Main-group pallasites: Thermal history, relationship to IIIAB irons, and origin

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Abstract

We have determined metallographic cooling rates below 975 K for eight main group (MG) pallasites from Ni profiles across taenite lamellae of known crystallographic orientation in metallic regions with Widmanstätten patterns. Comparison with profiles generated by modeling kamacite growth gave cooling rates ranging from 2.5 to 18 K/Myr. Relative cooling rates were also inferred from the sizes of cloudy zone particles in 28 MG pallasites (86–170 nm) and tetrataenite bandwidths in 20 MG pallasites (1050–2170 nm), as these parameters are positively correlated with each other and negatively correlated with the metallographic cooling rates. These three different techniques show that MG pallasites cooled below 975 K at significantly diverse rates. Since samples from the core–mantle boundary should have indistinguishable cooling rates, MG pallasites could not have cooled at this location. Group IIIAB irons, which were previously thought to be core samples from the MG pallasite body, have faster cooling rates (~50–350 K/Myr) and smaller cloudy zone particle sizes and tetrataenite bandwidths. This shows that IIIAB irons cooled faster than MG pallasites and could not plausibly be from the same body. The absence of related iron meteorites and achondrites and our thermal constraints suggest that MG pallasites cooled at diverse depths in a pallasitic body consisting of well-mixed olivine and metallic Fe–Ni. Such a body may have formed during an impact on a differentiated asteroid or protoplanet that mixed olivine mantle fragments with residual Ir-poor molten metal from the outermost part of a core that chemically resembled the IIIAB core and was ~80% fractionally crystallized. Separation of the solid core and most of the associated mantle may have resulted from a grazing hit-and-run impact with a larger protoplanet or asteroid. Thermal calculations suggest that the radius of the pallasitic body was 400 km but the likely presence of a regolith would reduce this estimate considerably.

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1. INTRODUCTION

Pallasites are stony-iron meteorites containing ~65 vol% olivine, ~30 vol% metallic Fe–Ni, and ~5 vol% of chromite, phosphate, and troilite (Buseck, 1977; Ullf-Møller et al., 1998), and are widely thought to have formed by mixing of molten Fe–Ni from the core with olivine mantle in one or more differentiated asteroids (e.g., Scott, 1977a,b; Wasson and Choi, 2003; Haack and McCoy, 2003; Greenwood et al., 2006). However, formation at a core–mantle boundary is difficult to reconcile with the tendency for olivine crystals to separate gravitationally from molten metal even in asteroids, and the relatively large number of pallasites: 85 cf., ~1000 iron meteorites (Meteoritical Bulletin Database see http://tin.er.usgs.gov/meteor/methbull.php). In addition, concentrations of rare-earth elements in some phosphates and minor elements in olivine appear to require a near-surface origin for pallasites (Davis and Olsen, 1991; Hsu, 2003).

Large slices of most pallasites show millimeter to centimeter-sized fragments of olivine crystals embedded in metal with polycrystalline olivine masses up to 10–20 cm in size,
which appear to be disintegrating to form the olivine fragments (Scott, 1977b; Ulff-Møller et al., 1998; Wasson and Choi, 2003). This suggests that pallasites formed after impacts crushed olivine mantle and mixed in molten metal from the core. About 15–20% of pallasites show rather different textures: rounded olivines with equilibrated olivine–olivine and olivine–metal grain boundaries. Since pallasites with angular olivine fragments commonly show micro-mixing textures like those observed on a larger scale in pallasites with rounded olivines, the latter probably experienced more extensive annealing in the presence of residual S-rich Fe–Ni–S liquid (Scott, 1977b; Saiki et al., 2003).

Oxygen isotopic compositions of the olivine and trace element concentrations of the metallic Fe–Ni in pallasites show that they can be divided into several groups that probably come from separate parent bodies, some of which may also have supplied certain iron meteorites. Pallasites are divided into a main group (MG), which accounts for 90–95% of pallasites and has affinities with the largest group of irons—IIIAB, the Eagle Station trio, and several ungrouped pallasites including Milton (Lovering et al., 1957; Scott, 1977a; Davis, 1977; Clayton and Mayeda, 1996; Boesenberg et al., 2000; Wasson and Choi, 2003; Jones et al., 2003). Fractional crystallization models for the chemical variations within group IIIAB irons show that the metallic Fe–Ni portions of most MG pallasites, which are especially depleted in Ir, are a good compositional match for the liquid in the IIIAB body after ~80% of the metal crystallized (Scott, 1977c; Davis, 1977; Wasson and Choi, 2003).

A link between MG pallasites and IIIAB irons, if confirmed, would clearly favor a core–mantle origin for these pallasites. However, the oxygen isotopic compositions of the MG pallasites and the IIAB irons are not definitive evidence for a common source as they lie in a crowded region of isotopic space where unrelated meteorites may be superimposed, e.g., angrites and the ungrouped eucrite, Ibitira (Scott et al., 2009a). The siderophile element data also fail to provide definitive evidence for a common source as the compositional range of the metal in MG pallasites is much broader than in iron meteorite groups (excluding IAB and IIICD), and their Ga and Ge concentrations are not unlike those in many other meteorites. A genetic link between MG pallasites and IIIAB irons is not favored by their shock and reheating indicators: over ~80% of IIIAB irons have shock-hatched or recrystallized kamacite and many have extensively shock-melted troilites (Buchwald, 1975) but none of the MG pallasites show these features. In addition, the cosmic-ray exposure ages of the pallasites (≤ 200 Myr) are much less than those of IIAB irons, 600–700 Myr (Eugster et al., 2006).

Cooling rates of pallasites offer powerful constraints on their formation and possible associations with iron meteorite groups. Buseck and Goldstein (1968, 1969) used measurements of taenite edge compositions to infer that the pallasites cooled at uniformly slow rates of ~0.5–2 K/Myr below ~975 K, possibly near the core. These rates are much lower than the values of 50–350 K/Myr measured in IIAB irons arguing against a close link with MG pallasites (Yang and Goldstein, 2006). However, determinations of cooling rates from peak Ni concentrations in taenite are not accurate because the latter are sensitive to impingement effects and to the exact placement of the electron beam close to the kamacite/taenite interface. Nevertheless, pallasite metal appears to have cooled slower than IIAB irons as the peak Ni concentrations measured in taenite in MG pallasites exceed those reported in IIAB irons. In addition, high-Ni particle sizes in cloudy taenite, which are inversely correlated with cooling rate, are larger in MG pallasites than in IIAB irons (Yang et al., 1997; Yang and Goldstein, 2006).

The cooling rates of pallasites clearly need to be reinvestigated as metallographic cooling rate models have improved significantly in the last 40 years (Yang and Goldstein, 2005, 2006). In addition, the cooling rates of Buseck and Goldstein (1969) are not consistent with the cooling rate of ~20–40 K/Myr determined for the Omolon pallasite from the Mn–Cr age of the olivine (Ito and Ganguy, 2006) and the rates of ~20–200 K/yr and 0.001–100 K/yr determined by Miyamoto (1997) and Tomiyama and Huss (2006), respectively, from concentration profiles of Ca, Cr and other elements in olivine.

We have investigated the thermal history of pallasites and IIAB irons to constrain the origin of pallasites and to test the possible relationship between MG pallasites and IIAB irons. We determined the cooling rates of the pallasite metal below 975 K (~700 °C) by applying the metallographic method. We also obtained relative cooling rates below 675 K (~400 °C) by measuring the tetrataenite bandwidth and the size of the high-Ni particles in the cloudy zone of the taenite in pallasites and IIAB irons (Yang et al., 2008; Goldstein et al., 2009a). We also developed a thermal model of a pallasitic asteroid to obtain the size of MG pallasite parent body. Finally, we offer a schematic impact model to help explain how the MG pallasites may have formed.

2. METEORITE SAMPLES AND ANALYTICAL TECHNIQUES

Twenty-nine MG pallasites, three Eagle Station group pallasites, and two ungrouped pallasites were selected for study. In one MG pallasite, Phillips County (pallasite), the metallic Fe–Ni was too corroded to obtain any data. The remaining 33 pallasites are listed in Table 1 with their sources and catalog numbers. In addition, we studied cloudy taenite and tetrataenite in six IIAB iron meteorites that are listed in Table 2; five of the six have a metallographic cooling rates that were determined by Yang and Goldstein (2006).

Samples of pallasites and iron meteorites were prepared for reflected light microscopy and scanning electron microscopy (SEM) using standard metallographic procedures: mounting, grinding, polishing, and etching with 2% nital. SEM studies were performed with a Zeiss EVO 50 at the University of Massachusetts (UMass), a Hitachi S4300 FE-SEM at Lehigh University, and a Zeiss Ultra-55 FE-SEM at Harvard University. A low accelerating voltage (1.8–10 kV) was used to reveal the surface character of the various metal phases. The tetrataenite bandwidth and
Table 1
Sizes of cloudy zone high-Ni particles and tetrataenite bandwidths in 33 pallasites.

<table>
<thead>
<tr>
<th>Meteorite name</th>
<th>Source</th>
<th>Class</th>
<th>Ni in metal (wt%)</th>
<th>Cloudy zone particle size (±2SEM) (nm)</th>
<th>No. of particles</th>
<th>Tetraenite bandwidth (±2SEM) (nm)</th>
<th>No. of tetrataenite bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Admire USNM 2620a</td>
<td>MG</td>
<td>11.76</td>
<td>130 ± 8</td>
<td>30</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Ahumada ASU 354.1,1</td>
<td>MG</td>
<td>9.36</td>
<td>124 ± 6</td>
<td>91</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Albin (pallasite)</td>
<td>ASU 314.1a</td>
<td>10.84</td>
<td>112 ± 5</td>
<td>42</td>
<td>1560 ± 70</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>Argonia ASU 458.2</td>
<td>MG</td>
<td>12.36</td>
<td>127 ± 6</td>
<td>30</td>
<td>1910 ± 70</td>
<td>5</td>
<td>—</td>
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<td>Brahin USNM 7018a</td>
<td>MG</td>
<td>11.16</td>
<td>106 ± 9</td>
<td>8</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Brenham AMNH 989-3</td>
<td>MG</td>
<td>11.73</td>
<td>123 ± 3</td>
<td>203</td>
<td>1550 ± 80</td>
<td>33</td>
<td>—</td>
</tr>
<tr>
<td>Dora (pallasite)</td>
<td>AMNH 4394-2</td>
<td>11.55</td>
<td>136 ± 6</td>
<td>83</td>
<td>1760 ± 80</td>
<td>24</td>
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<td>Esquel AMNH 4761-2</td>
<td>MG</td>
<td>9.31</td>
<td>157 ± 11</td>
<td>23</td>
<td>2090 ± 250</td>
<td>3</td>
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<tr>
<td>Finmarken USNM 392c</td>
<td>MG</td>
<td>10.28</td>
<td>86 ± 2</td>
<td>238</td>
<td>1050 ± 100</td>
<td>14</td>
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<tr>
<td>Fukang SML 9.5*</td>
<td>MG</td>
<td>9.5</td>
<td>129 ± 10</td>
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<td>Giroux USNM 1574a</td>
<td>MG</td>
<td>10.67</td>
<td>120 ± 7</td>
<td>35</td>
<td>1760 ± 300</td>
<td>2</td>
<td>—</td>
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<tr>
<td>Glorieta Mountain</td>
<td>USNM</td>
<td>11.67</td>
<td>170 ± 6</td>
<td>92</td>
<td>2170 ± 90</td>
<td>15</td>
<td>—</td>
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<tr>
<td>Hambleton OpenU</td>
<td>MG*</td>
<td>152 ± 6</td>
<td>28</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Huckitta USNM 2273</td>
<td>MG</td>
<td>8.5</td>
<td>127 ± 7</td>
<td>25</td>
<td>1770 ± 360</td>
<td>3</td>
<td>—</td>
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<tr>
<td>Imilac AMNH 896-2</td>
<td>MG</td>
<td>8.28</td>
<td>143 ± 4</td>
<td>133</td>
<td>1980 ± 120</td>
<td>15</td>
<td>—</td>
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<tr>
<td>Krasnojarsk ASU 182.2a</td>
<td>MG</td>
<td>8.3</td>
<td>145 ± 5</td>
<td>76</td>
<td>1870 ± 60</td>
<td>3</td>
<td>—</td>
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<tr>
<td>Marjalahti AMNH 4088-2</td>
<td>MG</td>
<td>8.75</td>
<td>118 ± 3</td>
<td>201</td>
<td>1530 ± 100</td>
<td>15</td>
<td>—</td>
</tr>
<tr>
<td>Molong AMNH 2463-2</td>
<td>MG</td>
<td>9.99</td>
<td>142 ± 4</td>
<td>145</td>
<td>2020 ± 210</td>
<td>9</td>
<td>—</td>
</tr>
<tr>
<td>Mount Dyrring unk</td>
<td>MG*</td>
<td>118 ± 6</td>
<td>20</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Mount Vernon USNM 300e</td>
<td>MG</td>
<td>10.91</td>
<td>127 ± 5</td>
<td>44</td>
<td>1850 ± 420</td>
<td>3</td>
<td>—</td>
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<tr>
<td>Newport AMNH 4407-3</td>
<td>MG</td>
<td>11.5</td>
<td>109 ± 3</td>
<td>138</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Otinapa AMNH 4600-2</td>
<td>MG</td>
<td>10.86</td>
<td>114 ± 9</td>
<td>16</td>
<td>1550 ± 220</td>
<td>3</td>
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<tr>
<td>Rawlinna 001 ASU 677.1</td>
<td>MG</td>
<td>13.53</td>
<td>158 ± 12</td>
<td>11</td>
<td>2090 ± 200</td>
<td>3</td>
<td>—</td>
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<tr>
<td>Santa ASU 599.1,2</td>
<td>MG*</td>
<td>10.1</td>
<td>153 ± 7</td>
<td>18</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Seymchan USNM 7200a</td>
<td>MG*</td>
<td>9.51</td>
<td>122 ± 5</td>
<td>77</td>
<td>1390 ± 100</td>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>Somervell County AMNH 1408a</td>
<td>MG*</td>
<td>11.3</td>
<td>133 ± 11</td>
<td>20</td>
<td>1800 ± 70</td>
<td>4</td>
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<tr>
<td>South Bend USNM 2616a</td>
<td>MG</td>
<td>9.22</td>
<td>115 ± 5</td>
<td>51</td>
<td>1320 ± 70</td>
<td>6</td>
<td>—</td>
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<tr>
<td>Springwater AMNH 2641-4</td>
<td>MG</td>
<td>12.18</td>
<td>132 ± 3</td>
<td>121</td>
<td>1630 ± 170</td>
<td>11</td>
<td>—</td>
</tr>
<tr>
<td>Cold Bay USNM 636</td>
<td>EST</td>
<td>20.6</td>
<td>90 ± 8</td>
<td>11</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Eagle Station USNM 275b</td>
<td>EST</td>
<td>15.3</td>
<td>a</td>
<td>—</td>
<td>—</td>
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</tr>
</tbody>
</table>

(continued on next page)
the size of the high-Ni particles in the cloudy zone next to the tetrataenite band were measured from SEM images (e.g., Fig. 1d) using the methodology developed by Goldstein et al. (2009a).

Samples were prepared for electron probe microanalysis using the same procedures except that the samples were not etched. Local bulk compositions of the metal phases in pallasites were determined by analyzing kamacite, taenite, and phosphide for Fe, Ni, Co, and P. Nickel gradients across taenite lamellae were analyzed in 1–2 μm steps for cooling rate measurements. Analyses were made with a Cameca SX-50 electron probe micro-analyzer (EPMA) at the University of Massachusetts (see Yang et al., 2008).

<table>
<thead>
<tr>
<th>Table 1 (continued)</th>
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<tbody>
<tr>
<td><strong>Meteorite name</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Itzawisis</td>
</tr>
<tr>
<td>Milton</td>
</tr>
<tr>
<td>Vermillion</td>
</tr>
</tbody>
</table>

Dashed line: tetrataenite bandwidth unavailable as the orientation relative to the polished surface was not known.

Class abbreviations: MG, Main Group; EST, Eagle Station Grouplet; Ungr, Ungrouped.

Errors are ±2× standard error of the mean, ±2SEM.

Source abbreviations: USNM, US National Museum of Natural History; AMNH, American Museum of Natural History; OpenU, Open University, UK; ASU, Arizona State University; UMass, University of Massachusetts; SML, Southwest Meteorite Laboratory; NHM, Natural History Museum, London.

* Classification and Ni content from Wasson and Choi (2003) except for the following: Fukang, classification from Greenwood et al. (2006), Ni content from Lauretta et al. (2006); Hambleton (Johnson et al., 2006); Mount Dyrring (Mason, 1963; Buseck and Goldstein, 1969); Santa Rosalia (Scott, 1977a); Seymchan (van Niekerk et al., 2007); SomervellCo. (Davis, 1977), and Milton (Jones et al., 2003). The classification of Mount Dyrring is uncertain as its metal and its oxygen isotopic composition have not been analyzed.

* No cloudy zone particle size as SEM image of poor quality.

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<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sizes of cloudy zone high-Ni particles, and widths of tetrataenite bands in six IIIAB irons.</td>
</tr>
<tr>
<td><strong>Meteorite name</strong></td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Bella Roca</td>
</tr>
<tr>
<td>Buenaventura</td>
</tr>
<tr>
<td>Casas Grandes</td>
</tr>
<tr>
<td>Chupaderos</td>
</tr>
<tr>
<td>Point of Rocks (iron)</td>
</tr>
<tr>
<td>Uruachic</td>
</tr>
</tbody>
</table>

Errors are ±2× standard error of the mean, ±2SEM.

Source abbreviations: UNM, University of New Mexico; FMNH, Field Museum of Natural History; UCLA, University of California at Los Angeles; USNM, US National Museum of Natural History.


+ Tetrataenite bandwidth omitted as the orientation relative to the polished surface was not known.

# Sources of Ni concentrations: a, Buchwald (1975); b, Wasson (1999); c, Scott et al. (1973); d, Wasson et al. (1998).
3. COOLING RATE MODELING

In pallasites, the nature of the kamacite that forms depends on the dimensions of the metal regions between the olivine grains. In rare cases, for example in Brenham, Glorietta Mountain, and Seymchan (Fig. 2a and b), in regions where the olivine-bearing regions are many centimeters apart, the oriented kamacite plates form a Widmanstätten pattern like those in iron meteorites from a single crystal of taenite. However, in most pallasites, olivines are generally separated by metal regions only a few millimeters or less in thickness and only the largest metal regions typically larger than 5 mm across contain oriented kamacite plates (Fig. 1a). We have measured metallographic cooling rates only from these large metal areas where the Widmanstätten pattern formed from a single crystal of taenite and taenite grain boundaries were absent.

To obtain metallographic cooling rates from the Widmanstätten pattern kamacite plates, we need to know how the kamacite plates nucleated, the nucleation temperature, the effect of impingement by adjacent kamacite plates, the Fe–Ni and Fe–Ni–P phase diagrams, and the interdiffusion coefficients which control the growth of the Widmanstätten pattern (Yang et al., 2008). In order to apply the metallographic cooling rate model developed for iron meteorite groups IIIAB, IVA, and IVB (Yang and Goldstein, 2006; Yang et al., 2010), we need to be sure that the Widmanstätten pattern in pallasites formed in the same way as in iron meteorites, viz., from single crystal, P-bearing taenite. Additional minor elements that could influence nucleation and diffusion-controlled growth must have been absent, and major shock events that could modify kamacite nucleation and diffusion could not have taken place during cooling.

The chemical composition of the metal in most MG pallasites is very close to that of Ni-rich IIIAB irons although a few are somewhat richer in Ni, Co, Cu, Ir, Ga, As, or Au and a couple have slightly lower concentrations of Co or Ga (Wasson and Choi, 2003). The metallic portions of main group pallasites also contain comparable P concentrations to those in IIIAB irons: 0.3–0.6 wt% P, some in solid solution within the metal and some in schreibersite and rhabdites (Buseck, 1977; Davis, 1982; Ulf-Møller et al., 1998; Lauretta et al., 2006). As in Ni-rich IIIAB irons, carbides and graphite appear to be absent in MG pallasites and significant amounts of C have not been reported. We conclude that the kamacite nucleation temperature in MG pallasites was controlled by the bulk Ni and P contents, as in IIIAB irons, and the Ni diffusion rates in the metal are dependent on the Ni, Fe, and P content and are not measurably influenced by any metal impurity.

Olivine crystals in pallasites are enclosed by swathing kamacite (Figs. 1a and 2b). For metal less than ~1 cm across, the swathing kamacite commonly approaches a millimeter in width and wider than the adjacent oriented kamacite plates (Fig. 1a). This observation implies that
on cooling, kamacite nucleates initially on taenite–olivine boundaries because of the lowering of surface energy between taenite and olivine. Rapid diffusion of Fe and Ni along the metal–olivine boundary as envisioned for chondrite metal (Reisener and Goldstein, 2003) may also play a role in forming the swathing kamacite. At slightly lower temperatures, kamacite nucleates homogeneously within the remaining taenite to form either a Widmanstätten pattern of oriented kamacite plates or, if the remaining taenite is too small, plessite at lower temperatures (see Fig. 1). The prior growth of swathing kamacite in the metal regions that are less than ~1 cm across raises the Ni concentration in the residual taenite above the bulk value of the Fe–Ni metal. In this case the nucleation temperature of the oriented kamacite plates (or plessite in small taenite regions) is lowered. Consequently, the nucleation temperature for the Widmanstätten kamacite plates can vary throughout the pallasite according to the proximity to the olivine crystals. For large metal regions, greater than ~1 cm across, the metal regions are so large that the Ni build up in the taenite and consequent depression of the nucleation temperature are negligible. In these regions, the swathing kamacite is comparable in width to the oriented kamacite plates (Fig. 2b).

We determined the local bulk Ni and P concentrations around oriented kamacite plates by electron microprobe.

Fig. 2. (a) Polished and etched slice of the Seymchan main group pallasite showing three different types of material: 5–10 cm wide olivine-free metal regions with Widmanstätten patterns, 5–15 cm long angular regions with Brenham-like pallasite material consisting of rounded olivine aggregates with interstitial metallic Fe–Ni (left and center), and a 10 cm wide zone on the right side with seemingly isolated, mostly angular olivines in metal. The isolated olivines may have been detached from Brenham-like angular regions or from large polycrystalline olivine masses (see Meteoritical Bulletin Database links at http://tin.er.usgs.gov/meteor/metbull.php). Longest dimension of the slice is 48 cm. (b) Oblique view of the region marked in (a) under different lighting conditions showing oriented kamacite plates, swathing kamacite (S) around olivine, and small dark inclusions of the phosphide, schreibersite (P) in metal. Photographs taken by R.A. Langheinrich.
analysis for Ni and P point by point from the middle of the kamacite (α) band at one side of a taenite band (γ) to the middle of the kamacite on the other side of taenite, following the method of Rasmussen (1981). As we shall see in Section 4.1, the local bulk Ni concentrations increase modestly up to 3 wt% Ni from the bulk Ni concentrations in the metallic Fe–Ni where kamacite plates form. In most pallasites, the bulk Ni concentration in metallic Fe–Ni is 8–14 wt%; Cold Bay and a few others have higher bulk Ni concentrations, possibly up to ~20% Ni (Wasson and Choi, 2003; Table 1). Thus local bulk Ni concentrations in the pallasite metal are almost all below 17 wt%. The effect of a higher local bulk Ni content, although relatively minor, needs to be considered in measuring the metallographic cooling rates.

The local bulk P concentrations that we measured in MG pallasite metal, typically 0.04–0.08 wt%, are much smaller than the bulk P in metal since the measured local bulk P did not include the P content in any nearby phosphides. The P is at the solubility limit in both kamacite and taenite as temperature decreases, and the metal composition is in the three phase field (α + γ + phosphide, Ph) in the Fe–Ni–P phase diagram. Based on the solubility of P in taenite and the measured local bulk Ni (<16 wt%), the local bulk P at the time of the Widmanstätten kamacite nucleation is above 0.1 wt% (Yang and Goldstein, 2005). From the Fe–Ni–P phase diagram and the local bulk Ni and P values, we infer that phosphides form before the Widmanstätten kamacite plates nucleate and their formation is controlled by mechanism II: \( γ \rightarrow γ + Ph \rightarrow α + γ + Ph \) (Yang and Goldstein, 2005). Kamacite nucleation temperatures range between 975 and 875 K (~700 and 600 °C). Swathing kamacite also nucleated after the phosphides formed. Note that in chondrites, swathing kamacite is not observed at metal/olivine interfaces since P is not present in the metal (Reisener and Goldstein, 2003).

Aside from the effect of swathing kamacite in raising the local bulk Ni in nearby metal that was described above, the olivine grains do not appear to have affected the growth of the Widmanstätten pattern. For example, photos of olivine-poor Brenham and Seymchan (Fig. 2a and b) samples show that the Widmanstätten pattern has uniform kamacite plate thickness right up to the swathing kamacite around the olivine. We see no evidence for localized strain in the metal near the metal–olivine boundary that might locally enhance diffusion rates—a possibility raised by one of the reviewers of this paper. There is also no evidence for shock that might have affected the nucleation temperature of the Widmanstätten pattern and the Ni diffusion rates. Olivine crystals show sharp optical extinction, aside from kink bands caused by annealing at high temperature after deformation (Klosterman and Busack, 1973), and olivine and metal have low dislocation densities (Matsui et al., 1980; Desrousseaux et al., 1997). Kamacite in pallasites lacks the shock-hatched structure that is visible on etching in many IIIAB irons that were shocked above 13 GPa (Buchwald, 1975).

The Wood method, which is usually employed for the measurement of the metallographic cooling rates (Wood, 1964), cannot be applied for cooling rate measurements in the pallasites because it assumes that the taenite is compositionally homogeneous when the kamacite plates nucleate. We therefore used the Ni profile matching method (Goldstein and Ogilvie, 1965) taking into account the local Ni content of the parent taenite. In this method, a unique cooling rate is obtained for each taenite plate when the measured Ni concentration profile across the plate matches the calculated profile. Nickel profiles were calculated for the pallasites using the same set of diffusion coefficients and phase diagrams that were used in our studies of IVA and IVB irons (Yang et al., 2010). Our study of IVA irons showed that results from the Ni profile matching method are entirely consistent with those of the Wood method when taenite is chemically homogeneous at the time that the Widmanstätten kamacite plates nucleate.

4. RESULTS

4.1. Metallographic cooling rates of pallasites

Eight samples of pallasites, which are all MG members, contain metal regions with Widmanstätten pattern kamacite suitable for cooling rate analysis. The remaining 20 MG pallasite samples either did not have an observable Widmanstätten pattern in our sample or we could not determine the crystallographic orientation of the taenite bands. We measured the “M” shaped Ni profile across 7–10 taenite bands in each of these eight pallasites (Table 3). Since accurate cooling rate determinations require that the Ni profiles are measured perpendicular to the plane of the kamacite–taenite boundary, the measured taenite distance on the polished sample surface was corrected for orientation effects by determining the crystallographic orientation of the kamacite and taenite plates (Yang and Goldstein, 2006).

Fig. 3a shows a backscattered electron image of a microprobe trace in the Giroux pallasite across one of the taenite bands. In Fig. 3a and some other cases, the trace of the Ni profile was not oriented perpendicular to the taenite band in the plane of the polished section and an additional correction was made to the distance measurements to derive the Ni profile perpendicular to the kamacite plate. Fig. 3b shows the measured “M” shaped Ni profile across the taenite band in Fig. 3a after correction for the orientation of the plates relative to the polished surface and the orientation of the Ni profile to the taenite band in the polished section.

In order to obtain the cooling rate for each pallasite, we first plotted the orientation-corrected Ni profile for each taenite band. We then measured the local bulk Ni content of the kamacite–taenite bands. Finally, Ni profiles were calculated for a set of varying cooling rates using the measured local bulk Ni content until a match was obtained for the measured profile (e.g., Fig. 3b). Fig. 4 shows the measured and the calculated matching Ni profiles for 10 taenite bands in the Giroux pallasite. The local bulk Ni content and nucleation temperature for each band is also shown in Fig. 4. For the 10 taenite bands analyzed in Giroux, the cooling rate of the matching profile ranges from 5 to 10 K/Myr. The mean cooling rate for Giroux and the other
pallasites was calculated using the logarithm of the measured cooling rates for all the taenite bands. For example, the logarithmic average, which equals the geometric mean, of the 10 cooling rates for Giroux is 0.83 equivalent to a cooling rate of 6.8 K/Myr with a two standard deviation (2\sigma) value of ±0.17, which is equivalent to an uncertainty

<table>
<thead>
<tr>
<th>Meteorite name</th>
<th>Source</th>
<th>Ni in metal (wt%)</th>
<th>Wid. pattern cooling rate (±2SEM) (K/Myr)</th>
<th>2\sigma uncertainty factor</th>
<th>No. of taenite bands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brenham</td>
<td>AMNH 989-3</td>
<td>11.73</td>
<td>6.2 ± 0.9</td>
<td>1.4</td>
<td>8</td>
</tr>
<tr>
<td>Dora (pallasite)</td>
<td>AMNH 4394-2</td>
<td>11.55</td>
<td>4.7 ± 1.3</td>
<td>1.9</td>
<td>7</td>
</tr>
<tr>
<td>Finmarken</td>
<td>ASU 47</td>
<td>10.28</td>
<td>18.2 ± 8.7</td>
<td>2.4</td>
<td>7</td>
</tr>
<tr>
<td>Giroux</td>
<td>USNM 1574a</td>
<td>10.67</td>
<td>6.8 ± 1.0</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>Glorieta</td>
<td>UMass</td>
<td>11.67</td>
<td>2.5 ± 0.3</td>
<td>1.4</td>
<td>9</td>
</tr>
<tr>
<td>Mountain</td>
<td>USNM 7200a</td>
<td>9.51</td>
<td>7.1 ± 1.2</td>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td>Seymour</td>
<td>USNM 2616a</td>
<td>9.22</td>
<td>8.9 ± 1.2</td>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>Springwater</td>
<td>AMNH 2641-4</td>
<td>12.18</td>
<td>5.1 ± 0.7</td>
<td>1.4</td>
<td>7</td>
</tr>
</tbody>
</table>

Errors are ±2\times standard error of the mean, ±2SEM.
Source abbreviations are given in Table 1 footnotes.

Fig. 3. (a) Backscattered electron image of an oriented taenite lamellae in a Widmanstätten pattern in the Giroux main group pallasite showing the position of the electron microprobe trace. The two arrows indicate the starting and ending points of the trace. (b) Ni composition profile (open circles) along the trace with distances measured normal to the plane of the kamacite–taenite interface. Three calculated cooling rate curves are plotted for the local bulk content of 12.2 wt% Ni and 0.3 wt% P, and a kamacite nucleation temperature of 905 K. The data closely match the Ni profile for a cooling rate of 6 K/Myr.
Fig. 4. Ni concentration vs. distance profiles across 10 taenite bands in the Giroux main group pallasite measured at intervals of 1–2 μm together with matching calculated cooling rate curves (solid curves). The local bulk Ni concentration and kamacite nucleation temperature for each band are marked on the side of each profile. For the 10 taenite bands, the local bulk Ni concentration varies from 11.0–13.8 wt% Ni and the kamacite nucleation temperature varies from 885 to 930 K. The mean value of the matching cooling rate curves is 6.8 ± 1.0 K/Myr (∓2× standard error of the mean).
factor in the cooling rate of 1.5 (i.e., 4.5–10.2 K/Myr). We also list 2× the standard error of the arithmetic mean (SEM) of the cooling rate measurements, which for Giroux was 1.0 K/Myr (See Table 3).

Fig. 5 shows the mean cooling rates vs. the bulk Ni content for the 8 MG pallasites and error bars showing twice the standard error of the mean (2× SEM in Table 3). These cooling rates vary from 2.5 to 18 K/Myr and are much lower than the cooling rates for the IIAB irons, which are ~50–350 K/Myr (Yang and Goldstein, 2006). The negative correlation between bulk Ni and the logarithmic cooling rate for the 8 MG pallasites is significant at the ~90% level. However, cloudy zone particle size and tetrataenite band width data for 28 and 20 MG pallasites, respectively (see below), show that these parameters are uncorrelated.

4.2. Tetrataenite bandwidth and cloudy zone particle size

The tetrataenite and cloudy zone regions of nearly all pallasites are well developed and preserved and there is no evidence for shock heating. However, the structure in Phillips County (MG pallasite) was corroded, and the SEM images in both Eagle Station (Eagle Station group) and Vermillion (ungrouped pallasite) were not of sufficient quality. Milton (an ungrouped pallasite) is unique as it contains no cloudy zone structure as shown by SEM and by TEM techniques and shows no evidence of reheating which might remove this low temperature microstructure. It appears that Milton cooled rapidly.

The width of 2–33 tetrataenite bands was measured in the SEM images of each of the 21 pallasites and four IIAB irons (Tables 1 and 2). For the remainder, either we could not determine the crystallographic orientation of the taenite region or the SEM image quality was insufficient. Since most of the taenite regions were not oriented perpendicular to the polished surface, the thickness of the tetrataenite band normal to the plane of the kamacite–taenite interface was inferred from the crystallographic orientations of kamacite and taenite which were determined by EBSD. The mean bandwidth and 2× the standard error of the mean (2SEM) were obtained for each meteorite (Tables 1 and 2). Fig. 6a shows a plot of tetrataenite bandwidth vs. bulk Ni. The tetrataenite bandwidth varies from 1050 to 2170 nm for 20 MG pallasites, and is 800 nm for the Itzawiss pallasite, a member of Eagle Station group. The tetrataenite bandwidth of the four IIAB irons is much smaller and ranges from 290 to 450 nm. There is no correlation between tetrataenite bandwidth and the bulk Ni of the metal in the MG pallasites.

The sizes of between 8 and 238 high-Ni particles in the cloudy zones of several taenite bands were measured for 28 MG pallasites, two Eagle Station group pallasites and six IIAB irons. The average particle size and the corresponding 2× the standard error of the mean (2SEM) are listed in Tables 1 and 2. The mean sizes of the cloudy zone particles range from 86 to 170 nm for 28 MG pallasites, and from 82 to 90 nm in two Eagle Station group pallasites (Fig. 6b). The high-Ni particle sizes in the cloudy zone of six IIAB irons are much smaller with mean sizes ranging from 42 to 58 nm. There is no correlation between the high-Ni particle size and the bulk Ni of the metal regions in the MG pallasites. In fact, tetrataenite width and cloudy zone particle size in pallasites are closely correlated (Fig. 7), as observed for the IVA irons (Goldstein et al., 2009a).

4.3. Accuracy and precision of cooling rates

Errors in the measurement of the Ni profile and in the metallographic cooling rate model contribute to the total error of the metallographic cooling rates (Yang and Goldstein,
Fig. 6. (a) Tetrataenite bandwidth and (b) cloudy zone particle size vs. bulk Ni concentration in the metallic Fe–Ni of main group pallasites (MG Pall.), Eagle Station group pallasites (ES Pall.), and IIIAB irons. Error bars are $2\times$ the standard error of the mean.

Fig. 7. Tetrataenite bandwidth vs. cloudy zone particle size in 20 main group pallasites (MG Pall.) and four IIIAB irons. Error bars are $2\times$ the standard error of the mean.
The uncertainty factors caused by measurements of Ni concentration, taenite distance and kamacite–taenite orientation are 1.1, 1.2, and 1.2, respectively (Yang et al., 2008) and the combined uncertainty is at most a factor of 1.3. This uncertainty value is less than the mean 2σ uncertainty factors for the eight pallasites (Table 3).

The cooling rate uncertainty caused by model parameters such as kamacite nucleation mechanism and temperature, phase diagram and diffusion coefficients has been discussed in detail for iron meteorites (Yang et al., 2008). In this study, we used the same set of diffusion coefficients and phase diagrams that were used for the iron meteorite studies. For pallasites, we consider two possible effects on the measured cooling rate due to the uncertainty in the kamacite nucleation temperature. One effect is the uncertainty of the kamacite nucleation temperature for a fixed Ni and P. For the local bulk Ni in the metal of 8.5–15 wt%, the nucleation temperature for the Widmanstätten pattern is about 975–875 K (∼700–600 °C). For a ±10 K uncertainty in the nucleation temperature for a fixed local bulk Ni, the cooling rate is essentially the same. The second effect is the difference in nucleation temperature of Widmanstätten kamacite due to differences in local bulk Ni. Our measured local bulk Ni contents are 0–3 wt% higher than the overall bulk Ni for a given pallasite. The kamacite nucleation temperature for the Widmanstätten pattern may therefore vary across each pallasite. For example, kamacite will nucleate at 913 K (∼640 °C) for a local bulk Ni of 12 wt% while kamacite will nucleate at 873 K (∼600 °C) for another taenite region with a local bulk Ni of 15 wt%. After applying the Ni profile matching method to both taenite bands, we observe that the difference in the measured cooling rates for the two bands is negligible, despite the difference in local bulk Ni and nucleation temperature.

The values for 2× the standard error of the mean for each pallasite (2SEM in Table 3), expressed as a percentage of the mean cooling rate, vary between 12% and 50%. These values represent the precision of our cooling rates. The 2σ uncertainty factors in the cooling rates listed in Table 3 are 1.4–2.4 with a mean value of 1.6. The uncertainty factors, which are much larger than the precision, except for the Finmarken data, can be used to estimate the total error in the cooling rates.

4.4. Comparison with published pallasite cooling rates

Our cooling rates for pallasites of 2.5–18 K/Myr are much higher by a factor of 5–6 than the previously measured cooling rates (∼0.5–2 K/Myr) based on taenite edge compositions (Buseck and Goldstein, 1968, 1969). The metallographic cooling rates are now more consistent with the lower limit of 5 K/Myr that Pellas et al. (1983) inferred from Pu fission tracks in Marjalahi phosphate. The change in metallographic cooling rate is not surprising given the significant improvements, especially in understanding the effect of P on Widmanstätten growth and the improvement in the relevant diffusion coefficients and phase diagrams.

The Mn–Cr age of the olivine in the Omolon pallasite implies that it cooled at ∼20–40 K/Myr at ∼1000 °C, which is probably compatible with a metallographic cooling rate of 10–17 K/Myr (Lugmair and Shukolyukov, 1998; Ito and Ganguly, 2006). We did not measure the cooling rate of Omolon but since it is a MG pallasite, there does not appear to be a major conflict between the Mn–Cr age and the metallographic cooling rate.

Cooling rates for a few pallasites of ∼2–200 K/yr were derived from element zoning profiles (e.g., Cr, Ca, Mn, and Fe) in olivine by Miyamoto (1997) and Miyamoto et al. (2004). These rates, which are 10^4–7 times faster than the results of this study, were derived using an implausible model. The olivine crystals were assumed to be initially homogeneous and equilibrated at 1100 °C with the observed core compositions. Theoretical zoning profiles were derived by assuming that the olivine crystals were transferred to a totally different environment in which the surface compositions of the crystals were somehow fixed at their measured rim composition while the crystals cooled. However, chemical zoning profiles in pallasitic olivines, like those in kamacite and taenite, reflect kinetic and thermodynamic factors that change continually on cooling. To determine reliable cooling rates from a zoned olivine crystal, one needs to know what phases were reacting with olivine, their equilibrium phase compositions as a function of temperature, and the various diffusion rates in olivine, the reacting phases, and the medium that separated them. Although some improvements have been made to the olivine-based cooling rate model, the olivine cooling rates are still 1–3 orders of magnitude faster than the metallographic ones (Tomiyama and Huss, 2006).

5. DISCUSSION

5.1. Cooling rates of pallasites

Although we rely solely on the taenite Ni compositional data for quantitative cooling rates of pallasites (Fig. 5, Table 3), the sizes of cloudy zone particles and tetrataenite bandwidths provide excellent quantitative constraints on relative cooling rates as both parameters are inversely correlated with the cooling rates derived from oriented taenite lamellae. Fig. 8a and b shows that cloudy zone particle sizes and the tetrataenite bands in eight MG pallasites increase systematically with decreasing metallographic cooling rate as observed in other meteorite groups (Goldstein et al., 2009a). Since the pallasites with the lowest and highest cooling rates in Fig. 5 (Glorieta Mountain and Finmarken) lie at opposite ends of the MG range in Fig. 7, we infer that all 28 analyzed MG pallasites cooled through 975–775 K (∼700–500 °C) at between 2.5 and 18 K/Myr.

One might argue from Fig. 5 that the MG pallasites actually lie on an extrapolation of the IIAB trend to higher Ni concentrations. However, the data for the two IIAB irons with ∼10 wt% Ni show that the IIAB trend levels off with increasing bulk Ni. In addition, our measurements of the sizes of cloudy taenite particles and tetrataenite widths show that the cooling rates of MG pallasites are not correlated with bulk Ni (Fig. 6a...
and b). There is therefore no justification for extrapolating the trend in IIIAB irons with <8.5% Ni into the MG pallasites.

The inverse correlation between cloudy taenite particle size and metallographic cooling rate, Fig. 8a, validates our conclusion that the range of cooling rates we determined for the MG pallasites of 2.5–18 K/Myr is not an artifact resulting from errors in the phase diagram or diffusion coefficients. Fig. 8a also shows that the correlation trend defined by the MG pallasites is within error of that defined by all the meteorites including the mesosiderites, pallasites, IIIAB, IVA, and IVB iron meteorites (Goldstein et al., 2009a). The absence of any cloudy taenite in the Milton pallasite as shown by analytical transmission electron microscopy of several kamacite/taenite interfaces or any evidence for shock reheating shows that it cooled faster than 5000 K/Myr, the cooling rate of the irons with the finest observed cloudy taenite intergrowths (Goldstein et al., 2009a). Theoretical constraints on the formation mechanism of cloudy taenite and tetrataenite bands and the relation between cloudy taenite particle size, tetrataenite bandwidth and metallographic cooling rates are given in the Appendix A.

From our metallographic cooling rates and the constraints from cloudy taenite particle size and tetrataenite bandwidth we draw the following conclusions.

1) MG pallasites cooled at 2.5–18 K/Myr during kamacite growth below 975 K, more slowly than the IIIAB irons, which cooled at ~50–350 K/Myr.
(2) The range of cooling rates among MG pallasites is not an artifact of errors in the phase diagram or diffusion data or differences in kamacite nucleation temperature as the cooling rates are correlated with two other parameters: cloudy taenite particle size and tetrataenite bandwidth.

(3) Cooling rates among MG pallasites are not correlated with bulk Ni, as they are in IIIAB irons (also in group IVA and IVB).

(4) The range of cooling rates observed in MG pallasites shows that they were not located at the core–mantle boundary of a single parent body when kamacite, tetrataenite, and cloudy taenite formed as they cooled through the temperature range 975–575 K (~700–300 °C).

(5) The Eagle Station grouplet cooled at a rate comparable to that of the fast cooled MG pallasites, viz. ~15 K/Myr.

(6) The ungrouped pallasite, Milton, cooled at >5000 K/Myr.

For the remainder of this paper we focus solely on the origin of the MG pallasites.

5.2. Source(s) of main group pallasites

Could the diversity of cooling rates of the MG pallasites reflect their formation at the core–mantle boundaries of two or more bodies having differing sizes and compositions? Since MG pallasites are much more diverse than magmatic groups of iron meteorites in their concentrations of minor and trace elements in metal and other minerals and abundances of minerals like phosphate and trolilit, the possibility that they came from multiple sources needs to be readdressed using our cooling rate data. Wasson and Choi (2003) listed several MG pallasites with unusual properties, which we have identified on a plot of tetrataenite bandwidths vs. cloudy taenite particle sizes (Fig. 9a). They concluded that these pallasites formed in the same location as the other MG pallasites and that the mineralogical and chemical heterogeneity of this group reflects the complexity of processes operating within a single body, rather than derivation from multiple bodies (Wasson and Choi, 2003).

Most MG pallasites have 11–13.5 mol.% fayalite in their olivine but four are more Fe-rich with 16–19 mol.% fayalite. These pallasites with anomalous silicate compositions were called MG-as pallasites by Wasson and Choi (2003), who suggested that oxygen-rich magmatic gas in voids oxidized Fe and P causing a subsequent increase in Fe concentration in their olivine. This explanation might explain the presence in Springwater, the only multi-kg MG-as pallasite, of multi-cm wide regions where phosphates, mostly farringtonite Mg3(PO4)2, replaced metal between the olivine crystals (Buseck, 1977; Davis and Olsen, 1991). Two of the four MG-as pallasites, Springwater and Rawlinna, are plotted in Fig. 8a, and do not appear to have extreme cooling rates. In addition we found that fayalite concentration in olivine and cloudy taenite particle size are uncorrelated. Wasson and Choi (2003) identified six main-group pallasites with somewhat deviant metal compositions, which they called MG-am pallasites. Each one has anomalous concentrations of between one and three of the elements, Au, Co, Ga, Ge, and Ir. However, the concentrations of the other siderophiles appear quite typical for main-group pallasites. Of the five MG-am pallasites that we analyzed, Argonia, Brenham, Glorieta Mountain, Huckitta, and Krasnojarsk, only Glorieta Mountain has an extreme cooling rate (Fig. 9a). However, its cooling rate was very similar to that of the MG pallasite, Esquel, so that excluding Glorieta Mountain would not affect our conclusions about the origin of the MG pallasites in any way.

Wasson and Choi (2003) also identified on their inter-element diagrams three “unusual” MG pallasites, which have moderately high Ir concentrations. Our tetrataenite and cloudy taenite data in Fig. 9a show that the two we analyzed, Finmarken and Marjalahti, are both fast cooled MG pallasites: Finmarken clearly cooled much faster than any other MG pallasite in our set. However, tetrataenite and cloudy taenite dimensions are not correlated with bulk Ir concentrations, and excluding Finmarken from the MG would not affect our conclusions. Like Wasson and Choi (2003), we infer that the anomalous compositional features in these nine pallasites reflect local processes within the MG parent body such as solid–liquid metal mixing.

A single parent body for all MG pallasites is supported by the high precision oxygen isotopic analyses of olivine by Greenwood et al. (2006, 2008) who found uniform isotopic compositions in a set of 12 MG pallasites that included two MG-am, one MG-as, and two high Ir MG members. Ziegler and Young (2007) questioned whether MG pallasites could come from one source as they found a somewhat bimodal distribution of Δ17O values in seven MG pallasites. However, their total range of Δ17O values for MG pallasites is much wider than that of Greenwood et al. (2006) despite a smaller number of analyzed meteorites. Ziegler and Young (2007) also found that individual pallasites showed the same wide range of Δ17O values, contrary to Greenwood et al. (2006, 2008). We conclude that the oxygen isotopic compositions of MG pallasites are probably consistent with a single body.

Since the shape of olivine grains in pallasites probably reflects the degree of annealing of olivine–metal mixtures when they contained residual S-rich Fe–Ni–S liquid (Scott, 1977b; Saiki et al., 2003), one might expect that the main-group pallasites with rounded olivines cooled in separate locations from those with angular olivines. However, the five MG pallasite samples that contain rounded olivine, Rawlinna, Krasnojarsk, Springwater, Brenham, and Seymchan, have cooling rates that are spread throughout the MG range (Fig. 9b). In addition, Seymchan contains regions with angular olivine fragments and regions with rounded olivines (Fig. 2a). It therefore seems likely that the rounded olivine texture was formed by annealing before olivine fragmentation and slow cooling.

Although MG pallasites have diverse properties, there is no evidence that this requires that they formed in multiple parent bodies. Their diverse cooling rates are best interpreted as evidence that they cooled at different depths in one body rather than at the core–mantle boundaries of several bodies.
5.3. Possible relationships between main group pallasites and other meteorites

5.3.1. IIIAB irons

Three different techniques show that the IIIAB irons all cooled significantly faster than the MG pallasites (Figs. 5, 7, 8, A1, and A2), and that the latter therefore did not cool at the core–mantle boundary of the parent body of the IIIAB irons. Given the oxygen isotope and siderophile abundance data supporting a common source, we also need to ask whether the MG pallasites and the IIIAB irons could be derived from a common precursor body. Since the IIIAB irons cooled in a core surrounded by only a very thin layer of silicate under a few kilometers in thickness (Yang and Goldstein, 2006; Goldstein et al., 2009b), is it possible that the impact that mixed olivine and residual molten metal to make the MG pallasites also removed the IIIAB solid core so that it cooled with little mantle?

If the IIIAB core had solidified outwards, then a common ancestral body for the IIIAB irons and MG pallasites would be feasible. But the cooling rate data of Yang and Goldstein (2006) (see Fig. 5) preclude outwards solidification as the low-Ni irons, which formed first, cooled faster than the high-Ni irons. Our measurements of the sizes of the high-Ni cloudy taenite particles in IIIAB irons and tetrataenite bandwidths confirm this inverse correlation between bulk Ni and cooling rate (Fig. 6a and b). Thus three techniques suggest that IIIAB solidified inwards so that the residual Ir-poor liquid was near the center of the core. Removal of the residual liquid would have required...
that the solid core was broken open, destroying any relationship among IIIAB irons between bulk Ni concentration and burial depth. We conclude that MG pallasites did not form from residual liquid from the IIIAB core.

5.3.2. Other iron meteorites and olivine achondrites

If IIIAB irons are not derived from the core of the MG pallasite parent body, is it possible that another group of irons sampled the core? Since Seymchan was once classified as a IIE-anomalous iron before olivine-rich samples were recognized (Wasson and Wang, 1986), a link between MG pallasites and IIE irons might be suspected on the basis of metal compositions. However, silicates in the two groups have very different oxygen isotopic compositions (Franchi, 2007). In addition, IIE irons have lower Co concentrations and almost uniformly higher Ir concentrations (Wasson and Wang, 1986). Group IIE irons show a very minor compositional overlap with the MG pallasites. However, IIE irons nearly all have lower Ni, Co, Au, and As concentrations as well as carbides which are absent in the pallasites (Wasson et al., 1998). Group IIICD irons are also close in composition to metal in a few MG pallasites but their rare chondritic silicates have different oxygen isotopic compositions (Clayton and Mayeda, 1996) arguing against formation in a common body. Although the metal in MG pallasites has the low-Ir concentrations that favor formation from the core of a body that fractionally crystallized, no group of iron meteorites appears to be derived from the same parent body.

Three MG pallasites have olivine-free regions of metal that are several tens of centimeters in size—Brenham, Glorioeta Mountain, and Seymchan—and Seymchan was classified as an ungrouped iron before olivine-bearing samples were discovered. Is it possible, therefore, that other ungrouped irons may have been derived from olivine-free metal zones in the MG pallasite body? Although two ungrouped irons, Ban Rang Du and Tres Costillos, have compositions that approach that of Pavlodar, which is the MG pallasite with the lowest Ni, Au, and As and the second highest Ir concentration (Wasson et al., 1998; Wasson and Choi, 2003), there are currently no ungrouped irons with compositions close to the majority of MG pallasites, which have low-Ir concentrations. Lonaconing, which was once classified as an ungrouped iron, closely matches the compositions of Fe–Ni in many MG pallasites but was transferred to a subgroup of the IAB complex by Wasson and Kallemeyn (2002).

Olivine achondrites that might be linked to the MG pallasites are rare. Mineralogically, the dunite, NWA 2968, might qualify but its oxygen isotopic composition shows it is not from the same body as the MG pallasites (Greenwood et al., 2006; Scott et al., 2009b). We conclude that few if any ungrouped irons or olivine achondrites are related to the MG pallasites. Since the olivine-free metal regions should survive impacts better than pallasites, we infer that olivine-free metal zones were small and rare in the body that supplied the MG pallasites. Assuming the MG pallasites are representative of the body in which they cooled, its mean composition should be similar to that of large pallasite slices: viz., 65% olivine and 35% metal and associated phases (Buseck, 1977; Ulff-Møller et al., 1998).

5.4. Formation of main group pallasites

Although our cooling rate data effectively negate the compositional arguments in favor of a link with IIIAB irons, it remains probable that the metal in MG pallasites was largely derived from residual molten metal during the final stages of crystallization from a IIIAB-like source (Scott, 1977b; Wasson and Choi, 2003). Only by invoking fractional crystallization of ~80% of a metallic Fe–Ni in a core can one plausibly explain the highly fractionated, low-Ir metallic compositions in most MG pallasites, which show Ir/Ni ratios that are 0.05–0.005× those found in chondrites. Since the associated iron meteorites appear to be absent in meteorite collections, we infer that the core of the body that supplied the metal in the main-group pallasites crystallized outwards, like the IVB core (Yang et al., 2010), so that the solid inner core could have been separated from the surrounding residual molten metal by an impact. Fig. 10 shows schematically how the MG pallasites may have formed from a mixture of mantle fragments and the ~20 vol% of residual molten Fe–Ni. We suggest that removal of the solid core may have occurred in a glancing hit-and-run collision when the differentiated MG pallasite body struck a larger body (Asphaug et al., 2006). If all of the 20 vol% of residual molten metal had been mixed with twice the volume of mantle fragments, the pallasitic body would have had ~60 vol% of the original core in the differentiated body in Fig. 10a, or ~84% of the core’s radius.

Since the pallasites with rounded olivines did not cool below 925 K any slower than the pallasites with angular olivines, we suggest that the former owe their shape to prior annealing at the core–mantle boundary before the impact (Fig. 11). The rounded olivines may have formed either from olivine fragments created at the boundary by earlier milder collisions, or from olivine crystals that were subducted into the molten core by the weight of the olivine mantle (Davis, 1977; Wood, 1978, 1981). Pallasites like Pavlodar with relatively high Ir concentrations, near chondritic Ir/Ni ratios, and rounded olivines could have formed in the pallasitic layer prior to the impact that broke up the differentiated body. For pallasites like Brenham with low-Ir metal and rounded olivines, the metal may have solidified around the rounded olivine intergrowth in the pallasite body after the impact. The presence of olivine-free metal veins in Brenham is compatible with such an origin. Pallasites like Seymchan that have regions with rounded olivines and regions with angular olivines (Fig. 2a) appear to have formed from a mixture of fragments of olivine mantle, rounded olivine intergrowth (Fig. 11), and molten metal. How pallasites with angular olivines but high Ir concentrations, like Finmarken, formed is not known.

Unlike other models that envisage formation and cooling of pallasites at the core–mantle boundary, our model can account for the incorporation of some material originally located well above the core–mantle boundary. For example, some phosphates in MG pallasites contain high concentrations of rare-earth elements and negative Eu anomalies and appear to have crystallized from residual silicate melt (Davis and Olsen, 1991; Hsu, 2003). Traces of residual silicate melt from cooler regions could have been
mixed with mantle olivine and residual molten Fe–Ni when the pallasitic body accreted. In addition, cooler olivine mantle fragments that were originally located far above the core–mantle boundary may have been added to the pallasitic mixture causing incipient crystallization of molten metal around the olivine, hindering the tendency for molten metal and olivine to separate gravitationally.

5.5. Thermal model for main group pallasite body

A thermal model of the pallasite parent was developed, assuming that the MG pallasite parent body is composed of mantle olivine and metal with similar proportions to the large slices. The pallasite material was treated as a particulate composite with olivine as particle and metal as matrix.
We assume that the pallasite body has an olivine/metal volume ratio of 2/1, and that the mixture rule can be used to obtain the density and specific heat of pallasites. The thermal conductivity of pallasites can be calculated by an empirical equation given by Kaviany (2002) for particulate composite, giving a thermal conductivity of 7.5 W/m-K.

We also assume that a hot isothermal and spherical pallasite body was exposed to space after the collision took place and that regolith was absent. An initial temperature of 1750 K and a surface temperature of 200 K were assumed, and any internal heat generation in the body during cooling (for example by $^{60}$Fe decay) was neglected. The thermal conductive equation for these assumed conditions was solved using the code developed by Yang et al. (2007).

The calculation shows that if the center of the body cooled at 2.0 K/Myr, equivalent to the slowest cooled MG pallasites (Table 3), the pallasite body was 400 km in radius. If we assume that pallasite body contained 20 vol% of original core that was liquid and twice the volume of olivine mantle fragments, the protoplanet in Fig. 10 would have been about 950 km in radius. However, the pallasite body and protoplanet would have been much smaller if the pallasite body cooled under a silicate regolith, as seems plausible (see Haack et al., 1990).

6. SUMMARY

We have determined metallographic cooling rates below 975 K (~700°C) for eight MG pallasites by measuring Ni profiles across taenite lamellae of known crystallographic orientation in metallic Fe–Ni regions with Widmanstätten patterns and comparing these profiles with those calculated for diverse cooling rates. Local bulk concentrations of Ni and P were determined for each taenite lamella to correct for variations due to prior growth of swathing kamacite around olivine grains. Mean cooling rates for each pallasite, which were determined by averaging rates inferred for 7–10 taenite lamellae, ranged from 2.5 ± 0.3 K/Myr for Glorieta Mountain to 18 ± 9 K/Myr for Finmarken. The quoted uncertainties, which are twice the standard error of the mean, are 0.3–1.3 K/Myr, except for Finmarken. Total errors due to analytical errors and errors in measuring distances normal to the plane of the kamacite–taenite interface are probably less than the mean 2σ uncertainty factor of 1.6 in the cooling rates determined for each pallasite.

Sizes of high-Ni particles in cloudy taenite at the tetra-taenite interface in 28 MG pallasites (86–170 nm) and the widths of the tetra-taenite bands in 20 MG pallasites (1050–2170 nm) are positively correlated with each other and negatively correlated with the metallographic cooling rates. Results from three different techniques show that the MG pallasites cooled below 925 K (~700°C) at rates that differed by a factor of 5 or more. Since samples from a core–mantle interface should have indistinguishable cooling rates, we infer that the MG pallasites did not cool at the core–mantle interface of a differentiated asteroid.

Cooling rates for 28 MG pallasites inferred from cloudy taenite particle sizes are not correlated with bulk Ni concentration in metallic Fe–Ni or with the FeO concentration and oxygen isotopic composition of the olivine. (There is a very weak inverse correlation between log Ir in the metal and cloudy taenite particle size, but this is very dependent on the two end-members, Finmarken and Glorieta Mountain.) Since all the MG pallasites, including those with extreme metal or olivine compositions, appear to have come from a single body, the MG pallasites probably cooled at various depths in a single body.

Six group IIIAB irons with 7.7–10.0% Ni and cooling rates of ~50–350 K/Myr (Yang and Goldstein, 2006) have cloudy taenite particle sizes of 40–60 nm and tetra-taenite bandwidths of 300–450 nm. These data confirm that cooling rates of IIIAB irons are faster than those of MG pallasites and decrease with increasing bulk Ni. The widespread belief that MG pallasites formed and cooled at the core–mantle interface of the IIIAB core (Mittlefehldt et al., 1998; Wasson and Choi, 2003) is incompatible with the following observations: (a) IIIAB irons have cooling rates, tetra-taenite widths and cloudy zone particle sizes showing that their cooling rates decrease with increasing bulk Ni; (b) MG pallasites have cooling rates, tetra-taenite widths and cloudy zone particle sizes which show that their cooling rates differ by a factor of five or more; and (c) three techniques show that all the MG pallasites cooled more slowly than the IIIAB irons. Formation of IIIAB irons and MG pallasites in a single body by mixing residual core melt with mantle material prior to impact destruction and core–mantle separation is incompatible with the inverse correlation between bulk Ni and cooling rate for IIIAB irons, which shows that the IIIAB core crystallized inwards. We infer that MG pallasites and IIIAB irons are not derived from a common parent body even though they have indistinguishable oxygen isotopic compositions (Clayton and Mayeda, 1996; Franchi, 2007).

We suggest that MG pallasites formed from an impact that mixed residual Ir-poor molten metal from the outermost part of a IIIAB-like core that was ~80% fractionally crystallized from the center (like the IVB core; see Yang et al., 2010) with roughly twice the volume of olivine mantle fragments. The absence of associated iron meteorites or olivine achnodrites suggests that olivine-free metal regions and metal-free olivine zones were relatively rare in the MG pallasite body after it had solidified. Separation of the solid core and most of the associated mantle may have resulted from a grazing hit-and-run impact with a larger protoplanet or asteroid (Fig. 10). Such an impact would have been more effective than a head-on collision in separating core and mantle material without intense shock (Asphaug et al., 2006). The possibility that a hit-and-run collision created more than one MG pallasite parent body cannot be excluded.

Since MG pallasites with rounded olivines did not cool any slower than those with angular fragments of olivine, we infer that the annealing of olivine and metal that converted angular to rounded olivine occurred prior to the impact that created the pallasite body. Thermal calculations show that if the pallasite body lacked a regolith and cooled at 2 K/Myr at its center, like the slowest cooled MG pallasite, the pallasite body would have been 400 km in radius. However, it would have been considerably smaller if it had a silicate regolith, as seems likely.
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APPENDIX A. THEORY OF CLOUDY TAENITE AND TETRATAENITE FORMATION

A1. Cloudy zone particle size

The widths of the cloudy zone particles at the tetrataenite interface in several chemical groups of iron meteorites and stony irons are related to the cooling rate determined from the growth of Widmanstätten kamacite as shown in Fig. A1. The equation which best fits the data is

$$d_{cz}^2 = \frac{m}{CR}$$

(A1)

where $d_{cz}$ is the cloudy particle size in nm, $m$ is constant which equals to 7,620,000, and $CR$ is the metallographic cooling rate in K/Myr. Fig. 8a shows that this line is within error of the best fit line for the MG pallasite data.

We should not expect all meteorites in Fig. A1 (and A2) to define a single line as the taenite compositions that determine the metallographic cooling rate reflect cooling rates at temperatures that are about 200 K higher than the formation temperatures of cloudy zone and tetrataenite. The cooling rates during formation of cloudy zone particles and tetrataenite should be slower than the cooling rates during Widmanstätten growth by an amount that depends on the nature of the body. For the IVA irons, the thermal model of the asteroid (Yang et al., 2007, 2008) indicates that the cooling rate below 675 K (~400 °C) is a factor of ~1–5 slower than the cooling rate below 875 K (~600 °C) for a metallic body. But for a slow cooled parent body like the pallasite asteroid, the cooling rate below 675 K is most likely ~1–3x slower than the cooling rate below 875 K.

The cloudy zone microstructure formed by spinodal decomposition followed by Oswald ripening. If we neglect the initial particle size before coarsening, the cloudy zone particle size should follow the power law for the coarsening growth process where

$$D^n = mt$$

(A2)

and $D$ is the size of the particle, $m$ is the coarsening rate constant, and $t$ is time. The parameter $n$ is a constant which depends on the mechanism which controls the coarsening process. A classical view of the coarsening process under isothermal conditions suggests that $n = 4$ for an interface-controlled growth process (Zhu et al., 1999), $n = 3$ for a bulk diffusion-controlled growth process (Lifshitz and Slyozov, 1961; Wagner, 1961), and $n = 2–3$ for a trans-interface-controlled growth process (Ardell and Ozolins, 2005).

The cloudy zone particle size follows a power law, given by Eq. (A1), where $n = 2.9$. For a continuous cooling process $t = AT/CR$, where $AT$ is the temperature interval for

Fig. A1. Cloudy zone particle size vs. metallographic cooling rate for iron and stony-iron meteorites: IVA irons (Goldstein et al., 2009a), IIIAB irons (Yang and Goldstein (2006) and this study), main group pallasites (this study), IVB irons (Yang et al., 2010) and mesosiderites (Hopfe and Goldstein, 2001).
spinodal decomposition and the coarsening process. For cloudy zone formation $\Delta T$ is about 150 K. Since $n = 2.9$ is very close to either a bulk diffusion-controlled ($n = 3$) or a trans-interface controlled ($n = 2–3$) growth process, the empirical expression of power law for growth of cloudy zone particle given by Eq. (A1) is consistent with coarsening theory.

A2. Tetrataenite bandwidth

The widths of the tetrataenite bands in three groups of iron meteorites and the MG pallasites are inversely correlated with the cooling rates determined from the growth of Widmanstätten kamacite as shown in Fig. A1.

The equation of the best fit line to the data plotted in Fig. A1 is

$$d_{2.3}^n = \frac{k}{CR}$$  \hspace{1cm} (A3)

where $d_{2.3}$ is the tetrataenite bandwidth in nm, $CR$ is cooling rate in K/Myr, and $k$ is constant which equals to 14,540,000.

The isothermal diffusion-controlled growth of one phase in a two-phase alloy obeys the parabolic law

$$x^2 = Kt$$  \hspace{1cm} (A4)

where $x$ is the thickness of new phase, $K$ is a constant and $t$ is time. The exponent 2.3 in Eq. (A3) is very close to the exponent 2 in Eq. (A4) above and is consistent with the parabolic law for growth of the tetrataenite band.

REFERENCES


Fig. A2. Tetrataenite bandwidth vs. cooling rate for iron and stony-iron meteorites: IVA irons (Goldstein et al., 2009a), IIIAB irons (Yang and Goldstein, 2006 and this study), main group pallasites (this study), and IVB irons (Yang et al., 2010).


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