Thermal history and origin of the IVB iron meteorites and their parent body

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Abstract

We have determined metallographic cooling rates of 9 IVB irons by measuring Ni gradients 3 μm or less in length at kamacite–taenite boundaries with the analytical transmission electron microscope and by comparing these Ni gradients with those derived by modeling kamacite growth. Cooling rates at 600–400 °C vary from 475 K/Myr at the low-Ni end of group IVB to 5000 K/Myr at the high-Ni end. Sizes of high-Ni particles in the cloudy zone microstructure in taenite and the widths of the tetrataenite rims, which both increase with decreasing cooling rate, are inversely correlated with the bulk Ni concentrations of the IVB irons confirming the correlation between cooling rate and bulk Ni. Since samples of a core that cooled inside a thermally insulating silicate mantle should have uniform cooling rates, the IVB core must have cooled through 500 °C without a silicate mantle. The correlation between cooling rate and bulk Ni suggests that the core crystallized concentrically outwards. Our thermal and fractional crystallization models suggest that in this case the radius of the core was 65 ± 15 km when it cooled without a mantle. The mantle was probably removed when the IVB body was torn apart in a glancing impact with a larger body. Clean separation of the mantle from the solid core during this impact could have been aided by a thin layer of residual metallic melt at the core-mantle boundary. Thus the IVB irons may have crystallized in a well-mantled core that was 70 ± 15 km in radius while it was inside a body of radius 140 ± 30 km.

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1. INTRODUCTION

The IVB iron meteorites are ataxites with microscopic Widmanstätten patterns consisting of kamacite platelets <20 μm in width, which appear in section as platelets embedded in matrices of plessite, a fine mixture of kamacite and taenite. The small size of the kamacite platelets reflects the high bulk Ni concentrations of the IVB irons, 15–18 wt.%. Low-Ni IVB irons have very few kamacite platelets, and phosphides whereas high-Ni IVB irons have many more kamacite platelets and phosphides (Fig. 1). Although only 13 IVB irons are known (Meteoritical Bulletin Database see http://tin.er.usgs.gov/meteor/metbull.php), the group is well studied, as the irons appear to be a fairly representative suite of samples from the core of an interesting asteroid with a relatively simple history.

The IVB irons are chemically unique as they contain exceptionally low concentrations of moderately volatile elements and high Ni contents: element/Ni ratios are depleted relative to CI chondrites by factors of 10–10 4 and decrease in order of increasing volatility: Au, P and As, Cu and Ga, and Ge (Kelly and Larimer, 1977; Rasmussen et al., 1984; Wasson, 1985). The low volatile abundances reflect high nebular temperatures when their parent body accreted or volatile loss during one or more impacts (Goldstein et al., 2009a). The high Ni concentrations in group IVB favor formation in an oxidizing environment (Campbell and Humayun, 2005). Despite the unusual bulk composition of group...
The purpose of this study was to obtain accurate cooling rates during kamacite formation for a diverse suite of IVB irons by measuring Ni gradients at the kamacite–taenite boundary with the analytical transmission electron microscope in thin sections cut from oriented samples with a focused ion beam instrument. These Ni profiles are then compared with calculated Ni profiles generated by modeling kamacite growth (Yang and Goldstein, 2006). In addition, we wanted to measure the dimensions of the cloudy taenite and the kamacite platelet formed below the kamacite bandwidths have been interpreted as evidence for core formation and cooling in a small parent body with a radius of 2–4 km (Rasmussen, 1989; Chabot and Haack, 2005; Walker et al., 2008).

The fast cooling rates for IVB irons inferred from their kamacite bandwidths have been interpreted as evidence for core formation and cooling in a small parent body with a radius of 2–4 km (Rasmussen, 1989; Chabot and Haack, 2006). However, the inferred radius of 2–4 km is much smaller than the minimum radius of 10–20 km for a body to be melted and differentiated by $^{26}$Al decay (Hevey and Humayun, 2006; Hevey and Humayun, 2005; Walker et al., 2008), there are significant differences among the measured values, especially the P content. Therefore, we re-measured the bulk Ni and P content of each meteorite using X-ray area scans obtained with wavelength dispersive spectrometers on a Cameca SX-50 electron probe microanalyzer (EPMA) at the University of Massachusetts. An operating voltage of 15 kV and a beam current of 40 nA were used. Two major elements (Fe and Ni) and two minor elements (Co and P) were measured. Pure Fe, Ni, Co and (Fe–Ni)$_3$P in the Grant meteorite (15.5 wt.% P) were used as standards. The bulk Fe, Ni, Co and P compositions within the group are well modeled by simple fractional crystallization in a vigorously convecting core using experimentally determined solid–liquid distribution coefficients (Rasmussen et al., 1984; Campbell and Humayun, 2005; Walker et al., 2008).

Although much is known about the formation of the IVB irons, the direction of crystallization of the IVB core and its subsequent thermal and collisional history is poorly known. Precise metallographic cooling rates are difficult to obtain for the IVB irons with the 1 μm spatial resolution of the electron probe microanalyzer (EPMA) because the Ni gradients in taenite at the boundary with the kamacite platelets are 3 μm or less in length. In addition, the kamacite platelets are too far apart for impingement to occur so that M-shaped profiles are not generated in the intervening taenite. Given these limitations, the conventional taenite central Ni vs half width Wood method (Wood, 1964), and the profile matching method for taenite lamellae (Goldstein and Ogilvie, 1965) cannot be applied. Cooling rates for the IVB irons have been obtained from the measurement of kamacite bandwidths and have values as high as 10,000 K/Myr (Rasmussen, 1989). However, the measured band-widths and the corresponding cooling rates have large and unknown uncertainties because the orientation of the kamacite platelets with respect to the polished surface was not measured and their nucleation temperatures were poorly constrained.

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We examined 9 out of the 13 known IVB irons (Table 1). Samples were first prepared by standard metallographic procedures, mounting, grinding, polishing, and etching with 2% nital, and observed using light optical microscopy. Samples for electron probe microanalysis were prepared the same way but without etching.

In order to determine the nucleation mechanism and the nucleation temperature of the kamacite platelets, it is necessary to have accurate bulk Ni and P contents for each meteorite. Although bulk Ni and P contents of the IVB irons have been measured (Moore et al., 1969; Buchwald, 1975; Campbell and Humayun, 2005; Walker et al., 2008), there are significant differences among the measured values, especially the P content. Therefore, we re-measured the bulk Ni and P content of each meteorite using X-ray area scans obtained with wavelength dispersive spectrometers on a Cameca SX-50 electron probe microanalyzer (EPMA) at the University of Massachusetts. An operating voltage of 15 kV and a beam current of 40 nA were used. Two major elements (Fe and Ni) and two minor elements (Co and P) were measured. Pure Fe, Ni, Co and (Fe–Ni)$_3$P in the Grant meteorite (15.5 wt.% P) were used as standards. The bulk Fe, Ni, Co and P composi-
tions were measured by averaging 8–27 side by side 100 × 80 μm² area scans for each IVB iron. The total area scanned for each meteorite was dependent on its structure and ranged from 64,000 μm² to 216,000 μm² (Table 1). Since few kamacite platelets and phosphides are present in the low-Ni IVBs, their Ni and P compositions are relatively homogeneous and 8 area scans were adequate for each meteorite. For the high-Ni irons, which have larger amounts of kamacite and phosphide, larger X-ray scan areas were needed to obtain representative bulk compositions and up to 24 area scans were made.

Ni profiles in taenite and adjacent kamacite across kamacite–taenite interfaces were measured by using the analytical electron microscope. A dual beam FEI focused ion beam (FIB) instrument at Sandia National Labs was used to obtain transmission electron microscope (TEM) thin sections generally 50–100 nm thick and approximately 10 μm long and 5 μm in depth. These TEM sections were cut perpendicular to kamacite–taenite interfaces of the kamacite platelets in the polished and etched meteorite sample surface (Fig. 2). Using this methodology, the kamacite–taenite interface of the platelet in the thin section is perpendicular to the surface. Selected kamacite–taenite interface regions in the thinnest areas of each FIB section were analyzed using a FEI Tecnai F30ST field emission transmission – analytical electron microscope (TEM–AEM) at Sandia National Labs or a VG 603 scanning transmission electron microscope (STEM) instrument at Lehigh University both operated at 300 keV. To obtain Ni composition gradients in kamacite and taenite at the two phase boundary, X-ray scans were taken with an energy-dispersive spectrometer (EDS) in micrometer-sized regions of the thin foil. Quantitative Ni X-ray gradients 0.5–2 μm in length in taenite were measured in a direction normal to the plane of the kamacite–taenite interface using the stored EDS X-ray scan data. The X-ray data in each pixel were converted to composition using the Cliff–Lorimer method (Cliff and Lorimer, 1975) with X-ray spatial resolution of 2–4 nm. A \( \frac{K_{Ni}}{K_{Fe}} \) factor in the Cliff–Lorimer method of 1.10 was measured at 300 keV using a 25 wt.% Ni–Fe standard.

The size of the high-Ni particles in the cloudy zone next to the cloudy zone/tetraetaenite boundary (Yang et al., 1997) was measured directly from the STEM image or the Ni X-ray scan obtained from the thin foil. The measurement of the size of the high-Ni particles in the cloudy zone was made next to the cloudy zone/tetraetaenite boundary since the local Ni content at that position is constant at 40–42 wt.% Ni (Yang et al., 1997). High-Ni particles farther away from the cloudy zone/tetraetaenite boundary were not measured as the high-Ni particle size and Ni content of taenite decrease with increasing distance from the cloudy zone/tetraetaenite boundary (Yang et al., 1997). The measurement of the size of the high-Ni particles is dependent on the geometry of the particles as discussed by Goldstein et al. (2009b) for cloudy zone in the IVA irons. The lack of a large sample of high-Ni particles limits the accuracy of the measurement of the mean size of the high-Ni particles.

The width of the outer taenite rim or tetraetaenite region between the cloudy zone and the kamacite–taenite interface was also measured at several points along the kamacite–taenite interface in each FIB section. The widths are measured directly from STEM images or Ni X-ray scans. No correction for orientation effects was necessary since the tetraetaenite width was measured in a direction normal to the plane of the kamacite–taenite interface (See Fig. 2).

In order to measure the cooling rates, information about the nucleation process of the Widmanstätten pattern, the nucleation temperature, the effect of impingement by adjacent kamacite plates, the Fe–Ni and Fe–Ni–P phase diagrams, and the interdiffusion coefficients that control the growth of the Widmanstätten pattern are needed (Yang et al., 2008). According to Yang and Goldstein (2005), the Ni and P contents of the IVB irons indicate that the Widmanstätten oriented platelets in the IVB irons nucleated by mechanism II \((\gamma \rightarrow \gamma + Ph \rightarrow x + \gamma + Ph)\) for high Ni–high P members of the IVB group where phosphides form in taenite during cooling before kamacite nucleated. For low Ni–low P members of the IVB group kamacite nucleation is controlled by mechanism III \((\gamma \rightarrow (x + \gamma) \rightarrow x + \gamma + Ph)\), where kamacite nucleation is suppressed during cooling until the meteorite enters the 3 phase field \(x + \gamma + Ph\). Our bulk Ni and P content of each IVB iron meteorite along with the Fe–Ni–P phase diagram were used to determine the nucleation mechanism and the nucleation temperature for each meteorite.

The Ni profile matching method (Goldstein and Ogilvie, 1965) was used to obtain a cooling rate for each individual measured taenite zoning profile. In this method, the measured Ni composition vs distance profile across taenite adjacent to a kamacite platelet is compared to Ni profiles calculated for several assumed cooling rates. A match between the observed and calculated profiles allows a unique cooling rate to be determined for each meteorite (Yang and Goldstein, 2006).

3. RESULTS

3.1. Bulk Ni and P contents

The bulk Ni and P contents that we determined for the nine IVB irons are listed in Table 1 and are plotted in Fig. 3a. The bulk Ni varies from 15.5 to 17.8 wt.% and
the bulk P varies from 0.05 to 0.25 wt.%. Literature data are shown in Fig. 3b for comparison. Fig. 3a also shows the Ni–P composition regions where mechanisms II \((\gamma \rightarrow \gamma + \text{Ph} \rightarrow z + \gamma + \text{Ph})\) and III \((\gamma \rightarrow (z + \gamma) \rightarrow z + \gamma + \text{Ph})\) are applicable for the nucleation of kamacite platelets in IVB irons (Yang and Goldstein, 2005). Irons with bulk Ni and P located above the dashed line nucleate kamacite by mechanism II while irons with bulk Ni and P located below the dashed line nucleate kamacite at lower temperatures by mechanism III. Nucleation temperatures for kamacite formation in each meteorite were obtained from the Fe–Ni–P phase diagram (Romig and Goldstein, 1980) and are listed in Table 1. They increase with increasing Ni and P content from 470 to 590 °C. We note that Rasmussen (1989) proposed that taenite was saturated in P so that schreibersite formed in all IVB irons before kamacite formed as the equilibrium phase. This assumption is incorrect for the low P IVB irons as shown in Fig. 3a and leads to inaccuracies in cooling rate measurements.

### 3.2. Measured metallographic cooling rates

A Ni X-ray scan taken in a 2000 × 500 nm region of the low-Ni Hoba meteorite is shown in Fig. 4a. The Ni X-ray scan shows the kamacite (black—low Ni), the tetrataenite (light gray—high Ni) and the cloudy zone composed of an intergrowth of high-Ni particles (light gray) and kamacite (dark gray). The measured Ni profile across the kamacite–taenite boundary shown in Fig. 4a is plotted in Fig. 4b.

Another Ni profile from Hoba is given in Fig. 4c along with two Ni profiles from the high-Ni IVB iron, Warburton Range, Fig. 4d and e. About 500 measurements of the Ni concentration were made for each 1–2 μm profile with a spatial resolution of ~4 nm/pixel depending on specimen thickness. The Ni content in tetrataenite in Hoba and Warburton Range exceeds 50 wt.% at the kamacite–taenite interface indicating continuous slow cooling to temperatures of 300 °C or below. One composition profile was measured for 3 meteorites, two composition profiles for 5 meteorites, and four composition profiles for 1 meteorite. The 17 measured Ni composition profiles were then compared with profiles calculated for various assumed cooling rates (Yang and Goldstein, 2006). The two compositional profiles for Hoba in Fig. 4b and c give average cooling rates of 400 and 900 K/Myr for a mean value of 650 K/Myr. With the exception of analyses in the tetrataenite rim and a few data points near the edge of the cloudy taenite, the Ni concentration data for Hoba scatter from 300 to slightly above the 1000 K/Myr curves. The two Warburton Range profiles in Fig. 4d and e both give cooling rates of 3000 K/Myr with virtually all the data in the cloudy zone scattering between the 1000 and 9000 K/Myr cooling rate curves.

The Ni profiles of two IVB irons, Skookum and Santa Clara, show evidence of re-heating at the kamacite/taenite interface (Fig. 5). For Skookum, the taenite Ni gradient within 300 nm of the kamacite–taenite boundary shows evidence of re-heating (Fig. 5a). The Ni profile in tetrataenite decreases rather than increases approaching the kamacite–taenite boundary and the maximum Ni content in tetrataenite is ~40 wt.%. The taenite Ni gradient beyond 300 nm, however, is not substantially influenced by re-heating so that the cooling rate can still be measured. For the Santa Clara IVB iron (Fig. 5b), the Ni gradient in taenite within 100 nm of the kamacite–taenite interface shows a diffusion profile suggesting a more modest shock re-heating than in Skookum. The maximum Ni content in tetrataenite is about 47 wt.%. The Ni gradient beyond 100 nm is not substantially influenced by re-heating so that the cooling rate can still be determined. In the case of Skookum, it is likely that heating occurred after atmospheric entry (Buchwald, 1975) but for Santa Clara we suspect earlier shock heating.

Table 1 lists the measured cooling rates for each of the 17 Ni profiles and the average cooling rate for the 9 IVB irons. Since so few cooling rates are measured for each meteorite, we also list the range of the cooling rates which fit the Ni composition data for each meteorite e.g., 300–1200 K/Myr for Hoba and 1000–9000 K/Myr for Warburton Range (Fig. 4). Fig. 6 shows the measured cooling rates vs the bulk Ni content for the 9 IVB irons. The vertical bars are not error bars but show the cooling rate ranges, e.g., 300–1200 K/Myr for Hoba. The mean cooling rates differ by a factor of 10 ranging between 475 and 5000 K/Myr and increase systematically with increasing Ni content.

### 3.3. Cloudy zone particle size and tetrataenite bandwidth measurements

The cloudy zone regions and tetrataenite bands in all but two IVB irons are well developed and preserved with...
no evidence of re-heating. For Skookum and Santa Clara no cloudy zone regions were observed, consistent with evidence of re-heating observed in the Ni taenite gradient near the kamacite–taenite boundary (Fig. 5). Figs. 4a and 7 show examples of Ni X-ray area scans from which the high-Ni particle size of the island phase of the cloudy zone microstructure and the tetrataenite bandwidths were measured. For each image, a limited number of high-Ni particles in the cloudy zone from several taenite bands were measured and the average particle size and its 1σ standard deviation were obtained (Table 2). The relationship between the cloudy zone high-Ni particle size and the bulk Ni of each IVB meteorite is plotted in Fig. 8a. The high-Ni particle size in the cloudy zone varies from 19 to 33 nm and decreases with increasing Ni content. The width of the tetrataenite bands measured in each of the images and the average tetrataenite width for each meteorite are also given in Table 2. The relationship between the

Fig. 4. Ni analyses and cooling rate measurements in two IVB irons Hoba (low-Ni, low P) and Warburton Range (high Ni, high P). (a) Ni X-ray scanning image of the surface of a FIB thin section of Hoba with an X-ray resolution of ~4 nm/pixel obtained using the analytical transmission electron microscope. The scanning image shows from left to right: cloudy zone intergrowth, a 200 nm wide band of tetrataenite (white) and the edge of the kamacite platelet (black). The dashed rectangle shows the region over which the Ni profile shown in Fig. 4b was obtained. (b and c) Ni concentration profiles across the kamacite–taenite interfaces in Hoba. (d and e) Ni concentration profiles across the kamacite–taenite interfaces in Warburton Range. The vertical arrow marks the boundary between the cloudy taenite and the tetrataenite rim where some data points plot below the curves. Cooling rates were determined by comparing the observed Ni profiles in the cloudy taenite with those calculated for a range of cooling rates.
tetrataenite bandwidth and the bulk Ni is shown in Fig. 8b. The tetrataenite bandwidth varies from 150 to 265 nm for the 7 meteorites and decreases with increasing Ni content. A positive correlation between cloudy zone particle size and tetrataenite bandwidth was also observed, like in IVA irons (Goldstein et al., 2009b).

4. ERRORS AND COMPARISON WITH PUBLISHED DATA

4.1. Bulk composition and metallographic cooling rate

Our bulk Ni and P contents are very consistent with the data of Campbell and Humayun (2005) and most other analysts (Fig. 3), but are significantly different from those of Walker et al. (2008) who obtained bulk P contents from 0.025 to 0.66 wt.%. This range is much broader than the

range of 0.04–0.2 wt.% P found by Campbell and Humayun (2005) and other authors. The difference in bulk Ni and P composition from these two studies can be attributed to the total areas from which the data were obtained. Campbell and Humayun (2005) used the laser ablation - inductively coupled plasma – mass spectrometry technique to

Fig. 6. Variation of the metallographic cooling rate with Ni content for 9 IVB irons. The vertical bars show the range of cooling rates determined from individual Ni analyses in taenite, e.g., 1000–9000 K/Myr for Warburton Range (Fig. 4d and e). These ranges are very conservative estimates of the 2σ precision limits for the cooling rates derived for each iron (see text). The dashed line shows the inferred relationship between cooling rate and bulk Ni.

Fig. 7. Ni X-ray scanning images of the low-Ni IVB iron, Cape of Good Hope (a) and the high-Ni iron, Warburton Range (b) showing right to left kamacite (black), tetrataenite (white) and cloudy taenite intergrowth. The wider tetrataenite rim and coarser cloudy taenite intergrowth in (a) show that Cape of Good Hope cooled slower than Warburton Range around 300 °C. The dashed rectangle in (a) shows the region over which the Ni concentration profile was obtained.

Fig. 5. Ni concentration profiles across the kamacite–taenite interface in (a) Skookum and (b) Santa Clara. These profiles show kamacite–taenite boundaries that are less well defined than those in Fig. 4 with lower maximum Ni concentrations of 40–45% cf. 50% or higher in the other IVB irons. This difference reflects re-heating that caused redistribution of Ni within the vicinity of the interface. The regions between the dashed lines were used to obtain the cooling rates.
measure the bulk composition from a scanned area of 250,000 μm² for each meteorite (50 μm diameter laser beam, 1 mm scan length, 5 scans). Walker et al. (2008) used the same technique to measure the bulk composition from scanned areas of 16,000 or 30,000 μm² for each meteorite (8 or 15 μm diameter laser beam, 0.5 mm scan length, 4 scans). In our study, we measured the bulk composition in each iron meteorite from total scanned areas from 64,000 to 216,000 μm² with larger areas for the high-Ni irons. We found that the scanned areas of Walker et al. (2008) were not large enough to cover a representative area for the high Ni and P iron meteorites. The Ni and P trend shown by the dotted line in Fig. 3a is consistent with a process of fractional crystallization in the core of the parent asteroid (Campbell and Humayun, 2005; Walker et al., 2008).

We cannot estimate the precision of the cooling rate data for each IVB iron because the number of taenite Ni gradients obtained for each meteorite was limited. As noted above, we show in Fig. 6, the cooling rate ranges given in Table 1 which give some estimate of the reproducibility of the measured cooling rates. Since the spread in the cooling rates derived from individual profiles from the same meteorite is smaller than these ranges, we take the plotted error bars to be very conservative estimates of the 2σ precision limits for the cooling rates derived for each iron. For example, the mean cooling rate derived from the four Ni profiles for Weaver Mountain is 3500 ± 1000 K/Myr. The 2σ uncertainty in the mean extends from 2500 to 4500 K/Myr, which is considerably smaller than the total range of 1000–9000 K/Myr which is plotted in Fig. 6. The errors in the cooling rates of the IVB irons are much larger than the errors estimated for the IVA and IIIAB irons where it was possible to measure Ni gradients in taenite with the EPMA (Yang and Goldstein, 2006; Yang et al., 2008).

Our results indicate that the cooling rates in group IVB irons increase systematically by a factor of 10 from ~475 K/Myr at the low-Ni end of the group to ~5000 K/Myr at the high-Ni end. By contrast, Rasmussen et al. (1984) and Rasmussen (1989) inferred from their data that cooling rates did not vary with bulk Ni in group IVB. However, the cooling rate data of Rasmussen (1989) are actually more consistent with our results as his Fig. 2 shows a significant positive correlation between bulk Ni and cooling rate for 10 IVB irons.

As pointed out previously, the bandwidth method employed by Rasmussen et al. (1984) and Rasmussen (1989) has significant errors due to the use of an incorrect kamacite nucleation mechanism for the low Ni–P irons. In addition, these two studies lack accurate bandwidth sizes since the orientation of the kamacite platelets with respect to the polished surface of the sample was not obtained. Our study avoided these sources of error as we used oriented samples and correct kamacite nucleation temperatures and mechanisms.

The cooling rate of a metallic core surrounded by a well insulating silicate mantle decreases with falling temperature. For the IVB irons, we should expect some increase of cooling rate with bulk Ni even if they had cooled in a well insulated core because of the increase in kamacite nucleation temperature of ~100 °C with increasing bulk Ni. However, this effect should only cause a 15% variation in cooling rate (Haack et al., 1990), much less than the 10-fold variation we observe across the group. Our analysis for the IVA iron shows that a 10-fold variation in cooling rate cannot be attributed to uncertainties in the parameters used to calculate cooling rates (Yang et al., 2007, 2008).

4.2. Cloudy zone particle size and tetrataenite bandwidth

Cloudy zone particle sizes and metallographic cooling rates of IVB irons (Tables 1 and 2) are plotted in Fig. 9a, together with other data from mesosiderites, IIIAB and IVA irons and the main-group pallasites (Yang et al., 2007; Goldstein et al., 2009a). Data for the IVB irons closely follow the general cooling rate vs particle size relationship.

The data for metallographic cooling rate and tetrataenite bandwidth in several groups, IVA (Goldstein et al., 2009b), IVB (this study), IIIAB and MG pallasites (Yang et al., 2009), are shown in Fig. 9b. The IVB data are clearly consistent with the overall trend in which cloudy zone particle size and tetrataenite bandwidth decrease with increasing cooling rate. The fact that cloudy zone particle size and tetrataenite

![Fig. 8. Bulk Ni concentrations of seven IVB irons plotted against (a) the size of the high-Ni particles in their cloudy zone, and (b) the tetrataenite bandwidth. Both plots show negative correlations. Since high-Ni particle size and tetrataenite width are both inversely related to cooling rate, these data confirm that the high-Ni IVB irons cooled faster than the low-Ni IVB irons, as was inferred from kamacite growth modeling (Table 1). The bars for the cloudy zone particle size for each meteorite represent 1σ of the analyses. The bars for the tetrataenite width for each meteorite show the range of measured values.](image-url)
bandwidth also decrease with increasing Ni content in the IVB irons (Fig. 8) strongly supports the positive correlation between metallographic cooling rate and bulk Ni shown in Fig. 6. As noted above, the relatively large cooling rate ranges for each measured IVB cooling rate, which are plotted in Fig. 6, are very conservative estimates of the uncertainty in the cooling rates for the IVB irons.

5. DISCUSSION

Fractionally crystallized iron meteorite groups like IVB are widely thought to be derived from the cores of asteroids that crystallized and cooled while they were surrounded by silicate mantles (Haack and McCoy, 2004). In such bodies, iron meteorite samples from diverse positions in the core would have nearly identical cooling rates because of the high thermal conductivity of metal compared with that of mantle and crust materials. However, in groups IVA and IIIAB, the irons cooled below 600°C at diverse rates and could not therefore have cooled inside a mantled core (Yang and Goldstein, 2006; Yang et al., 2007, 2008). The IVA irons appear to have formed in a metallic body with virtually no silicate mantle following a glancing impact (Yang et al., 2007).

Our data from three independent techniques show that there is a significant range of cooling rates among IVB irons and that these cooling rates correlate with Ni content. Therefore the IVB irons could not have cooled in an insulated core. In group IVB, the Ni-poor members, which crystallized early, cooled slower than the Ni-rich members suggesting they were located closer to the center, contrary to what was observed in groups IIIAB and IVA. If the IVB core crystallized concentrically, these data suggest that it grew outwards from the center. Below we discuss various constraints on the mode of crystallization of asteroidal cores.

5.1. Core crystallization of an asteroid: outside-in vs inside-out

In planetary cores, the direction of crystallization of a planetary core depends on the relative magnitudes of the liquidus temperature gradient and the actual temperature gradient, which should approach the adiabatic gradient assuming ideal convection. In the Earth’s core where pressures exceed 100 GPa, the adiabatic thermal gradient is shallower than the liquidus gradient so that crystallization proceeds outwards. Under these conditions, rejection of
light-elements like S and release of latent heat promote convection and dynamo action. For much smaller bodies like asteroids which have central pressures <1 GPa, the situation is much less clear. Haack and Scott (1992) and Williams (2009) infer that the adiabatic gradient across the core would be steeper than the liquidus gradient and that the core should therefore crystallize inwards. However, uncertainties in the properties of liquid Fe–Ni–S and kinetic factors discussed below may negate this conclusion.

The adiabatic temperature gradient can be defined by Eq. (1) (Jacobs, 1987; Haack and Scott, 1992; Boehler, 1993),

\[
\frac{dT}{dP} = \frac{\alpha T}{\rho C_p} \tag{1}
\]

where \(\alpha\) is the pressure-dependent coefficient of volume thermal expansion, \(T\) is the temperature, \(\rho\) is the density, and \(C_p\) is the specific heat at constant pressure. The largest uncertainty in these parameters is for the thermal expansion coefficient \(\alpha\). A value of \(\alpha = 9.2 \times 10^{-5} \text{K}^{-1}\) for pure iron has been widely adopted (Anderson and Ahrens, 1994). However, Williams (2009) prefers the value for \(\alpha\) of \(13.2 \times 10^{-5} \text{K}^{-1}\) recommended by Assael et al. (2006). If the smaller \(\alpha\) value is used, \(\frac{dT}{dP} = 28.4 \text{K/GPa}\) at the melting point of pure iron, but the larger \(\alpha\) value gives \(\frac{dT}{dP} = 40.8 \text{K/GPa}\) at melting point.

To derive the melting point gradient for pure iron, Williams (2009) prefers the data of Strong et al. (1973) up to 5 GPa, which give a gradient of 35 K/GPa. However, additional data for pressures up to 5–10 GPa favor a slightly higher melting point gradient of 39 K/GPa (Boehler, 1993; Saxena et al., 1994; Saxena and Dubrovinsky, 2000).

To illustrate the very small temperature differences expected across convecting asteroidal cores, we show in Fig. 10, adiabatic and liquidus gradients calculated for a pure Fe core in an asteroid of radius 150 km. Pressures were calculated using the hydrostatic equation (Jacobs, 1987) assuming the metallic core has half the radius of the body. The densities of core and mantle materials were taken as 3000 kg/m³ for the silicate mantle (Haack and Scott, 1992) and 7019 kg/m³ for liquid iron (Anderson and Ahrens, 1994). The curves in Fig. 10 were derived using the

| Table 2 | Cloudy zone (CZ) high-Ni particle size and tetrataenite (Tt) bandwidth measurements for 7 IVB irons. |
|---|---|---|---|---|
| Meteorite | Ni (at.%) | CZ particle size (nm) | (±1σ)(nm) | Tt (nm) |
| Iquique | 15.5 | 33.1 | 2.4 | 282 |
| | | 33.1 | 2.4 | 264 |
| Hoba | 15.6 | 26.1 | 2.5 | 202 |
| | 26.9 | 2.6 | 183 |
| | 26.5 | 2.6 | 193 |
| Tlacotepec | 15.9 | 29.3 | 4.5 | 232 |
| Cape of Good Hope | 16.0 | 31.5 | 4.1 | 237 |
| | 27.1 | 2.4 | 268 |
| | 20.7 | 2.9 | 169 |
| | – | – | 266 |
| | 26.4 | 3.1 | 236 |
| Weaver Mtn | 17.5 | 16.0 | 4.2 | 130 |
| | – | – | 127 |
| | 16.4 | 1.7 | 152 |
| | 17.4 | 2.8 | 147 |
| | 20.0 | 2.5 | 185 |
| | 26.3 | 2.6 | 188 |
| | 19.2 | 2.8 | 155 |
| Tawallah Valley | 17.5 | – | – | 162 |
| | – | – | 140 |
| | – | – | 144 |
| | 23.3 | 1.9 | 155 |
| | 23.2 | 1.9 | 151 |
| Warburton Range | 17.8 | 17.4 | 2.1 | 152 |
| | 23.4 | 1.9 | 181 |
| | 21.1 | 2.9 | 180 |
| | 20.6 | 2.3 | 171 |

'–' Indicates the image quality was not sufficient for an accurate measurement of CZ particle size.

Fig. 9. Metallographic cooling rates of irons in groups IIIAB, IVA, and IVB and the stony-iron meteorites, main-group pallasites (MG Pall.) and mesosiderites (Meso.), show an inverse correlation with (a) the sizes of high-Ni particle in the cloudy zone microstructure and (b) the tetrataenite bandwidths. Although there is more scatter at the fast-cooled end of the line, the IVB data are quite consistent with the trends established by the other groups showing that tetrataenite bandwidth and cloudy zone particle size can be used to infer relative cooling rates at ~300°C in diverse meteorites.
lower $x$ value of $9.2 \times 10^{-5}$ K$^{-1}$ and a melting point gradient of 39 K/GPa. With these data, one would predict outwards growth of the core assuming equilibrium crystallization. The use of the higher $x$ value would indicate inwards equilibrium crystallization. Williams (2009) has investigated the effects of Ni and S and infers that even with the lower $x$ value, asteroidal cores with >5 wt.% S should crystallize inwards under equilibrium conditions.

Despite uncertainties in the adiabatic and liquidus temperature gradients, it is clear that temperature differences across asteroidal cores assuming ideal convection should not have exceeded a few degrees K. The mode of crystallization may therefore have depended on other factors. For example, Haack and Scott (1992) infer that lateral temperature variations at the base of the mantle resulting from mantle convection or topographic variations may have exceeded the temperature variation across the core. As a result, crystallization may have commenced at the coldest sites at the base of the mantle. Once crystallization starts, S is rejected from the growing solid and may build up in the adjacent liquid without vigorous convection. Since 1 wt.% S will lower the liquidus temperature by ~20 K (Li and Fei, 2003), even minor S gradients can quickly affect the course of crystallization. Concentric inwards growth in a mantled core would enhance the S concentration in the outer layer precluding global convection and fractional crystallization. Alternatively, Haack and Scott (1992) suggested that S-build up promoted the formation of inwards growth of dendrites with lengths approaching the core radius. Convection may then have been driven by S-rich liquid rising along the dendrites.

Another factor that may have affected the crystallization mode in asteroidal cores is the availability of nuclei for Fe–Ni crystals. Homogeneous nucleation of solid iron in liquid iron requires undercooling of ~300 K (Turnbull and Cech, 1950). Alternatively, solid iron may have nucleated heterogeneously on solid metal, silicate or oxides. Silica inclusions are present in the IVB iron, Santa Clara (Teshima and Larimer, 1983), but their concentration around sulfide nodules suggest they may not have nucleated solid Fe–Ni. Solid Fe–Ni nuclei may have reached the core from dendrites that grew on the core-mantle boundary and became detached (Wasson, 1993). Alternatively, peak core temperatures may never have exceeded the liquidus temperature so that residual metal crystals were available at the center for outwards growth.

Olivine nuclei would also have been plentiful at the core-mantle boundary, but the activation energy barrier for heterogeneous nucleation ($\Delta G_{\text{Fe-Ni}}^* = S(\theta) \Delta G_{\text{mol}}^*$) on olivine is much higher than for solid metal because of the difference in wetting angle, which determines the shape factor $S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4$. The wetting angle $\theta$ between liquid iron and olivine is about 94° (Eckhardt, 1995) so the shape factor $S(\theta) = 0.55$. The wetting angle between liquid iron and solid iron is unknown but it is expected to be close to 0° (Eustathopoulos et al., 1999). Assuming $\theta = 5^\circ$, then the shape factor for solid metal nucleation $S(\theta) = 1.2 \times 10^{-5}$. Thus the activation energy barrier for heterogeneous nucleation on solid Fe–Ni is 5 orders of magnitude less than on olivine.

In summary, adiabatic and thermal gradients in asteroidal cores may have favored inwards growth except possibly in low-S cores. However, the small temperature gradients across asteroidal cores suggest that kinetic factors and initial conditions may have been more important than equilibrium relationships. Concentric inwards growth in a mantled core would enhance the S concentration in the outer layer precluding global convection and fractional crystallization. However, evidence for fractional crystallization in iron meteorites suggests that convection was vigorous. Inwards growth of multi-km-sized dendrites (Haack and Scott, 1992) remains speculative as cooling rate data for iron meteorites in groups IIIAB, IVA and IVB suggest concentric growth. Outwards growth in low-S cores may have resulted from incomplete melting of Fe–Ni and supercooling in the outer regions of the core due to the difficulty in nucleating on olivine at the core-mantle boundary.

5.2. Crystallization and origin of the IVB Irons

Although we cannot exclude the possibility that the IVB core grew inwards with multi-km long dendrites, the cooling rate data favor simple outwards concentric crystallization. Since the IVB meteorites have the lowest concentrations of troilite of any group (Buchwald, 1975), the low S abundance in the core may have promoted outwards growth. Outwards growth is also consistent with the chemical trends in IVB, which require fractional
crystallization (Walker et al., 2008), and vigorous convection. If outwards crystallization is typical of mantled asteroidal cores, the inwards crystallization of the IVA and IIIAB metallic bodies may simply result from mantle removal before crystallization rather than afterwards (Yang et al., 2007, 2008). Steep thermal gradients in the outer metallic portions may have promoted convection in the IIIAB and IVA bodies.

Our explanation for the diverse cooling rates of the IVB irons requires that the mantle was removed after the IVB irons crystallized. Fractional crystallization modeling suggests that the IVB irons sample only ~70–80% of the whole core (Walker et al., 2008). Thus the IVB mantle could have been removed before the outer 20–30% of the core had crystallized. Mantle removal by a glancing hit-and-run impact when the outer 20–30% was still liquid seems more plausible than post-solidification removal as the latter would presumably have fragmented much of the outer parts of the core.

Our proposed history for the IVB irons is shown schematically in Fig. 11. Before core solidification, the parent body had a liquid or largely liquid core with radius \( R \) surrounded by a mantle (Fig. 11a). During cooling, the solid Fe–Ni grew from the center of the core (Fig. 11b). When the radius of the solid core was \( R' \) (Fig. 11c), a glancing impact with a larger body (Fig. 11d) exposed the solid core and dispersed the residual molten metal (Fig. 11e). The solid inner core of radius \( R' \) cools to lower temperatures without a surrounding mantle (Fig. 11f). Below we estimate the radii of the solid and liquid cores (\( R' \) and \( R \)) and the locations of the IVB irons using fractional crystallization and thermal models.

Fractional crystallization of the IVB irons was modeled using elemental distribution coefficients that vary with S concentration (Chabot and Jones, 2003). Since the chemical trends in group IVB are well modeled using bulk S contents of 0–2 wt.% (Walker et al., 2008; Goldstein et al., 2009a), we assumed S contents of the liquid core of 1 and 2 wt.% S. The Ni content of the liquid core was fixed at 17.6 wt.% Ni so that the first solid to crystallize had a Ni concentration equal or close to that of the lowest Ni IVB iron (15.5%). Following the procedure used by Yang

![Fig. 11. Cartoon showing the evolution of the group IVB asteroid. (a) Parent body with a liquid core (red) of radius \( R \) surrounded by a mantle (blue). (b) Fractional crystallization of the core begins in the center of the metallic core (brown). (c) Fractional crystallization continues until about 80% of the original liquid core has solidified and the solid core has a radius \( R' \). (d) Glancing impact with a much larger asteroid breaks up the IVB parent body forming in (e) the exposed solid core (brown), dispersed liquid metal (red), and mantle fragments (blue). (f) The solid inner core of radius \( R' \) cools to lower temperatures without a surrounding mantle and is subsequently broken up to form the IVB meteorites. We infer from thermal and fractional crystallization models that the radius (\( R \)) of the liquid core in (a) was ~70 km while the radius (\( R' \)) of the solid core in (c–f) was ~65 km. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 12. Ni concentration in solid Fe-Ni metal as a function of radial distance \( r \) from the center of a liquid core of radius \( R \) that crystallizes from the center of the core outwards. Initial bulk S concentrations of 1 and 2 wt.% are assumed. Dashed lines (\( r/R = 0 \) to \( r/R = 0.9 \)) show the range of bulk Ni concentrations, 15.5–18.5 wt.% (Campbell and Humayun, 2005; Walker et al., 2008) in group IVB irons. The IVB irons are core samples taken from the center to \( r/R = 0.9 \). The unsampled shaded section where \( r/R = 0.9–1.0 \) accounts for ~25% of the core volume.](image-url)
et al. (2008) for the IVA irons, we generated a relationship between the Ni content of the solidified iron and the fraction of the core that has solidified (f) for the two S contents. Assuming outwards growth, the Ni content in the solidified core was then obtained as a function of the normalized radius r/R (Fig. 12). In this model, the IVB iron meteorites with the highest bulk Ni contents (18.5 wt.%; Campbell and Humayun, 2005; Walker et al., 2008) would have crystallized at a radial position r/R = 0.90 when ~75% of the original liquid had crystallized. We assume that residual liquid between R' and R was dispersed in the impact that removed the mantle (Fig. 11e).

5.3. Thermal history of the IVB metallic asteroid

The cooling rate of the IVB metallic asteroid was investigated using the thermal model developed for the IVA asteroid in which the initial temperature was taken as 1760 K (Yang et al., 2008). Assuming that the IVB iron with the slowest cooling rate of 475 K/Myr (Table 1) was located close to the center of the metallic body and that the metal core essentially lacked a silicate mantle, we calculate that the metallic core in which the kamacite plates formed had a radius (R') of 65 km (Fig 11f). Since the kamacite nucleation temperatures of the IVB iron vary with Ni content from 740 to 860 K (Table 1), we calculated the cooling rate at the kamacite nucleation temperature vs r/R from the thermal model. Fig. 13 shows the calculated cooling rate as a function of the normalized radial distance r/R from the center of the core (upper abscissa) as well as the radial distance r/R in the original core (lower abscissa). The relationship of Ni content to r/R for this calculation is given by the Ni vs r/R plot (Fig. 12). Using Fig. 13, we determined that the IVB irons with the fastest cooling rate of 5000 K/Myr were located at a radial distance r/R = 0.95, or 62 km from the center of the solid body. The fastest cooled IVB iron have Ni contents of 17.5 to 17.8 wt.%Ni (Table 1). Using the calculated Ni distribution in the solidified core as a function of the normalized radius r/R (Fig. 12), it is observed that meteorites with the fastest cooling rates are located at a position r/R of ~0.88. Since r is 62 km, the original liquid core radius is ~70 km.

By combining the results from the fractional crystallization model (Ni content vs r/R, Fig. 12), and the thermal model (cooling rate vs r/R, Fig. 13), we calculate the cooling rate vs bulk Ni relationship for samples from a solid metallic core of radius 65 km that crystallized outwards in a molten core with a radius 70 km and a bulk S concentration of 1 and 2 wt.% (Fig. 14). Fig. 14 shows an excellent match between the calculated cooling rate vs bulk Ni variations and that obtained from the metallographic cooling rates of the IVB irons (Table 1). Although both S contents match the data, the 1 wt.% curve is a better fit.

The metallographic cooling rate range for the four low-Ni IVB irons is about 350–900 K/Myr (Column CR (K/Myr) in Table 1). By using this cooling rate range to determine the uncertainty in the calculation of the inner core size, we calculate that the radius of the solid metallic body size was between 50 km and 80 km. Therefore, the radius of the inner core was 65 ± 15 km, and that of the original liquid core was 70 ± 15 km. Assuming that the original liquid core was half the radius of the differentiated body (Fig. 11a), we infer that the original IVB body was 140 ± 30 km in radius before breakup.

5.4. Possible relation with angrites

Campbell and Humayun (2005) suggested that the IVB irons might be derived from the same body as the angrites,
which are more depleted in Na, K and other volatile elements than any other basalts. The angrites record magnetic fields on the order of 10 μT that lasted for at least 8 Myr (Weiss et al., 2008) around the time when the IVB irons crystallized (Walker et al., 2008). Indeed, the IVB body may well have had a dynamo-generated magnetic field during core crystallization, as fractional crystallization and dynamos both require efficient convection (Nimmo, 2009). However, oxygen isotope data for IVB irons and more siderophile element data for angrites are needed to test this possible link.

6. SUMMARY

We produced electron transparent thin sections of kamacite–taenite interfaces from the polished surfaces of nine group IVB iron meteorites. This allowed us to measure the 2–3 μm long Ni concentration profiles normal to the plane of the kamacite–taenite interface with a resolution of 2–4 nm using analytical transmission electron microscopy. By comparing these profiles with those generated from computer modeling of kamacite growth using our measurements of bulk Ni and P concentrations, we have determined that the nine IVB irons cooled at rates of between 475 and 5000 K/Myr during kamacite growth at 600–400 °C. These cooling rates are faster than those of most other iron and stony-iron meteorites and are correlated with the bulk Ni concentrations.

Seven of the nine IVB irons have cloudy taenite intergrowths and tetrataenite layers between the cloudy taenite and the kamacite platelets. Sizes of the high-Ni particles in the cloudy taenite at the interface with the tetrataenite rim and widths of the tetrataenite rims in the IVB irons are inversely correlated with bulk Ni concentrations. Since the widths of cloudy taenite particles and the tetrataenite rims in a wide variety of iron and stony-iron meteorites are inversely correlated with the cooling rates during kamacite growth, these data strongly support our conclusion from kamacite growth modeling that the cooling rates of IVB irons are correlated with their bulk Ni concentrations. In addition they confirm that IVB irons cooled faster than nearly all other iron and stony-iron meteorites.

The two IVB irons, Santa Clara and Skookum, that lack cloudy taenite have lower peak Ni concentrations in taenite at the kamacite interface (40–45% cf. >50% in the other IVB irons) and less steep Ni profiles close to this peak indicating re-heating above 400 °C. Because their Ni profiles were undisturbed at distances 100 and 200 nm from the kamacite–taenite interface, cooling rates could still be determined from the rest of the taenite Ni profile. Skookum was probably heated after atmospheric entry (Buchwald, 1975), but for Santa Clara, which was much less affected, earlier shock heating is more probable.

If the group IVB irons had cooled in a core that was enveloped by a silicate mantle, their cooling rates would be uniform. The 10-fold variation in cooling rate for the IVB irons (Table 1) suggests instead that the IVB core cooled through 600 to 400 °C after the mantle had been removed. Although we cannot exclude the possibility that the IVB core grew inwards with multi-km long dendrites, the positive correlation between bulk Ni and cooling rate suggests simple outwards concentric crystallization. Then high-Ni irons that crystallized late would have been located nearer the surface and cooled more rapidly than low-Ni irons.

If the core grew concentrically outwards as we infer, our thermal and crystallization models suggest that the radius of the core was 65 ± 15 km when it cooled without a mantle. The mantle was probably removed when the IVB body was torn apart in a glancing impact with a larger body, as these “hit-and-run” impacts were probably the dominant mechanism for extracting core material from differentiated asteroids (Asphaug et al., 2006). Clean removal of the mantle from the solid core by a hit-and-run impact may have been aided by a thin layer of residual metallic melt at the core-mantle boundary, which was lost during the impact. The IVB irons may therefore have crystallized in a core that was slightly larger, 70 ± 15 km in radius, in a body that was probably around 140 ± 30 km in radius.

Outwards crystallization in asteroidal cores would have promoted convection but it is counter to the predictions of Williams (2009), who argued for top-down crystallization, except possibly in cores with low S (like the IVB core). However, inwards growth would have enriched S in the outer liquid zones inhibiting convection and fractional crystallization. Since the thermal gradient across the core would have been less than a few degrees K, it is possible that kinetic and other factors controlled crystallization of asteroidal cores rather than the relative gradients of the adiabatic and liquidus curves. The outside-in crystallization that we inferred for the IVA and IIIAB irons may have resulted from rapid cooling and crystallization following mantle removal (Yang et al., 2008).

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