Cooling rates of seven hexahedrites

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Abstract—Cooling rates for seven hexahedrites, (Uwet, Coahuila, Walker County, Lombard, Quillagua, Hex River Mountains and Tocopilla) have been determined using a ternary diffusion controlled phase growth analysis developed by the authors. The model is applied to the exsolution and growth of plate phosphides in the kamacite phase of hexahedrites during cooling of the meteorite in its parent body. The effects of cooling rate, bulk composition, nucleation temperature and diffusion field length are considered. A unique cooling rate was determined by comparing the Ni content and width of several phosphides in a given hexahedrite to computer-generated curves of Ni content vs phosphide width. Six hexahedrites have cooling rates of approximately 2°C/10^6 yr. One hexahedrite, Coahuila, has a somewhat higher cooling rate of 10°C/10^6 yr. These cooling rates fall within the range calculated by an independent method for octahedrites. The cooling rate analysis indicates that the hexahedrites, except for one possible exception, were formed in or close to the core of a parent body ~150 km in radius.

INTRODUCTION

IRON meteorites (irons) are alloys of Fe, Ni and P which contain minor amounts of Co, Cr, S, C and a variety of trace elements (MASON, 1962). The irons are sub-divided into three groups according to texture. Nickel rich ataxites are a fine mixture of α (kamacite or b.c.c. Fe-Ni) and γ (taenite or f.c.c. Fe-Ni). The octahedrites contain a coarse mixture of α and γ in the form of a Widmanstätten pattern. Hexahedrites contain 5–6 wt.% Ni and are large crystals of α. Because of the similarity of structure, composition and trace element content, the hexahedrites are placed in chemical group II A (WASSON, 1969).

Previous studies have determined cooling rates for a large number of octahedrites (GOLDSTEIN and SHORT, 1967a; WOOD, 1964). These cooling rate determinations were made using a mathematical model for the γ→α (Widmanstätten) transformation in the Fe-Ni system. This binary model, however, cannot be applied to the hexahedrites where the γ→α transformation has gone to completion. The purpose of this study is to determine cooling rates for a number of hexahedrites using the ternary phase growth model of RANDICH and GOLDSTEIN (1975) adapted to the Fe-Ni-P system. The growth of the accessory mineral schreibersite, (FeNi)_3P, in kamacite is simulated. The model predicts phase compositions and phase dimensions as a function of cooling rate. Measured and simulated data are then compared to define a unique cooling rate for each hexahedrite.

PHOSPHIDE FORMATION

Although hexahedrites contain many elements they can be approximated as ternary alloys comprised of Fe, Ni and P (GOLDSTEIN and SHORT, 1967b; DOAN and GOLDSTEIN, 1969; HORNBOGEN and KREYE, 1970). The range of Ni and P contents for the hexahedrites is 5.35–5.75 and 0.20–0.34 wt% respectively (BUCHWALD, 1975). A small amount of Co is present but appears to behave like Fe and thus has little influence on the system (DOAN and GOLDSTEIN, 1969). The minor alloying elements C, S, Cr and Si tend to segregate in inclusions such as cohenite [(FeNi)3C], troilite (FeS), daubréelite (FeCr,S4), graphite and silicates. Most of these inclusions form at high temperatures (>800°C) and therefore have a negligible effect on major metallic phase transformations. During cooling most P exsolves to form schreibersite, (FeNi)_3P (also called phosphide or Ph). This phase is the most abundant inclusion and most striking feature of hexahedrites (AXON and WAINE, 1972).

The macrostructures of two hexahedrites are shown in Fig. 1 and are used to illustrate the several basic morphological forms of phosphides which are present in hexahedrites. One form (Fig. 2a) occurs as widely scattered, relatively scarce irregular patches known as hieroglyphic phosphides which form at temperatures above 850°C (DOAN and GOLDSTEIN, 1969). The nature of their nucleation and early growth is unclear. Because of this and their irregular shape, the phase growth model developed by RANDICH and GOLDSTEIN (1975) cannot be used to simulate the growth of this form of phosphide.

Phosphide also occurs as thin plates or laths known as plate phosphides or rhabdites (Fig. 2b). These plates have thicknesses ranging from 2 to 50 μm (other dimensions being typically larger than 100 μm). This type of phosphide appears to form on distinct crystallographic planes in the α matrix (RANDICH and ECKELMEYER, 1976). As discussed in a subsequent section, the phase growth model of RANDICH and GOLDSTEIN (1975) can be used to simulate the growth of this type of lamellar precipitate morpho-

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The third form of phosphide is known as rhabdite. Rhabdites are short rods with rhomboidal cross sections having two dimensions typically less than 50 μm (Fig. 2b).

Phosphide formation in hexahedrites can be described with the aid of the Fe—Ni—P ternary diagram. This diagram has been recently redetermined by Doan and Goldstein (1969, 1970) for the temperature range 1100–550°C. Figure 3 is a vertical section of this diagram taken at 5.5 wt% Ni (the average hexahedrite Ni composition) showing the equilibrium phase regions as a function of temperature and wt% P. The approximate P range for hexahedrites is represented by the shaded area on the figure. This shaded area delineates the possible phase transformations which can occur as a hexahedrite cools.

There are two possible reaction paths for Ph formation (Note Fig. 3); (1) \( \gamma \rightarrow \alpha + \gamma + \alpha \rightarrow \alpha + \text{Ph} \), (2) \( \gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{Ph} \rightarrow \alpha + \text{Ph} \). In hexahedrites which contain less than \( \sim 0.35 \) wt% P, phosphide exsolves by reaction path (1) directly from \( \alpha \). Growth continues as temperature decreases because of the decreasing solubility of P in \( \alpha \). For hexahedrites containing more than \( \sim 0.35 \) wt% P, the phosphide exsolves by reaction path (2), from both \( \alpha \) and \( \gamma \). The amount of \( \gamma \) present when the phosphide nucleates is small however. As the temperature decreases the \( \gamma \) phase gradually dissolves leaving only \( \alpha + \text{Ph} \) below 650°C. Since reported P contents are \( \leq 0.35 \) wt% P in hexahedrites, phosphide formation follows reaction path (1).

**PHASE GROWTH MODEL**

**Description of the model**

The phase growth model which is used for simulating phosphide growth in hexahedrites was developed by Randich and Goldstein (1975) for diffusion controlled phase growth in ternary systems. It is a numerical model for one dimensional, plane front growth and can accommodate ternary interactions, non-isothermal phase transformations and overlapping diffusion fields or impingement effects. The model can be used for phase transformations in any ternary system, provided that pertinent phase diagrams and ternary diffusion coefficients are known at the temperatures of interest. The model predicts phase dimensions and compositional profiles for both the exsolving and matrix phases. The major assumption in the model is that local equilibrium is maintained at the interface between the exsolving phase and the matrix phase.

In this study, the Randich—Goldstein model was adapted to simulate the growth of phosphide from \( \alpha \) (Randich, 1975). The temperature dependence of the ternary diffusion coefficients for \( \alpha \) in the Fe—Ni—P system (Heyward and Goldstein, 1973) and for phosphide (Norkiewicz and Goldstein, 1975) was incorporated in the model. The Fe—Ni—P phase diagram has been experimentally determined between 1100 and 550°C (Doan and Goldstein, 1970). Figure 4 shows a series of isothermal sections which give the boundaries of the \( \alpha, \alpha + \gamma, \alpha + \text{Ph} \) and \( \alpha + \gamma + \text{Ph} \) phase regions at the Fe rich corner of the Fe—Ni—P diagram. Since temperatures as low as 250°C are considered in this study, an extrapolation of the \( \alpha + \text{Ph} \) phase field is made to 250°C. The \( \alpha + \text{Ph} \) phase field is assumed to change shape in the following manner (see Fig. 4): (1) the \( \alpha + \text{Ph}/\text{Ph} \) boundary is fixed at 25 wt% P (15.5 wt% P) since \((\text{FeNi})_3\text{P}\) is stoichiometric in P; (2) The \( \alpha + \text{Ph}/\alpha + \gamma + \text{Ph} \) boundary rotates clockwise to higher Ni contents as temperature decreases; (3) The decreasing solubility of P in \( \alpha \) (as temperature decreases) causes the \( \alpha + \text{Ph}/\alpha \) boundary to move towards the Fe—Ni boundary. The assumption of P stoichiometry for \((\text{FeNi})_3\text{P}\) is well established. Microprobe measurements of P in meteoritic and lunar phosphides which have cooled to temperatures well below 500°C have confirmed the stoichiometric value of P. Microprobe measurements of Ni in meteoritic schreibersite embedded in taenite borders, an association which is often observed in octahedrites and approximates the phosphide corner of the three phase field \( \alpha + \gamma + \text{Ph} \) (Fig. 4), range from 41 to 45 wt% at 550°C, the maximum Ni content in phosphide is only 19 wt%. Therefore the \( \alpha + \text{Ph}/\alpha + \gamma + \text{Ph} \) boundary should rotate to higher Ni contents as temperature decreases. The solubility of P in \( \alpha \) is small, and decreases from 2 wt% at 1000°C to 0.25 wt% at 550°C (Doan and Goldstein, 1970). As suggested by thermodynamic considerations (Swalin, 1962) and by several investigators (Reed, 1965; Clarke, 1976),
Cooling rates of seven hexahedrites measured solubility data can be used for extrapolation to lower temperatures. A plot of wt% P on a logarithmic scale vs 1/T yields an excellent straight line through the measured data (≥550°C, CLARKE, 1976) and a direct method of extrapolation to lower temperatures (<550°C). The endpoints of the α + Ph/α boundary, Y1 on the Fe-P binary and Y2 at the α + γ + Ph corner, as shown on Fig. 4, describe the detailed movements of the boundary. The values of Y1, Y2 and the intersection of the α + Ph/Ph and α + Ph/α + γ + Ph boundaries (the phosphide triple point) are listed for various isothersms in Table 1. In addition the equations which describe these changes with temperature are included in Table 1. The endpoint Y2 increases in Ni content down to 450°C but below 450°C it decreases in Ni content. This bending back of Y2 is inferred from the work of DOAN and GOLDSTEIN (1970) and follows the same bending back calculated for the Fe-Ni binary. The movement of the phosphide triple point parallels the projected α + γ/γ boundary of the Fe-Ni binary. Figures 4 and 5 show the important portions of the extrapolated ternary diagram at 500 and 250°C. The major uncertainties are in the Ni contents at Y2 and the phosphide triple point and the P contents at Y2. The effect of these uncertainties on the calculated cooling rates will be discussed in a later section of the paper.

Table 1. α + Ph phase field boundaries. Part A—solubility limits (wt%). Part B—solubility limit equations below 600°C (T in °C)

<table>
<thead>
<tr>
<th>Part A—Solubility Limits (wt%)</th>
<th>Part B—Solubility Limit Equations below 600°C (T in °C)</th>
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<tbody>
<tr>
<td>Temp. (°C)</td>
<td>Y1</td>
</tr>
<tr>
<td>------------</td>
<td>----</td>
</tr>
<tr>
<td>925</td>
<td>2.03</td>
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<tr>
<td>750</td>
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<td>600</td>
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<td>550</td>
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<tr>
<td>300</td>
<td>0.09</td>
</tr>
<tr>
<td>250</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Fig. 4. Isothermal sections at the Fe rich corner of the Fe-Ni-P system, 750, 500 and 250°C. The dotted lines are α + Ph tie lines. The solubility limits Y1, Y2 are discussed in the text.

Fig. 5. Growth of phosphide in the α + Ph two phase region of the 500°C Fe-Ni-P isotherm. The bulk Ni and P composition of the sample is assumed to be 5.5 wt% Ni, 0.5 wt% P. The tie line through the bulk composition is called the ETL (equilibrium tie line). Phosphide growth usually occurs with the α/Ph interface compositions given by a tie line, as shown at a position to the left of the ETL.
Permissible tie lines in the $\alpha + \text{Ph}$ phase field are determined as follows (some tie lines are shown for the 250°C isotherm in Fig. 4): (1) no tie lines intersect; each tie line is unique; (2) close to the Fe–P binary, the permitted tie line is parallel to the Fe–P binary (that is the tie line lies in the plane of the Fe–P binary); (3) the tie line permitted close to the $\alpha + \text{Ph}/\alpha + \gamma + \text{Ph}$ boundary is parallel to that boundary. As shown in Fig. 4, rotation of tie lines occurs in going from (2) to (3).

Since local equilibrium at the two phase $\alpha/\text{Ph}$ interface must be maintained according to the model, the Ni and P compositions of the $\alpha$ and Ph at the $\alpha/\text{Ph}$ interface for any temperature and time are assumed to lie on a tie line in the $\alpha + \text{Ph}$ phase field. Figure 5 shows the $\alpha + \text{Ph}$ phase field at 500°C as well as several tie lines in the two phase field. The tie line through the bulk Ni and P composition of a meteorite is called the Equilibrium Tie Line (ETL). While phosphide growth is occurring, the interface tie line will usually shift away from the ETL in order to achieve a balance of the Ni and P mass fluxes into the growing phosphide. During cooling, the tie line shift is to the left of the ETL or to lower Ni contents to accommodate the faster rate of P diffusion. The amount of tie line shift is dependent upon several factors including cooling rate and diffusion field length which is defined as half the distance between neighboring phosphide plates. Only at equilibrium, when there are no Ni or P gradients present in either phase, will the $\alpha/\text{Ph}$ interface compositions be given by the ETL. At equilibrium, the Ni content of the phosphide will be a maximum.

There are four variables which must be considered in applying the ternary phase growth model: (1) cooling rate; (2) bulk composition; (3) nucleation temperature of the phosphide; and (4) diffusion field length. The diffusion field length must be considered because there is competition for Ni and P from adjacent phosphides. For a given meteorite the bulk composition can be measured experimentally and can be eliminated as a variable in the growth model. To obtain a unique cooling rate for a given meteorite one of the two remaining factors, nucleation temperature and diffusion field length, must be well understood.

**Nucleation temperature of phosphides in hexahedrites**

The amount of undercooling which precedes phosphide nucleation is unknown. It could be as little as 1°C or perhaps as much as 200°C. Reed (1965) and Goldstein and Ogilvie (1963) have discussed the phosphide nucleation problem for iron meteorites. Goldstein and Ogilvie propose a sequential nucleation process in which phosphide plates (plate rhabdite) form at high temperatures and phosphide rhombohedrons (rhabdite) form at lower temperatures. A second possible nucleation process assumes that phosphide plates (plate rhabdite) and rhabdites nucleate simultaneously. In this process plates nucleate heterogeneously at $\alpha/\gamma$ interfaces while rhabdites nucleate homogeneously in supersaturated $\alpha$. Alternatively both plates and rhabdites nucleate homogeneously in $\alpha$. If the sequential nucleation process is correct, the modeling of phosphide growth becomes difficult since the nucleation temperatures of the phosphides cannot be specified.

To decide between these two nucleation processes calculations were made to determine the effects of undercooling on the initial growth of phosphide. The computer model of Randic and Goldstein (1975) for phosphide growth was applied to a hypothetical hexahedrite cooled through 500°C. The Ni and P gradients as well as the phosphide size were calculated as the function of nucleation temperature. The cooling rate and diffusion field length used were $10^{-4}/10^6$ yr and 1000 μm. Three nucleation temperatures (600, 550 and 501°C) which represent 100, 150 and 200°C of undercooling were considered. The Ni and P gradients and phosphide size were calculated as the hypothetical hexahedrite “cooled through” 500°C.

Clearly if nucleation temperature is an important variable, the Ni and/or P gradients will be different at 500°C.

The calculated results showed that the predicted Ni and P gradients as well as the phosphide size were identical for the three nucleation temperatures considered. There were virtually no Ni or P gradients in either phosphide or $\alpha$ indicating that all three simulated phosphides were essentially in equilibrium with the $\alpha$ matrix as they cooled through 500°C. Even if a phosphide nucleated at 501°C (200°C of undercooling), it was in equilibrium with the $\alpha$ matrix after cooling only 1°C. Therefore the nucleation temperature of phosphide is not important and need not be specified for hexahedrites as long as nucleation occurs above 500°C and the actual cooling rate is $10^{-4}/10^6$ yr.

The attainment of equilibrium at 500°C for all three nucleation temperatures illustrates several points with respect to the application of the phase growth model to hexahedrites. Any chosen nucleation temperature above 500°C will result in an equilibrium $\alpha + \text{Ph}$ phase assemblage at 500°C assuming a diffusion field length of $\leq 1000$ μm. Therefore as long as the phosphide nucleates at or above 500°C, a valid starting point for the model is an equilibrium $\alpha + \text{Ph}$ phase assemblage at 500°C. This condition is correct no matter how small or how large the amount of undercooling. In cases where the diffusion field length is less than 300 μm, equilibrium $\alpha + \text{Ph}$ phase assemblages occur even below 500°C. Therefore a valid starting temperature for the model in this case will be below 500°C. The fact that equilibrium is attained to 500°C and below for all the hexahedrites studied as confirmed by further calculations eliminates nucleation temperature as a variable in the phase growth.
Cooling rates of seven hexahedrites

In addition, all taenite has disappeared by 600°C (see Fig. 3). Since our calculations predict equilibrium as low as 500°C, any effect of the presence of γ [Path (2)] on the growth process at or below 500°C is also eliminated.

In the sequential nucleation process, if the plates nucleated before rhabdites, these plates would grow and in so doing would constantly deplete P and Ni from the α matrix. This P and Ni depletion would hinder rhabdite formation. At simulated plate spacings of 500 μm for the Coahuila meteorite the amount of P depletion in α would prevent even one rhabdite (which nucleated at some lower temperature between the plates) from thickening to >1 μm. In hexahedrites, numerous rhabdites with dimensions greater than 1 μm are found between plates separated by less than 500 μm. The simultaneous nucleation process for plates and rhabdites is therefore more consistent with observation and will be assumed for the phase growth model. This assumption applies to rhabdites only.

Hieroglyphic phosphides and micro-rhabdites did not nucleate simultaneously with the rhabdites. Hieroglyphic forms nucleated at high temperatures (>850°C) and micro-rhabdites probably nucleated at very low temperatures (<300°C). This last type of phosphide forms areas of frosty kamacite [Axon and Waine (1972)].

Cooling rate curves for hexahedrites

The two remaining variables, cooling rate and diffusion field length, L, allow one to determine unique cooling rates for hexahedrites of known Ni and P contents. To illustrate the effect of L on phosphide growth, two cases are discussed: first, the case for a very small L (50 μm) and second, the case for a very large L (1000 μm). In both cases the bulk Ni and P composition, cooling rate, starting temperature (T₁) and final temperature (T₂) are 5.5 wt.% Ni, 0.5 wt.% P, 10°C/10⁶ yr, 500 and 250°C respectively. In the first case of phosphide growth (L = 50 μm) the interface tie line shifts to the left of the ETL during cooling (Fig. 5). Since the diffusion distances are small, impingement of both Ni and P occurs rapidly and Ni and P are depleted over the total length L. Ni and P gradients in both the Ph and α phase approach zero and the interface tie line is always very close to the ETL. At T₂ the Ni content of the phosphide is only slightly less than that given by the ETL. The size of the phosphide is however limited by the amount of Ni and P present in 50 μm of α. Thus an L of 50 μm results in a small phosphide (~2 μm) with a high Ni content.

In the second case of phosphide growth, L is much larger, 1000 μm. During growth the interface tie line shifts to the left of the ETL. Since diffusion distances are very large, impingement does not occur and the Ni and P gradients in the α phase are appreciable. Therefore the phosphide Ni content is not close to equilibrium during cooling. At T₂ the Ni content of the phosphide is much less than that given by the ETL. The size of the phosphide is not limited by a lack of Ni and P from the surrounding α and therefore the phosphide width is much larger than the width obtained for L = 50 μm. In summary, if all other variables are held constant, a small, high Ni phosphide will form when the diffusion field length L is small and conversely, a large, low Ni phosphide will form when the diffusion field length L is large.

This relationship between phosphide size and Ni content of phosphides offers a simple way to determine the cooling rate of a hexahedrite. Figure 6 shows a family of “cooling rate curves” (CRC) for a hexahedrite containing 5.5 wt.% Ni and 0.5 wt.% P cooling at rates of 1, 10, 100 and 1000°C/10⁶ yr. Each curve is generated in the following manner. The cooling rate is held constant and simulations are made for several values of L. Each of these simulations grows a phosphide which has a unique Ni content and width at T₂. The calculated Ni content of the phosphide is essentially constant across the phosphide. To generate a CRC curve, the final phosphide Ni content at T₂ is plotted versus phosphide width, for each simulation. The points for L = 100, 300, 500 and 1000 μm are labeled on Fig. 6. Curves for different cooling rates are obtained in an analogous manner. Cooling rates falling between the curves can be interpolated on a logarithmic basis.

Figure 6 shows that all CRCs intersect at one phosphide Ni content when the phosphide width approaches zero. As the diffusion field length approaches zero, the phosphide width also approaches zero and equilibrium is maintained to T₂ regardless of cooling rate. The Ni content for this condition is given by the ETL at T₂. For the simulations in Fig. 6, T₂ is 250°C and the CRC intersection occurs at 37.5 wt.% Ni (solid lines in Fig. 6) for the bulk composition of 5.5 wt.% Ni and 0.5 wt.% P. Theoretically, as L approaches zero, equilibrium can be maintained to room temperature. The actual intersection will approach 45 wt.% Ni as predicted by the


Table 2. Cooling rates and compositions of hexahedrites examined in this study

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<thead>
<tr>
<th>Authors Copy</th>
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<tr>
<td>Cooling Rate</td>
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<tr>
<td>(°C/10^6 yr)</td>
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</tr>
<tr>
<td>Walker County (BH 33413)</td>
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<tr>
<td>Tocopilla (RM 1931.13)</td>
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<tr>
<td>Coahuila (NM 54242)</td>
</tr>
<tr>
<td>Quillagua (NMN 23126)</td>
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<tr>
<td>Lombard (USNM 1684)</td>
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<tr>
<td>Uvet (BH 1908.171)</td>
</tr>
<tr>
<td>Hex River Mts. (NMN 3815)</td>
</tr>
</tbody>
</table>

* BUCHWALD (1975).
++ MOORE et al. (1969).
** LEWIS and MOORE (1971).
* This study.

The effect of a lower $T_i$ is more important at slower cooling rates. For cooling rates greater than 1°C/10^6 yr the only portion of a CRC curve significantly affected by a $T_i$ of less than 250°C is for $L \leq 40$ μm. This corresponds to a phosphide width $\leq 3$ μm. Since the resolution of the electron microprobe limits experimental analysis to Ph plates $>2$ μm in width, the choice of $T_i = 250$°C is a reasonable assumption for cooling rates $\geq 1°C/10^6 yr$.

A hexahedrite cooling rate can be obtained using the CRC curves appropriate to that meteorite in conjunction with measured values of Ni content and phosphide width. The diffusion field length need not be measured or evaluated because each CRC family is generated using a range of suitable $L$ values. Measurements are typically made on several different size phosphides in a sample. When plotted on the CRC family for that hexahedrite, these data should uniquely define the cooling rate for the hexahedrite.

This method for cooling rate determinations is subject to one restriction. Only growth of plate phosphide can be simulated in the analysis. The method is not applicable to growth of small rhabdites because the mathematical model assumes one dimensional phase growth, in which the length of the simulated phosphide must be much greater than its width. Small rhabdites and hieroglyphic forms do not meet these dimensional requirements.

SAMPLE ANALYSIS

AXON and Waine (1972) have demonstrated the gross variation of structure that exists across large sections of hexahedrites. Therefore careful examination of such large metallographic sections must precede any attempt to obtain small sections of a hexahedrite for microprobe analysis. Large polished sections (ranging from ~100 to 750 cm^2 in area) of hexahedrites from the collections of the British Museum (London, England) and the National Museum of Natural History (Washington, DC) were polished and metallographically examined. Twenty-seven hexahedrite sections were examined. Only seven hexahedrites had sections which were suitable for analysis (Uvet, Coahuila, Walker County, Lombard, Quillagua, Hex River Mountains and Tocopilla). The remaining samples were rejected because of a lack of suitable plate rhabdites or the presence of abundant terrestrial corrosion. Representative samples of each of the seven hexahedrites were cut from the larger sections or chosen from existing museum samples. These specimens range from 10 to 30 cm^2 in surface area.

Each specimen was prepared by standard polishing techniques through 1/4 μm diamond paste and etched in 2% nital for metallographic examination. Suitable corrosion free plate phosphides were selected for microprobe analysis. Each specimen was sectioned with a diamond cut-off wheel and the widths of a number of phosphides were obtained by a two surface analysis. For thin phosphides, widths were measured using a scanning electron microscope. The precision of the corrected Ph widths is ±5% for all specimens except Walker County where terrestrial corrosion decreased the precision to ±20%.

An ARL-EMX electron microprobe was used for the analysis of each of the selected phosphide plates. Operating parameters were 20 kV accelerating voltage and 0.05 μA sample current. Because of the finite X-ray source size, plates smaller than 2 μm in width could not be analyzed reliably. To assure maximum resolution, 1/4 μm steps were taken across plates of ≤4 μm width.

A hieroglyphic phosphide of known Ni content in the hexahedrite Lombard was used as a P standard and chemically analyzed; annealed alloys of Fe and Ni were used as Ni standards. Background for Ni and P were obtained from a pure Fe standard. Errors due to counting statistics were <1%. A statistical calculation of P and Ni detectability limits, using the method of ZIEBOLD (1967), yields 125 and 340 ppm respectively. X-ray intensity data were corrected for matrix effects using the correction program of Rucklidge and Gasparini (1969).

Phosphide widths and Ni compositions were measured at the same point on each phosphide. The Ni composition vs phosphide width was plotted on a CRC curve for each hexahedrite. In all cases the phosphides were homogeneous in Ni across their widths. Approximately ten such data points were plotted for each meteorite.

The reported Ni and P bulk compositions of the hexahedrites studied are listed in Table 2. The compositions used in the computer simulations are underlined. In choosing these values we preferred using matched Ni-P pairs from the same study when available. When this was not possible, we chose the most recent values reported by BUCHWALD (1975) or WASSON (1969). For Tocopilla and...
Cooling rates of seven hexahedrites were determined by this method are \(0.43 \pm 0.03\) and \(0.39 \pm 0.04\) wt\% respectively and are listed in Table 2.

**RESULTS**

Input parameters for the computer program are the bulk composition of the hexahedrite, the nucleation temperature of the phosphide, the cooling rate, and the diffusion field length. The Ni and P bulk compositions used for the hexahedrite simulations are listed and underlined in Table 2. As discussed previously, a nucleation temperature of 500°C or below can be assumed for the phosphide. At least two cooling rates, 1 and 10°C/10\(^6\) yr, were simulated for each hexahedrite. For each cooling rate simulation at least three values of \(L\) were used; 100, 300 and 500 \(\mu\)m. The point of intersection of the CRC family at \(L = 0\) was calculated from the ETL at 250°C. Simulation results were plotted as CRC families, i.e. phosphide Ni content vs phosphide width for each cooling rate.

Figure 7 shows the measured microprobe data (phosphide Ni content vs width) for the hexahedrite Coahuila. A “best fit” curve drawn through the data is consistent with a CRC cooling rate curve of 10°C/10\(^6\) yr. Scatter in the data indicate a cooling rate range of 5–15°C/10\(^6\) yr as shown on Fig. 7. Figure 8 shows the measured data and CRC curves for the other six hexahedrites studied. Cooling rates were obtained from a “best fit” curve through the data and cooling rate ranges were obtained from the maximum scatter in the data for each hexahedrite.

![CRC analysis of Coahuila](image)

**Fig. 7.** CRC analysis of Coahuila. Data points are given as filled circles.

Quillagua bulk P compositions were unavailable. Quantitative metallography was used to obtain these values. In this technique one measures the area percent phosphide on one or more polished surfaces. This area per cent is then converted to wt\% P. The P remaining in solution in the kamacite (~0.03 wt%) is then added to the value obtained from the metallographic analysis. Before applying this technique to Tocopilla and Quillagua a check was run on the hexahedrite Coahuila. A phosphorus value of \(0.28 \pm 0.03\) wt% was found which is comparable to the measured chemical value, Table 2. The P values for Tocopilla and Quillagua determined by this method are \(0.43 \pm 0.03\) and \(0.39 \pm 0.04\) wt% respectively and are listed in Table 2.

![CRC analysis of Walker County, Hex River Mountains, Tocopilla, Quillagua, Uwet and Lombard](image)

**Fig. 8.** CRC analysis of 6 hexahedrites: Walker County, Hex River Mountains, Tocopilla, Quillagua, Uwet and Lombard.
Table 2 lists the measured cooling rates and cooling rate ranges of the seven hexahedrites studied. A variation in cooling rate from 0.8 to 10°C/10^6 yr was measured. The "best fit" cooling rates of six of the seven hexahedrites lie within a small range, 0.8 to 3°C/10^6 yr.

**DISCUSSION**

**Growth of phosphides**

Goldstein and Ogilvie (1963) reported electron microprobe analyses of various sized schreibersites in the Canyon Diablo, Breeze and Grant octahedrites. They observed an inverse correlation between phosphide Ni content and phosphide width. Reed (1965) confirmed this correlation by measuring the range of Ni values in schreibersites and rhabdites from a large number of meteorites. Although it is recognized that schreibersite growth is controlled by solid state diffusion, no theory currently exists to explain fully the relationship between phosphide Ni content and phosphide width.

The phase growth model of Randich and Goldstein (1975) predicts that for a given cooling rate the phosphide Ni content will increase as the phosphide width decreases (see Fig. 6). This variation is the basis of the cooling rate method that is used in this study. The diffusion field length between growing phosphides limits the supply of Ni and P available for growth and therefore controls the growth rate and the Ni contents of the (α and phosphide at the α/Ph interface. As the diffusion field length decreases, the tie lines which define the composition of the α/Ph interface approach the ETL. The phosphide Ni content is highest when the α + Ph tie line passes through the ETL. In other words, at one cooling rate, phosphides can develop very different Ni contents and sizes primarily due to the variation in diffusion field length, that is the distance between adjacent phosphide particles. The model has been applied strictly to hexahedrites but the general relationship no doubt applies to phosphide growth in other types of iron meteorites. The application of this cooling rate model to octahedrites is very complex however, and requires a knowledge of the Widmanstätten pattern (α + γ) growth as well.

**Precision and accuracy of the cooling rate analysis**

The phase growth model has two independent sources of error: (1) numerical approximations used in the solution of the diffusion equations; and (2) inaccuracies in the constants used in the program, the diffusion coefficients, and phase diagrams (Randich, 1975). These sources of error primarily effect the accuracy of the calculated CRC curves.

Because the model uses a numerical solution (rather than an analytical solution) to the mass flux equations, approximation and round off errors occur. These errors take the form of mass errors which accumulate during the simulation. For hexahedrites, simulation times can be as long as 2.5 × 10^8 yr. For this condition, a spurious relative mass increase of up to 10% in P and up to 4% in Ni was calculated. As mass leaks into the system the phosphide appears to grow more than it would if no mass leakage occurred. For a given phosphide Ni content (or L) this results in a phosphide width that is ~10% too large. This error is noticeable only at large phosphide widths. Mass leakage effects thus tend to artificially flatten the CRC curves at large phosphide widths. For measured phosphide widths of less than ~30 μm, mass leakage errors are not significant and can be safely ignored. Note that except for Hex River Mountains we have restricted our CRC analysis to phosphides not larger than 30 μm.

A second source of error in the phase growth model is the error associated with the constants used in the cooling rate model. The measured ternary diffusion coefficients (D_P, D_Ni in the α and Ph phases) have accuracies of ±20% (Heyward and Goldstein, 1973; Norkiewicz and Goldstein, 1975). The extrapolated ternary coefficients have much larger inaccuracies estimated to be ~±50%. The errors introduced into the cooling rate analysis by inaccuracies of ±50% in the diffusivities lead to calculated cooling rate variations of ±20%. The Fe–Ni–P diagram has not been experimentally determined at temperatures below 550°C. Therefore the α + Ph phase field was extrapolated from 550 to 250°C as discussed previously in the section on the phase growth model. The major uncertainties in the extrapolation are the Ni and P contents at Y2 and the Ni content at the phosphide triple point (Note Fig. 4). It is difficult to assess the errors inherent in the extrapolation method. However, several authors [Clarke (1976) and Moren (1978)] have independently made extrapolations of pertinent portions of the Fe–Ni–P diagram. Comparisons of calculated Ni and P concentrations at Y2 from these two studies and the present study are given in Table 3. The P solubilities in α below 500°C are substantially less than those used in this study and the Ni contents at Y2 by Moren (1978) follow the same general form but the maximum Ni solubility in α at 450°C is 0.4 wt% less than that used in this study. The errors introduced into the cooling rate analysis by extrapolations of the phase diagram can be estimated using the calculated diagrams of Clarke (1976) and Moren (1978). If the P solubilities of Moren (1978) are substituted in the cooling rate model for the P solubilities at Y1 and Y2 (Fig. 4) and the Ni values at Y2 and the Ph triple point are not changed, the calculated cooling rates will increase by ~10%. If the P and Ni solubilities at Y2 of Moren (1978) are substituted in the cooling rate model, the P solubility at Y1 is assumed equal to that at Y2, and the Ni value at the Ph triple point is assumed equal to the Ni content at Y2 multiplied by the factor FT used in this study (Table 1), the calculated cooling rates are increased by a larger amount ~20%. The errors due to the extrapolated phase diagram and diffusion coefficients will have a major effect up to ~±30% on the accuracy of the cooling rate values.
Table 3. Comparisons of α + Ph phase field boundaries at Y2 in the Fe–Ni–P phase diagram

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Ni (wt%)</th>
<th>P (wt%)</th>
<th>Ni (wt%)</th>
<th>P (wt%)</th>
<th>Ni (wt%)</th>
<th>P (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This Study</td>
<td>Moren (1978)</td>
<td>Clarke (1976)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>7.4</td>
<td>0.26</td>
<td>6.9</td>
<td>0.24</td>
<td>0.23</td>
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<tr>
<td>500</td>
<td>8.2</td>
<td>0.19</td>
<td>7.6</td>
<td>0.16</td>
<td>0.17</td>
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</tr>
<tr>
<td>550</td>
<td>8.3</td>
<td>0.14</td>
<td>7.9</td>
<td>0.09</td>
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</tr>
<tr>
<td>400</td>
<td>8.1</td>
<td>0.10</td>
<td>7.8</td>
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<tr>
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<tr>
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<td>6.5</td>
<td>0.04</td>
<td>5.3</td>
<td>0.006</td>
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</tr>
</tbody>
</table>

* Solubility Limit Equations below 600°C. \( \log Y_2 (\text{wt} \% P) = 2.34635 - 0.243898 \times 10^9 / T (\text{°K}) \). \( Y_2 (\text{wt} \% \text{Ni}) = -7.1714 + 0.12312 (T, \text{°C}) - 0.71242 \times 10^{-3} (T, \text{°C})^2 + 0.27950 \times 10^{-5} (T, \text{°C})^3 - 0.58455 \times 10^{-8} (T, \text{°C})^4 + 0.57933 \times 10^{-11} (T, \text{°C})^5 - 0.21612 \times 10^{-14} (T, \text{°C})^6. \)

obtained. Since the bulk Ni and P contents of the hexahedrites are similar, the relative magnitude and sign of these errors will be the same for all the meteorites and should not influence the relative values of the cooling rates.

The precision of the cooling rate values obtained by the CRC analysis depends on the assumption of a constant cooling rate, the accuracy of the measured hexahedrite bulk Ni and P compositions and the variation or scatter in the measured Ni content and widths of the analyzed phosphides for each meteorite. The phase growth model assumes a constant cooling rate. The temperature–time relationship in a parent body may not have been linear. The thermal models of Goldstein and Short (1967b) and Fricker et al. (1970) demonstrate that for the temperature range of interest (500–250°C) a linear cooling rate is a reasonable approximation.

Bulk Ni compositions listed in Table 2 have associated errors of approximately ±0.1 wt%. We estimate errors in the P values to be approximately ±0.05 wt%. Our quantitative metallography values of P also show this type of variation. Such bulk Ni and P composition errors will affect the position of the CRC family. The small compositional variations of the seven hexahedrites shown in Table 2 from all investigators (5.46–5.75 wt% Ni, 0.22–0.43 wt% P) could be interpreted as indicating that all these hexahedrites have approximately the same composition. Trace element data given in Table 2 do not substantiate this argument. However the error introduced in each CRC family due to bulk composition uncertainty can be examined by superimposing the measured microprobe data (phosphide Ni content vs width) for all seven hexahedrites on a CRC curve for the average bulk Ni–P content of these hexahedrites, 5.60 wt% Ni–0.31 wt% P. Figure 9 shows these data with the appropriate 1 and 10°C/10^6 yr CRC curves. A “best fit” curve drawn through the data for each hexahedrite gives a “best fit” cooling rate which differs by less than ±50% from the cooling rates listed in Table 2 and does not enlarge the upper and lower bounds of the cooling rate range for each meteorite.

Scatter in the measured Ni content and width of the phosphides in each hexahedrite is clearly the most significant factor in determining the precision of a cooling rate analysis (see Figs. 7–9). This is particularly true because Ni contents, calculated for CRC curves showing factor of ten variations in cooling rates, change by only small amounts, ~5 wt% Ni (note Figs. 7 and 8).

In summary, errors in bulk Ni and P composition, as well as scatter in the data for phosphide Ni contents and widths, make it difficult to establish the cooling rate of a hexahedrite with a precision of better than a factor of ±3. Considering the large cooling rate range now established for each meteorite (Table 2) it is not possible to argue that any one hexahedrite

Fig. 9. CRC analysis of average hexahedrite, 5.60 wt% Ni, 0.31 wt% P. The measured microprobe data from all seven hexahedrites are also plotted in the figure.
except perhaps Coahuila has a uniquely different cooling rate. The general range of cooling rates (0.8–10°C/10⁶ yr) for the hexahedrites is similar to the cooling rate range of the octahedrites (GOLDSTEIN and SHORT, 1967).

The hexahedrite Uwet requires special consideration. The bulk of Uwet's CRC data fall at 2°C/10⁶ yr, the same cooling rate as Lombard. However three data points, all at the smallest phosphide widths, fall well above the 2°C/10⁶ yr CRC. Uwet is unique among hexahedrites. It was heavily shocked and suffered a late cosmic reheating to temperatures of at least 300–400°C (BUCHWALD, 1975). Unlike the other hexahedrites, plate rhabdites in Uwet have both {001} and {112} habit planes (RANDICH and ECKELMEYER, 1977). Many rhabdites in Uwet are aligned in rows with a habit plane (112) and traverse the entire section (Fig. 1b). This alignment has been interpreted by RANDICH and ECKELMEYER (1977) as indicating a large mechanical deformation or shock event may have occurred simultaneously with the nucleation of plate rhabdites. The (112) plane is the twinning plane of kamacite and the twin boundary could be a preferred nucleation site for rhabdites. The late reheating event may have also affected the nucleation and growth processes, particularly for the smallest phosphides, where low temperature growth controls the phosphide Ni content.

Hexahedrite parent bodies

Considering the errors described in the computer analysis and data measurements for the seven hexahedrites studied, six of the meteorites with measured cooling rates from 0.8 to 3°C/10⁶ yr can be considered as having the same cooling rate ~2°C/10⁶ yr. Thermal models for meteorite parent bodies, as proposed by FRICKER et al. (1970) show that a cooling rate of 2°C/10⁶ yr (at 500°C) corresponds to the center of a parent body with a radius of ~150 km. The hexahedrite Coahuila has a cooling rate of 10°C/10⁶ yr which lies above the average cooling rate of the other six hexahedrites. However, the cooling rate range of Coahuila does overlap the cooling rate ranges of many of the other six hexahedrites (Table 2). Therefore a unique cooling rate for Coahuila cannot be positively established. However if the 10°C/10⁶ yr cooling rate for Coahuila is correct, the meteorite would be present at a fractional radius of 0.5 or greater in a 150 km radius body. It is interesting to note that the six hexahedrites of similar cooling rate also have similar Ir contents (2.3–4.4 ppm, Table 2), while Coahuila has an Ir content of 16 ppm.

Trace element analyses by WASSON (1969) have placed hexahedrites in the chemical group IIA. All members of IIA have Ga contents between 56 and 66 ppm and Ge contents between 170 and 190 ppm. These two elements are positively correlated with Ni while Ir shows a strong negative correlation with Ni. Because of the trace element correlation and close similarities in composition and microstructure, WASSON (1969) and SCOTT (1972) argue that the members of Group IIA (combined with those of IIB) form a single fractionation sequence. KELLY and LARIEMER (1977) have recently presented a comprehensive review of models for the formation of meteorite parent bodies and argue that members of Group IIAB formed by fractional crystallization presumably in a core of a parent body.

The interpretation of the chemical fractionation sequence for the hexahedrites is not yet clear. We have analyzed only 18% of the known hexahedrites. More samples, particularly of higher Ir content, should be analyzed. Our cooling rate analysis indicates that all the hexahedrites except for one possible exception were formed in or close to the core of one parent body.

SUMMARY

1. A computer model, developed by RANDICH and GOLDSTEIN (1975), for non isothermal ternary diffusion controlled growth was applied to the exsolution and growth of plate rhabdites, phosphides, in seven hexahedrites. The major assumption of the model is that of local equilibrium at the α (kamacite)–Ph (phosphide) interface. The four variables, cooling rate, bulk Ni and P composition, nucleation temperature and diffusion field length, which influence phosphide growth were considered in the model.

2. Computer simulations show that the effect of undercooling of phosphide above 500°C where γ (taenite) is present is unimportant. In addition a simultaneous nucleation theory appears to best describe the formation of rhabdites.

3. A cooling rate curve, CRC, analysis was developed in which a hexahedrite cooling rate can be determined simply by measuring the Ni content and width of several plate phosphides in one meteorite and by comparing these values to computer generated curves. The CRC analysis predicts that the smaller the phosphide width, the higher will be the Ni content of the phosphide. Such a correlation has been observed for phosphides in many types of iron meteorites.

4. Six of the seven hexahedrites have cooling rates of approximately 2°C/10⁶ yr. The seventh hexahedrite, Coahuila, has a somewhat higher but overlapping cooling rate of 10°C/10⁶ yr. These cooling rates fall within the range calculated by an independent method for octahedrites. Our cooling rate analysis indicates that the hexahedrites except for one possible exception were formed in or close to the core of a parent body approximately 150 km in radius.

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