The metallic microstructures and thermal histories of severely reheated chondrites

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Abstract—The metallographic structures of eight severely reheated chondrites (Farmington, Ramsdorf, Orvinio, Wickenburg, Lubbock, Rose City, Arapahoe and Tadjera) have been studied by optical, scanning electron microscope and electron microprobe techniques. Unreheated chondrites and experimentally heat treated chondritic material have also been examined. The following metallographic characteristics can be used to estimate the post-shock residual temperature of reheated chondrites: melted appearance of metal–troilite, presence of martensite, P enrichment of the metal, and the averaging of central metal grain compositions. Metallographic characteristics used to estimate the cooling rates of the severely reheated chondrites are the Ni content of troilite, the Ni gradients in metal grain rims, and the presence of secondary kamacite and phosphides. Farmington, Ramsdorf, Orvinio, Lubbock, Rose City and several of the heat treatment specimens have substantial P in solution in the metal grains (> 0.1 wt%). P enrichment is apparently caused by reduction of phosphates upon severe reheating and partial melting of metal–troilite areas in chondritic meteorites.

The eight severely reheated chondrites studied showed evidence of reheating to temperatures ranging from ~950°C to ~1250°C. Ramsdorf has the highest reheating temperature (1200–1250°C) and the fastest cooling rate ~100°C/day. Wickenburg has the lowest: reheating temperature (950–1000°C) and the slowest cooling rate, ~1°C/100 yrs. Cooling rate estimates correspond to post-reheating burial depths of less than 1 to ~1000 m.

INTRODUCTION

Reheated chondrites have been studied by several investigators (BUSECK et al., 1966; HEYMANN, 1967; WOOD, 1967; BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1969, 1971). It is commonly believed that the reheating among ordinary chondrites is related to shock. By studying the mineral and metal phases in selected shocked ordinary chondrites, estimates of the maximum reheating temperatures and cooling rates of these samples have been made (WOOD, 1967; BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1969, 1971). Reheating temperatures range as high as ~1350°C and cooling rates vary widely from ~0.05°C/sec to ~0.01°C/yr. Several microstructural characteristics of the metal phases of the shocked chondrites are used to estimate reheating temperatures and cooling rates. Among these characteristics are

(1) Martensite which is often called $\alpha_2$ and indicates shock reheating to $\geq$600°C (WOOD, 1967; TAYLOR and HEYMANN, 1971).

(2) Melted metal troilite microstructure which includes ovoid metal grains in troilite, rounded metal-troilite boundaries and tiny veins of metal–troilite within the silicate. The presence of melted metal–troilite structures indicates partial melting at or above 950°C (HEYMANN, 1967).

(3) Steep Ni gradients in $\alpha_2$ grain rims which indicate extensive remelting with subsequent fast cooling (BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1971).

(4) Secondary kamacite which nucleates and grows from taenite ($\gamma$) during cooling (TAYLOR and HEYMANN, 1971).

(5) Relative chemical homogeneity of metal grains which indicates extensive reheating of the original low Ni kamacite ($\alpha$) and high Ni taenite ($\gamma$) metal phases (BUSECK et al., 1966; HEYMANN, 1967; BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1971), and

(6) Phosphorus enrichment of the metal which occurs on reheating (BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1971) and the growth of phosphides during slow cooling.

In recent years metallic particles from lunar rocks and soils have been studied. Many of these particles have the same microstructural characteristics as noted for the metal in shocked chondrites (GOLDSTEIN and AXON, 1973; GOLDSTEIN et al., 1972; MISRA and TAYLOR, 1975). Therefore it appears that a better understanding of the metallic microstructure and thermal histories of severely reheated chondrites will also help in the interpretation of lunar samples. This study investigates the thermal history of eight severely shocked ordinary chondrites. In addition to using the metallographic characteristics already noted, equilibration temperatures of two phase kamacite–taenite, and metal–phosphide assemblages (AXON and GOLDSTEIN, 1972) are estimated.

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METHOD

Eight very strongly reheated or heavily shocked chondrites were selected for study: Farmington, Ramsdorf, Orvinio, Wickenburg, Lubbock, Rose City, Arapahoe and Tadjera. All the class 5, very heavily shocked samples studied by HEYMANN (1967) are included in the sample. The samples were mounted as polished sections and prepared for observation using standard metallographic polishing techniques. A 1% nital solution was used as an etchant to reveal metallographic structures.

An ARL electron probe microanalyzer was employed for elemental analysis of the opaque phases. Three types of measurements were made: (1) Ni, Co and P contents of a representative sample of metal grains, (2) Ni and P profiles across zoned metal grains and across phase boundaries with secondary kamacite and phosphide, and (3) Ni contents of the troilite. The X-ray scanning mode was used to study elemental distribution between phases and to identify phosphides and phosphates. An ETEC scanning electron microscope equipped with an energy dispersive detector was used to study the fine structure of the metallic phases and to search for and detect small (<1 μm) phosphides in the metal phases.

Several grams of the chondrite Knyahinya were used for the experimental heat treatments. This meteorite is a non-weathered, very lightly reheated, L5 chondrite and its structure and composition should be quite similar to that of the hypersthene chondrites before shock. Individual small pieces of Knyahinya were cut from the sample and heated to maximum temperatures varying from 900 to 1250°C and cooled at rates varying from 100°C/week (2 × 10^-4°C/sec) to a quench (≈ 500°C/sec). The rapidly cooled pieces were annealed in a vertical molybdenum furnace and were protected from oxidation by flowing argon through the furnace tube. The more slowly cooled samples were vacuum encapsulated in quartz tubes and heated in a horizontal resistance furnace. Cooling rates were controlled by a Trendtrak automatic programmer.

RESULTS AND DISCUSSION

Microstructural and chemical criteria

The following microstructural and chemical features were studied for each of the reheated chondrites: martensite, melted metal–troilite microstructure, phosphorus enrichment of metal, metal grain compositions, Ni gradients at the rims of metal grains, Ni content of troilite, the presence or absence of phosphides and secondary kamacite (α), and the compositions of phosphides and secondary kamacite. Table I gives a summary of the major microstructural and microprobe results for the eight reheated chondrites.

There are two basic groups of criteria: those that reveal information about the maximum reheating temperature caused by the shock process and those that reveal information about low temperature conditions from which cooling rates can be estimated. Martensite, melted metal–troilite microstructure, averaging of metal grain compositions and P enrichment of the metal indicate extensive reheating and in most cases remelting of the shocked chondrites. The presence of phosphides and secondary kamacite indicates relatively slow cooling rates. Composition and width measurements of these two phases can be used to estimate cooling rates. Ni gradients at the rims of metal grains and the Ni content of troilite indicate substantial reheating, but, more critically, reveal qualitative information on cooling rates.

Reheating temperatures

Martensite. Martensite or α2 was observed in all eight reheated chondrites and in most of the heat treated samples. Figure 1 shows the α2 structure in Farmington. Various morphologies of martensite were observed among the samples and were apparently due to differences in metal composition. Since α2 occurs upon relatively fast cooling of γ-Fe from a temperature ≥800°C (TAYLOR and HEYMANN, 1971), the presence of α2 in the chondrites indicates that these meteorites experienced temperatures ≥800°C. The presence of martensite apparently reveals no information about the maximum temperature of reheat-
ing or about the cooling rate except that the shocked chondrites have not cooled at an extremely slow rate such as that experienced by the iron meteorites.

**Melted metal–troilite microstructure.** The appearance of melted metal–troilite varied among the reheated chondrites and the heat treated samples. Ovoid metal grains agglomerated within troilite indicate extensive remelting. These structures are common in Ramsdorf (Begemann and Wlotzka, 1969), Orvinio (Taylor and Heymann, 1971), Rose City, and several of the heat treated samples (see Fig. 2). Metal in Lubbock, Farmington, Arapahoe and Tadjera typically occurs in irregularly shaped grains with rounded metal–troilite boundaries (see Fig. 1). Metal–troilite interfaces in Wickenburg are intermixed in a eutectic structure previously observed by Taylor and Heymann (1971), Fig. 3.

All of the shocked chondrites contain tiny blebs of metal–troilite dispersed in the silicate. Veinlets are plentiful in Tadjera, Arapahoe, and the moderately remelted samples of Knyahinya (Fig. 4). It appears that veinlets occur most plentifully in samples which were not extensively remelted and/or cooled fairly quickly. Samples of Knyahinya heated to a maximum temperature of 900°C showed very few signs of remelting. Therefore 900°C is probably a lower temperature limit for chondritic metal–troilite melting.

On the basis of the observed metal troilite microstructure, Ramsdorf was the most extensively remelted chondrite followed by Orvinio, Rose City, Lubbock, Tadjera, Arapahoe, Farmington and Wickenburg.

**Phosphorus enrichment.** Farmington, Lubbock, Orvinio, Ramsdorf and Rose City contain substantial P (>0.10 wt%) in the metal phase (Table 1). Wickenburg, Tadjera and Arapahoe have low P contents (<0.10 wt%) and compare with unreheated chondrites in this respect. Some of the artificially heated samples contain substantial P in the metal phase (0.15–0.83 wt%). Since the Knyahinya starting material contained <0.01 wt% P in the metal phase, these experiments showed that it is possible to enrich the metal phase in P upon reheating.

The reduction of phosphate is dependent upon the oxygen fugacity, \( f_{O_2} \), which must be low enough for a reduction reaction to occur (Olsen and Fuchs, 1967; Friel and Goldstein, 1976). Olsen and Fuchs (1967) proposed the following reduction reaction

\[
3\text{Ca}_2\text{Mg}[(\text{Si}_2\text{O}_5)_3] + 4\text{O}_2 + 3\text{Fe} + 2(\text{P})^{Fe} \\
\rightarrow \text{Ca}_3(\text{PO}_4)_2 + 3\text{MgFe}[(\text{Si}_2\text{O}_5)_3] (1)
\]

where \((\text{P})^{Fe}\) is the P content in the metal phase. This reaction can explain the relation of P in solution in the metal phase to metal–phosphate equilibrium in iron meteorites. Taylor and Heymann (1971) proposed a similar reaction for the reheated chondrites. Data from Williams (1971) indicate, however, that the \( f_{O_2} \) of ordinary equilibrated chondrites is too high for reduction via the above reaction to occur. Presumably during the shock process the local \( f_{O_2} \) in the chondrites is low enough to make reduction favorable. This low \( f_{O_2} \) may be caused by the presence of a reducing agent, such as C or CO (Taylor and Heymann, 1971). The P reduction in the experimental studies using the chondrite Knyahinya, may have been controlled by the presence of tantalum inside the sample capsules. The tantalum was used as an oxygen getter to protect the metal. The \( \text{Ta}_2\text{O}_5 – \text{Ta}_2\text{O}_3 \) equilibrium reaction probably buffered the \( f_{O_2} \) to well below the value needed for P reduction.

Once the \( f_{O_2} \) is favorable for P reduction, the amount of P which dissolves in the metal phase is probably most dependent on the volume ratio of phosphate to metal and the residual temperature \( (T_r) \) or maximum temperature of the chondrite after the shock event. The kinetics of P diffusion and the intimate contact of phosphate and metal would be increased during a partial melting stage. In general, the presence of increased P in the metal of reheated chondrites is consistent with other evidence of severe reheating. On the basis of the observed amount of P in the metal grains, Rose City, Orvinio and Ramsdorf have the highest maximum reheating temperatures followed by Lubbock, Farmington, Wickenburg, Tadjera and Arapahoe.

**Metal grain center compositions.** Previous investigators have noted that the Ni contents of metal grains in reheated chondrites are often similar from grain to grain (Heymann, 1967; Taylor and Heymann, 1971; Begemann and Wlotzka, 1969). The results of our measurements are illustrated in Fig. 5, where histograms of the number of grains vs central Ni content for an unreheated chondrite, Wellman, and for Orvinio, Farmington and Tadjera are given. Reheating–shock melting apparently has the effect of averaging out the original compositional differences between grains found in unreheated chondrites (Fig. 5a).

Begemann and Wlotzka (1969) proposed that such averaging out was due to melting, mixing, and redistribution of metal during shock reheating–remelting. This proposal is supported by the results of this study. The degree of compositional similarity of grain centers varies among the reheated chondrites studied (compare Fig. 5b–d) and coincides with the degree of remelting. Chondrites with extensively remelted metal–troilite (Ramsdorf, Orvinio, Rose City) have a narrow range of central Ni contents while the least remelted–reheated samples (Tadjera, Arapahoe, Farmington, Wickenburg) generally show a wide scatter. The veinlets observed in the least reheated chondrites (Fig. 4) indicate that molten metal and sulfide seeped through cracks in the silicate matrix and helped to some degree to mix the metal. For the more extensively remelted chondrites, molten metal and sulfide were able to mix thoroughly allowing a homogenization of the molten metal. Some time must have been available for this mixing to occur. Such a process however must proceed without allowing the metal–sulfide melt to separate from the surrounding silicate. Only minor amounts of solid state
By comparing and integrating results from the above criteria for the eight reheated chondrites, a relative ranking according to maximum reheating temperature can be made. Ramsdorf has the highest reheating temperature followed by Orvinio, Rose City, Lubbock, Farmington, Tadjera, Arapahoe and Wickenberg.

**Cooling rates**

**Ni rim gradients.** An increase in Ni at metal grain edges or rims of the reheated chondrites was measured (Table 2). The largest gradients are observed in Ramsdorf, Orvinio, Lubbock and Tadjera. Ni and P profiles are plotted in Fig. 6a for typical grain rims in Ramsdorf and in Fig. 6b for heat treated sample 15 (1250°C max temp, 100°C/day cooling rate). The Ramsdorf gradients are similar to those observed by Bögemann and Wlotzka (1969). Taylor and Heymann (1971) reported similar gradients in Orvinio and Lubbock. Bögemann and Wlotzka (1969) proposed that such gradients are due to Ni segregation during solidification of an Fe—Ni—S melt and this proposal is supported by the experimental heat treatments.

Given enough time or a slow cooling rate at high temperatures, the Ni gradients would be expected to be leveled out by solid state diffusion. Ni rim gradients are therefore indicators of relatively fast cooling, in accord with the steep Ni gradients observed in the artificially heated samples where the maximum temperature was >1050°C and the cooling rates were faster than 15°C/day (Fig. 6b).

**Ni in troilite.** The Ni contents of troilite in the reheated chondrites vary from <0.02 to 0.31 wt% (Table 1) and are higher than those of unreheated chondrites, which contain <0.02 wt%. Studies by Kullerud (1963) indicate that the Ni solubility in troilite decreases from <0.5 wt% at 900°C to <0.2 wt% at 650°C. Assuming that Henry's Law and the Neumann–Kopp Rule can be applied (Swalin, 1972), equilibrium solubilities of Ni in FeS for lower temperatures can be estimated by extrapolation from Kullerud's data. This extrapolation to the lower cooling temperatures of unshocked chondrites yields a solubility of ~0.01 wt% at 350°C. Therefore the increased Ni content of troilite in reheated chondrites is due to the reheating of metal–troilite assemblages, reequilibration of Ni into the sulfide, and the relatively fast cooling of the metal-troilite assemblage from high temperatures. Remelting of metal–troilite will increase the kinetics of the process. Slow cooling after shock melting would allow Ni to diffuse out of troilite and into the metal according to the solubility relations.

A semi-quantitative estimate of the cooling rate can be derived from the experimental samples, heat treated from 1050 to 1250°C. Their troilite contained substantial Ni (0.15–6.05 wt%), with the high Ni values in troilite obtained from samples cooled faster than 100°C/hr. Samples cooled at a rate of less than...
Fig. 1. Typical Farmington metal grain. $\gamma_2$ martensite (labeled M) is predominant structure. Troilite (T) and secondary $\alpha$ (a) are also present. Dark grey matrix is silicate. Nital etch. Marker = 25 $\mu$m.

Fig. 2. Typical Ramsdorf metal grain. Most of grain is $\gamma_2$. Light-etching high Ni rim (open arrow) surrounds $\gamma_2$. Troilite surrounds the metal. Nital etch. Marker = 25 $\mu$m.

Fig. 3. Metal and troilite of Wickenburg. The metal and troilite are finely intermixed in the central area of photo, indicating a eutectic structure. (Metal is lightest phase, troilite grey.) Major mass of metal is $\gamma_2$. No etch. Marker = 10 $\mu$m.

Fig. 4. Photo of Arapahoe featuring veinlets (arrows) of metal and/or troilite in silicate matrix (grey phase). Marker = 25 $\mu$m. Metal predominantly $\gamma_2$ with light-etching (high Ni) rim. Nital etch. Marker = 25 $\mu$m.

Fig. 9. Metal and troilite in heat treatment sample No.15 (1250 °C, 100 °C/day).
samples contained more than 0.15 wt% Ni. From these results, the cooling rates of the shocked chondrites are slower than 25°C/hr.

*Secondary kamacite (α). Secondary kamacite (α), was formed from the γ phase during cooling from maximum shock temperatures. It was observed in Farmington, Wickenburg, Rose City, Lubbock and Arapahoe (see Fig. 1). This phase was observed previously*
Table 3. Description of two phase (α/γ and phosphide/metal) particles in reheated chondrites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Build Composition</th>
<th>Precipitating Phase</th>
<th>Other Phase</th>
<th>Phase Diagram Employed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rose City</td>
<td>9 -0.50 α</td>
<td>6.15±0.20 0.30±0.05</td>
<td>γ &gt;18</td>
<td>Fe-Ni-P</td>
</tr>
<tr>
<td>Arapahoe</td>
<td>10 0.02 α</td>
<td>6.72±0.20 -0.02</td>
<td>γ</td>
<td>Fe-Ni</td>
</tr>
<tr>
<td>Lubbock</td>
<td>11 0.17 α</td>
<td>7.05±0.10 0.24±0.05</td>
<td>γ &gt;10</td>
<td>Fe-Ni-P</td>
</tr>
<tr>
<td>Farmington</td>
<td>12 0.13 α</td>
<td>7.05±0.20 0.17±0.05</td>
<td>γ &gt;10</td>
<td>Fe-Ni-P</td>
</tr>
<tr>
<td>Wickenburg</td>
<td>13 0.06 α</td>
<td>6.60±0.20 0.09±0.02</td>
<td>γ &gt;15</td>
<td>Fe-Ni-P</td>
</tr>
<tr>
<td>Rose City</td>
<td>9 -0.50 ph</td>
<td>22±12 15.5</td>
<td>α -6.0</td>
<td>Fe-Ni-P</td>
</tr>
<tr>
<td>Farmington</td>
<td>17 0.13 ph</td>
<td>-35 15.5</td>
<td>α -6.0</td>
<td>Fe-Ni-P</td>
</tr>
</tbody>
</table>

* Interface values too difficult to obtain.

25°C/hr show Ni contents below 0.3 wt%. Even at a slow cooling rate of 4°C/hr, the experimental in Farmington by WOOD (1967) and BUSECK et al., (1966) and in Wickenburg by TAYLOR and HEYMANN (1971). Secondary kamacite typically occurs along the edges or grain boundaries of α2 with silicate, troilite or other metal grains since these locations provide favorable sites for heterogeneous nucleation (Fig. 1). The presence of secondary α indicates that the cooling rate of the metal was slow enough to allow α to nucleate and grow from γ during cooling. The presence of P in the metal facilitates α nucleation and growth, since P is an α stabilizer (GOLDSTEIN and DOAN, 1972), and increases the diffusion coefficient of Ni in Fe–Ni (HEYWARD and GOLDSTEIN, 1973).

The Ni and P distributions at α/γ interfaces can be used to approximate the final temperature of equilibration (Teq) of the two phase assemblage α–γ. The method employed by AXON and GOLDSTEIN (1972) for determining Teq of lunar two-phase particles was applied in the present work. Interface Ni and P compositions of α were fit to the appropriate Fe–Ni or Fe–Ni–P phase diagram to estimate Teq. Point analyses were made using the microprobe along a line crossing the interface between the two phases. Figure 7 shows such a profile in the Farmington chondrite.

Interface compositions and Teq estimates are listed in Table 3 for those chondrites which contain α. The Ni composition on the γ side of the interface near the α/γ interface decreases rapidly (Fig. 7) due to low diffusion rates in the γ. It is therefore difficult to obtain an accurate interface value for γ. Accordingly Teq estimates are based mainly on the α compositions. The values of Teq can be used to give a relative ranking of chondrite cooling rates; a sample with a lower Teq has a slower cooling rate.

Cooling rate estimations were made by calculating the times of secondary kamacite growth. The following assumptions were made for the growth calculation: (1) growth is diffusion controlled; (2) chemical equilibrium exists at the α/γ interface; (3) growth is one dimensional; (4) no impingement occurs, and (5) growth can be considered as having occurred at one temperature, called the optimum growth temperature.

With these assumptions, the following analytical solution can be used to solve Fick's second law for the Ni concentration in α and γ:

$$C_\alpha(x,t) = A_\alpha + B_\alpha \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$  \hspace{1cm} (2)

$$C_\gamma = c^*$$  \hspace{1cm} (3)

Fig. 7. Ni and P profiles across secondary α in Farmington.
Metallic microstructures and thermal histories

$A_{\beta} = c' - a'_x \text{erf} \gamma \quad \quad B_{\beta} = a' - c'$

where

$D$ is the diffusion coefficient, $x$ the distance, $t$ the growth time, $C_p$ the composition in the taenite parent phase, $c'$ the equilibrium Ni content of the precipitate, $c''$ the equilibrium Ni content of the parent phase, $a'$ the bulk Ni content of parent phase, and $\gamma$ a dimensionless parameter (Jost, 1952). The location of the interface between the precipitate and parent phases, $\xi$, is given by:

$$\xi = 2\sqrt{Dt}$$

(Jost, 1952). The $\gamma$ term is found by inserting the general solutions for $C_p$ and $C_{\beta}$, equations (2) and (3), into the mass balance expression

$$\frac{d(c'' - c')}{dx} = D_{\beta} \left( \frac{\partial C_{\beta}}{\partial x} \right)_{\xi} - D_{\alpha} \left( \frac{\partial C_{\alpha}}{\partial x} \right)_{\xi}$$

(5)

where

$$\left( \frac{\partial C_{\beta}}{\partial x} \right)_{\xi}$$

is the concentration gradient in $\beta$ at the $\beta/\alpha$ interface, $\xi^-$ and

$$\left( \frac{\partial C_{\alpha}}{\partial x} \right)_{\xi}$$

is the concentration gradient in $\alpha$ at the $\beta/\alpha$ interface $\xi^+$. After minor rearranging of terms one has:

$$\sqrt{\pi(\gamma e^{\gamma})}(1 - \text{erf} \gamma) = \frac{a' - c'}{c'' - c'}$$

which is solved for $\gamma$ iteratively using a standard Newton-Raphson technique (McCracken, 1965). The interface distance or precipitate width $\xi$ can then be calculated for desired times using equation (4). The diffusion coefficients used in this calculation were obtained from Heyward and Goldstein (1973).

There are two variables that control precipitate growth, diffusion coefficient and driving force, which have opposing effects with respect to temperature. The diffusion coefficient decreases with decreasing temperature and the driving force increases with decreasing temperature (Remo-Hill, 1964). The temperature at which these effects balance is called the optimum growth temperature. At this temperature the $\alpha$ phase growth will be a maximum.

The optimum temperature for each case was found by performing isothermal calculations over a range of temperatures between the theoretical nucleation temperature and $T_{eq}$. Once the optimum growth temperature was found for each meteorite, calculations were performed to find the time needed to grow $\alpha$ to a width of the order of that observed in the sample. Due to geometry considerations accurate $\alpha$ phase widths could not be measured and a best value was estimated. The temperature range between the nucleation temperature and $T_{eq}$ was divided by the calculated time needed for growth at the optimum temperature. This result yields an approximate cooling rate for each meteorite. These cooling rates vary from $\sim 1^\circ C$/yr to $1^\circ C$/100 yr. Table 4 lists such cooling rates along with the temperatures and times employed in the calculations.

No secondary $\alpha$ was observed in the heat treated samples. This is not surprising as the experimental cooling rates were much faster ($>5000^\circ C$/yr) than those calculated for the shocked chondrites.

**Phosphides.** Phosphides were observed in Ramsdorf, Orvinio, Rose City, Farmington, and Lubbock (all the chondrites with $P > 0.1$ wt% in the metal). This phase was previously observed in Ramsdorf (Begemann and Wlotzka, 1969) and Orvinio (Taylor and Heymann, 1971). The phosphides apparently nucleate mostly at the $\alpha$-troilite or former $\gamma$-troilite boundaries during cooling. Rose City and Farmington contain phosphides large enough ($>2 \mu m$) for compositional measurements across phosphide/metal interfaces. Ni and P profiles across phosphides in these two meteorites are shown in Fig. 8. By applying the method of Axon and Goldstein (1972), $T_{eq}$'s for Rose City and Farmington phosphide/metal were estimated as $\sim 575$ and $<550^\circ C$ respectively (Table 3). The phosphides in Lubbock are generally $\sim 2 \mu m$ wide and the phosphides in Ramsdorf and Orvinio are $<2 \mu m$ wide. Rose City, Lubbock and Farmington have the largest phosphides, contain secondary kamacite, and therefore have slow cooling rates.

Table 4. Estimates of cooling rates for reheated chondrites, based on the growth of secondary kamacite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{nuc.}}$</th>
<th>$T_{eq}$</th>
<th>$T_{\text{opt}}$</th>
<th>Growth time at $T_{\text{opt}}$</th>
<th>Width</th>
<th>Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rose City</td>
<td>700°C</td>
<td>575°C</td>
<td>675°C</td>
<td>100 yrs.</td>
<td>10 µm</td>
<td>$-1^\circ C$/yr.</td>
</tr>
<tr>
<td>Arapahoe</td>
<td>700°C</td>
<td>550°C</td>
<td>685°C</td>
<td>1000 yrs.</td>
<td>8 µm</td>
<td>$&gt;1^\circ C$/10 yrs.</td>
</tr>
<tr>
<td>Lubbock</td>
<td>650°C</td>
<td>550°C</td>
<td>600°C</td>
<td>1000 yrs.</td>
<td>7 µm</td>
<td>$-1^\circ C$/10 yrs.</td>
</tr>
<tr>
<td>Farmington</td>
<td>650°C</td>
<td>500°C</td>
<td>600°C</td>
<td>1000 yrs.</td>
<td>8 µm</td>
<td>$-1^\circ C$/10 yrs.</td>
</tr>
<tr>
<td>Wickenburg</td>
<td>675°C</td>
<td>500°C</td>
<td>625°C</td>
<td>10,000 yrs.</td>
<td>10 µm</td>
<td>$&lt;1^\circ C$/100 yrs.</td>
</tr>
</tbody>
</table>

1 Approximate nucleation temperature, no undercooling.
2 Approximate final equilibrium temperature, Table 3.
3 Calculated optimum growth temperature.
4 Approximate secondary kamacite width.
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Upon resolidification. Also the presence of phosphides in a heat treatment sample 1050°C, 100°C/day indicates that phosphides can occur in metal which cooled as fast as 100°C/day.

THERMAL HISTORIES OF REHEATED CHONDRITES

Ramsdorf has probably experienced the highest reheating temperature of the chondrites studied. The metal troilite assemblages indicate extensive remelting. The central Ni contents of the metal grains are similar to each other and the high P content of the metal also indicate a high shock-reheating temperature. A comparison of the metal structure of Ramsdorf with the experimental heat treatment samples (Fig. 9) indicates a reheating temperature of 1200–1250°C.

Troilite in Ramsdorf contains an average Ni content of 0.11 wt%, which indicates a relatively fast cooling rate. The presence of steep Ni rim gradients and the absence of secondary α also indicate a relatively fast cooling rate. A comparison of Ramsdorf with the structure of the heat treated samples (Fig. 9) and the results from cooling rate criteria study lead to an estimate of ~100°C/day as the cooling rate for Ramsdorf. BEGEMANN and WLOTZKA (1969) propose a cooling rate of ~3°C/min at a reheating temperature of >1200°C. Such a value was based on a calculation of solid state diffusion in the grain rims of Ramsdorf at temperatures above 1000°C. Evidence from our heat treatment studies shows that metal–troilite melts at a temperature of 1000°C and the rims of the metal grains in Ramsdorf did not solidify until they cooled below 1000°C. This result invalidates the solid state diffusion method for T > 1000°C. Calculations of BEGEMANN and WLOTZKA (1969) indicate however that a cooling rate of ~100°C/day is possible if solidification occurs below 1000°C.

Orvinio has a metal–troilite structure which appears to have been extensively remelted. Results from the study of high temperature criteria in Orvinio and comparison to the heat treated sample lead to a maximum reheating temperature of ~1200°C. The cooling rate of Orvinio must have been fast enough to prevent secondary α growth and also to retain some Ni rim radii. The Ni content of troilite (0.08 wt% av) is somewhat lower than that of Ramsdorf indicating a slower cooling rate. Orvinio’s cooling rate is estimated as ~100°C/day to ~15°C/day.

Tadjera contains only some metal–troilite that appears remelted. The metal in this sample contains a relatively low amount of P, and the central Ni content of the metal grains varies greatly (Figure 4). Tadjera contains a high density of veinlets, which again indicates a less severe remelting process.

The maximum reheating temperature is estimated as ~1000–1050°C. The relatively high Ni content of troilite (0.31 wt% av), the inhomogeneity of individual metal grains (including some Ni rim gradients), and

0.1–1°C/yr (Table 4). The presence of phosphides in Ramsdorf and Orvinio, although they are smaller, might indicate slow cooling for these meteorites. However these two meteorites have been extensively remelted, they have the highest reheating temperature ≥1200°C and the highest P content in the metal. It is possible that the phosphides formed during the remelting stage and a small amount of phosphide–metal eutectic nucleated at the edges of the troilite upon resolidification.
Metallic microstructures and thermal histories

A summary of the estimated thermal histories of the eight reheated chondrites is presented in Fig. 10. The maximum reheating temperatures and cooling rates of the chondrites are obtained from the preceding discussions of appropriate criteria and the cooling rate data from Table 4. Error bars indicate the degree of uncertainty in the estimated thermal histories. Ramsdorf, Orvinio and Tadjera have relatively fast cooling rates while the remaining chondrites cooled slowly (<1°C/yr). Previous investigators have related the cooling rates of the reheated chondrites to their depth of burial after the shock event (BEGEMANN and WLOTZKA, 1969; TAYLOR and HEYMANN, 1971). Material with a slower cooling rate is buried deeper in the parent body. Correlations between cooling rate curves and burial depths have been made by TAYLOR and HEYMANN (1971) and their data is applied to the cooling rate estimates of the present study. The bottom scale in Fig. 10 indicates the depth of burial of the eight reheated chondrites. These chondrites were apparently buried at depths ranging from ~0.5 to 1000 m beneath the surface of their parent bodies.

CONCLUSIONS

(1) The following metallographic criteria can be used to estimate the post shock residual temperature of severely reheated chondrites: melted metal–troilite appearance, presence of martensite, phosphorus enrichment of metal and averaging of central metal grain compositions.

(2) The presence of phosphides and secondary kamacite are due to slow post-shock cooling rates. These exsolved phases can be used to estimate cooling rates. Ni rim gradients indicate both extensive remelting of metal grains and relatively fast cooling.

(3) Ramsdorf had the highest post shock residual temperature (1200–1250°C) followed by Orvinio and Rose City (~1200°C), Lubbock (~1100–1150°C), Farmington (1050–1100°C), Tadjera and Arapahoe (1000–1050°C), and Wickenburg (950–1000°C).

Fig. 10. Thermal history summary for eight severely reheated chondrites (samples identified by their initials).
Estimates of cooling rates are: Tadjera ~100–500°C/day, Ramsdorf ~100°C/day, Orvinio ~100°C/day to ~15°C/day, Rose City ~1°C/yr, Lubbock, Farmington and Arapahoe ~1°C/100 yr and Wickenburg ~1°C/100 yr. These chondrites were buried at depths ranging from 0.5 to 1000 m beneath the surface of their parent bodies.

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