Fast grain growth of olivine in liquid Fe–S and the formation of pallasites with rounded olivine grains

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Abstract

Despite their relatively simple mineralogical composition (olivine + Fe–Ni metal + FeS ± pyroxene), the origin of pallasite meteorites remains debated. It has been suggested that catastrophic mixing of olivine fragments with Fe–(Ni)–S followed by various degrees of annealing could explain pallasites bearing solely or prevalently fragmented or rounded olivines. In order to verify this hypothesis, and to quantify the grain growth rate of olivine in a liquid metal matrix, we performed a series of annealing experiments on natural olivine plus synthetic Fe–S mixtures. The best explanation for the observed olivine grain size distributions (GSD) of the experiments are dominant Ostwald ripening for small grains followed by random grain boundary migration for larger grains. Our results indicate that olivine grain growth in molten Fe–S is significantly faster than in solid, sulphur-free metal. We used the experimentally determined grain growth law to model the coarsening of olivine surrounded by Fe–S melt in a 100–600 km radius planetesimal. In this model, an impact is responsible for the mixing of olivine and Fe–(Ni)–S. Numerical models suggest that annealing at depths of up to 50 km allow for (i) average grain sizes consistent with the observed rounded olivine in pallasites, (ii) a remnant magnetisation of Fe–Ni olivine inclusions as measured in natural pallasites and (iii) for the metallographic cooling rates derived from Fe–Ni in pallasites. This conclusion is valid even if the impact occurs several millions of years after the differentiation of the target body was completed.

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1. INTRODUCTION

Pallasites are a group of stony-iron meteorites with a simple, yet vexing mineralogical composition. Buseck (1977) found pallasites to contain 64.9 vol% olivine, 31.0% metal, 2.3% troilite (FeS), 1.2% schreibersite ((Fe,Ni)\textsubscript{3}P), 0.4% chromite, and 0.2% phosphates on average. An occasionally present additional phase is phosphorite olivine. Texturally, pallasites consist of olivine surrounded by a metal matrix with a few additional minor phases. Recent findings provided pallasites bearing up to 40 vol% pyroxene, e.g., North West Africa NWA 1911 (Bunch et al., 2005), changing the classic definition. Originally separated into a Main Group (MG) and an Eagle Station group (ES) (Scott, 1977a), pallasites (the Meteoritical Bulletin website lists 103 pallasite records) are nowadays subdivided into 5–7 groups based on the oxygen isotopes signatures, trace element concentrations in the Fe–Ni metal, and mineralogical composition (Scott, 2007; Yang et al., 2010; Boesenberg et al., 2012).

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A further characteristic feature is the morphology of the olivines, which varies between angular and rounded, and constitutes a key to deciphering the mechanism of pallasite formation. Macroscopically, there are pallasite specimens bearing solely or prevalently well-rounded, well-sorted olivine grains, and samples with almost only angular fragments of olivine (fragmental pallasites; Buseck, 1977; Scott, 1977a). The former are commonly attributed to prolonged annealing, the latter could be the result of a violent mixing or fracturing event. Among pallasites bearing fragmental olivines, it is possible to distinguish those with a prevalence of large euhedral or subhedral crystals, often broken into several pieces and/or crossed by multiple fractures (e.g., the Esquel pallasite), and those with a preponderance of shattered fragments in the sub-millimetre range (Huckitta). Even in highly fragmental pallasites, the smallest fragments are invariably moderately- to well-rounded. Specimens bearing exclusively one type of olivine are uncommon, while a combination of two morphologies is frequent. The Seymchan pallasite is one of the rare samples containing all morphological olivine types. A classification of pallasites based on olivine textures was presented by Scott (1977b). Nevertheless, there is hardly any correlation between olivine type and chemical and mineralogical features, only a tendency that pallasites with more differentiated metal compositions and higher sulphur contents (Yang et al., 2010) contain rounded olivine slightly more frequently than fragmented olivine (Buseck, 1977; Scott, 1977a).

The peculiar characteristics of this meteorite family led to a number of formation theories. On one hand, the genesis of pallasites was ascribed to magmatic differentiation within a single chondritic body in a region located near the core mantle boundary (CMB) (Ringwood, 1961; Lovering, 1962; Mason, 1963; Anders, 1964; Scott, 1977a,b; Wasson and Choi, 2003; Boesenberg et al., 2012). Other authors suggested formation scenarios involving an external source of heat and/or matter related to impacts of various asteroids into the pallasite parent body (Mittlefehldt, 1980; Malvin et al., 1985; Scott and Taylor, 1990; Ulff-Møller et al., 1998; Scott, 2007; Yang et al., 2010).

The composition of the metal fraction in pallasites, in particular the low Ir content, is consistent with fractional crystallization of the liquid in the IIIAB iron meteorite parent body after crystallization of 80% of the metal (Scott, 1977c; Wasson and Choi, 2003). Nevertheless, there is no unequivocal evidence of a common origin for IIIAB iron meteorites and pallasites, as indicated by oxygen isotopes (Scott et al., 2009), the concentration of siderophile elements (Yang et al., 2010), and cosmic ray exposures ages (Eugster et al., 2006). Moreover, minor element abundances in olivine and REE concentrations in phosphates are best modelled by low pressure crystallization (Davis and Olsen, 1991; Hsu, 2003), difficult to reconcile with incomplete silicate-metal separation at the boundary of a growing core or with mixing of an olivine layer and metal at the CMB of an already differentiated planetesimal in the aftermath of a disturbance generated by impacts (Malvin et al., 1985). Similar, the metallographic cooling rates of 2.5–18 °C/Ma and 13–16 °C/Ma, determined for Main Group and Eagle Station pallasites, respectively, are not compatible with annealing in proximity of the CMB (Yang et al., 2010).

Tarduno et al. (2012) detected a remnant magnetisation in microscopic Fe–Ni inclusions in olivine crystals of two Main Group pallasites (Bryson et al., 2015). The measured magnetic intensities were ascribed to the presence of dynamo action in their parent body, proposed to be active throughout their formation and cooling below the Curie temperature of these Fe–Ni particles (~360 °C). Since the temperature in the proximity of the CMB, while the dynamo is active, is many hundreds of degrees above the Curie temperature of Fe–Ni alloy (Tarduno et al., 2012), the region where pallasite-type material was formed has to be placed at shallower depths.

In this model a collision event resulted in the fragmentation of olivines in the target body mantle mixing with the metal from the impactor. Fragmentation is followed by olivine annealing at relatively shallow depths. In this scenario, the depth range at which the mixed material cools down determines the olivine textures, with fragmented or shattered olivines being little annealed at the shallowest depths while rounded olivines form by longer and hotter annealing deeper in the planetesimal’s mantle. This hypothesis could be tested, if annealing of small fragments in the shallow mantle is shown to result in rounded grains with a grain size comparable to that observed in pallasite meteorites before temperatures decrease such that the annealing kinetics becomes insignificant.

Saiki et al. (2003) performed annealing experiments on a mixture of olivine and solid Fe–Ni, demonstrating that rounding of angular olivine fragments in hot solid metal is efficient for the smallest fragments, but inefficient over meaningful time spans for large fragments >1 mm. Saiki et al. (2003) also pointed out that the absence of sulphur in their experiments might have slowed down the rate of textural annealing.

A different approach is to test whether grain growth of olivine fragments in a metal matrix might yield the texture and maximum grain size of olivines observed in pallasites with rounded olivine. Guignard et al. (2012) exposed forsterite plus solid nickel aggregates to high temperatures, finding that forsterite growth in a solid Ni matrix could yield textures similar to those of pallasites, but growth rates were too small. A direct comparison of Guignard et al.’s (2012) experiments with actual pallasites is difficult, since their starting material was Fe- and S-free.

Our investigation aims to assess the grain growth kinetics of olivine fragments in a Fe–S melt. Moreover, we evaluate the grain size distribution (GSD) of the experimentally grown olivines. For comparison, we determine the GSD of three pallasites bearing rounded olivine and two with fragmented olivines in order to discuss their origin and formation conditions. Finally, we elaborate a model of olivine growth in a Fe–S matrix in a planetesimal (following the impact of a differentiated body). In this model, the liquid portion of the impactor core is injected into an olivine layer of the planetesimal’s mantle, leading to the formation of pallasite meteorites.
2. METHODS

2.1. Experimental technique

The starting materials were mixtures of San Carlos olivine and Fe–S powders in proportions of 60:40–90:10 vol%. Three runs with Fe–S served to test for carbon diffusion from the graphite capsule into the molten Fe–S. Olivine powder was obtained through crushing and subsequent milling for a few hours. The final grain size was measured through laser diffraactometry on dispersed solutions (“Mastersizer 2000” instrument, Malvern Instruments Ltd.) resulting in a mean of 1.8(5) μm. The Fe–S mixture corresponds to the composition of the eutectic in the iron–sulphur binary at 1 GPa, i.e. 70.5 wt% Fe and 29.5 wt% S (T_{eute} = 990 °C; Brett and Bell, 1969; Usselman, 1975; Fei et al., 1997), referred to hereafter as Fe–S. The desired Fe–S composition was obtained by mixing sulphur pieces (99.999% purity, CeramTM Inc.) and iron powder (99.9% purity, mesh 5 μm CeramTM Inc.).

Olivine and the Fe–S powder were mixed in the desired proportion, stored in vacuum at 50 °C for several days, and loaded into graphite capsules. The graphite capsules of 4.0 mm height and 2.0 mm diameter were fitted into platinum capsules that were sealed by arc welding. All experiments were performed in an end-loaded piston cylinder press with a 14 mm bore. Piston cylinder assemblies consisted of external NaCl- or Talc-Pyrex sleeves, mostly a straight graphite furnace of 36 mm length and 1 mm wall thickness, and inner crushable MgO cylinders containing the capsule and a nullite thermocouple ceramics. Only for runs OFS-nf-I and -14 (Table 1) the graphite heaters were stepped, with the top and bottom thirds having a reduced thickness of 0.5 mm. B-type Pt–Rh thermocouples were employed to control the temperature with an accuracy of ±5 °C. The thermocouple was separated from the Pt-capsule by a 0.6 mm thick corundum disk. Run pressure was calibrated against fayalite + quartz = orthoferrosilite (Bohlen et al., 1980) and the quartz-coesite transition (Bose and Ganguly, 1995). Heating was terminated by shutting off power, resulting in a cooling rate of ca. 50 °C/s down to <300 °C. Run conditions and composition of the starting mixture for each run are reported in Table 1.

2.2. Compositional analysis of olivine and Fe–S

Polished sections of the run products were imaged with backscattered electrons (BSE) and chemically characterised with wavelength dispersive spectrometry (WDS) employing a JEOL JXA-8200 electron microprobe. Olivine + Fe–S samples were graphite coated, whereas the Fe–S only samples were analysed uncoated to measure carbon.

WDS analyses of olivine were operated with a 15 kV, 20 nA focused beam. To improve the quality of the Fe–S analyses the accelerating voltage was increased to 20 kV and a beam size of 5–50 μm was used, the latter to average across the finely spaced quench features of the Fe–S melt. In run OFS-15, a 5–10 μm size sub-triangular to spherical phase was measured with a focussed beam at 20 kV and 20 nA. For the Fe–S phase, we employed native iron, haematite or wüstitte, and troilite or pyrite for standardization of the microprobe, for olivine, forsterite and fayalite were used for standardization. Energy Dispersive X-ray Spectroscopy (EDS) was employed to detect the presence of carbon in the quenched Fe–S alloy on non-graphite-coated samples, to a detection limit of ~0.5 wt%.

2.3. Image analyses

To determine the abundance of Fe–S in each experimental sample, BSE images were converted to binary images, resulting in white for Fe–S and black for olivine (Fig. 1e). Each BSE image was divided into 150 × 250 μm slices, resulting in 15–21 frames per sample. Then, binarisation was obtained by applying a threshold filter, and the black and white areas were measured. Repeating the filtering process and the measurement of the black and white areas three times for each frame resulted in an uncertainty <0.2%, while the overall error on the Fe–S mode was ~0.6% (Table 1).

Average olivine grain sizes and grain size distributions were obtained starting from binary images whose dimensions varied between 70 × 100 and 300 × 500 μm, depending on the size of olivine grains. Olivine grains in direct contact had to be manually separated in grey-scale BSE images, prior to binarisation, in order to enable the image processing software ImageJ (public domain, Wayne Rasband, NIH, USA) to recognise each olivine as a separate object (Fig. 1e and f).

A similar procedure was applied to quantify olivine grain sizes in several slabs from pallasite meteorites. The following criteria were employed to select rounded olivine-bearing pallasites for comparison of their olivine populations with the experimental ones: (a) One or more sections with well-rounded olivine grains were available;

<table>
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<th>Run</th>
<th>T (°C)</th>
<th>Duration (h)</th>
<th>Metal fractionb (vol%)</th>
</tr>
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<td>72</td>
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<td>1200</td>
<td>72</td>
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</tr>
<tr>
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<td>1300</td>
<td>72</td>
<td>19.3 (6)</td>
</tr>
<tr>
<td>OFS-4</td>
<td>1300</td>
<td>72</td>
<td>9.4 (4)</td>
</tr>
<tr>
<td>OFS-5</td>
<td>1300</td>
<td>72</td>
<td>14.9 (6)</td>
</tr>
<tr>
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<td>150</td>
<td>19.9 (5)</td>
</tr>
<tr>
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<td>1300</td>
<td>39</td>
<td>20.2 (8)</td>
</tr>
<tr>
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<td>145</td>
<td>19.5 (7)</td>
</tr>
<tr>
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<td>1100</td>
<td>300</td>
<td>20.3 (8)</td>
</tr>
<tr>
<td>OFS-nf-14</td>
<td>1430</td>
<td>8</td>
<td>19.7 (4)</td>
</tr>
<tr>
<td>OFS-15</td>
<td>1300</td>
<td>72</td>
<td>45.2 (26)</td>
</tr>
</tbody>
</table>

Table 1: Experimental conditions and melt abundance after image analyses.

a Assembly with a stepped furnace; nf = new furnace.

b Metal abundance from digital image analyses of run products. The error from repeated measurements is reported between brackets.
(b) The number of olivine grains in the sections had to be >100–150, to obtain a statistically significant GSD; (c) Olivine, FeS and Fe–Ni should represent >90% of the section’s area; (d) Olivine abundance should not exceed 90% and Fe + FeS abundance should not exceed 50%. High quality images of pallasites satisfying these criteria were available for the meteorites Brenham, Seymchan, and Springwater. We also analysed the size distribution of fragmental pallasite Brahin and a different portion of Seymchan. For these slabs, image analyses started from photographs instead of BSE images. Grain size was equated to the diameter of each object’s circle-equivalent area. 2D apparent grain sizes were corrected for sectioning effects of a sphere with the formula: \( d_{3D} = d_{2D}/(\pi/4) \) (Kong et al., 2005).

Roundness and the ratio between perimeter and circle equivalent diameter are used to quantify the shape of the grains in experimental samples and rounded pallasite slabs. Note that roundness is a measure for equi-dimensionality and not for smoothness of the surface. The quantitative formulation of roundness follows Waddell (1932): \( 4\pi A/MA^2 \), where \( A \) is the area of the grain and \( MA \) is the length of the major axis. The circle equivalent diameter is: \( 2(A/\pi)^{1/2} \).

2.4. Some background on grain growth

In an aggregate of grains a decrease of grain surface area via grain growth leads to a reduction of the surface to volume ratio and stabilizes the system by reducing its Gibbs free energy. This is a direct consequence of the grain boundary energy per unit volume \( E \) being inversely proportional to the grain radius \( r \): \( E \propto \gamma/r \), where \( \gamma \) is the specific surface energy of the coarsening phase (Evans et al., 2001).
Grain coarsening could be interpreted as a consequence of normal grain growth, which is expressed by the merging of multiple grains to form larger ones (Atkinson, 1988). Normal grain growth theory is usually employed for the study of mono-phase aggregates. Ostwald ripening theory explains the growth of grains dispersed in a solid or liquid matrix (Lifshitz and Slyozov, 1961; Wagner, 1961). Normal grain growth in the presence of a second phase is not influenced by the volume fraction of the coarsening phase, whereas Ostwald ripening depends on the ratio of the coarsening phase and matrix (Yoshino and Watson, 2005; Faul and Scott, 2006; Guignard et al., 2012).

Whatever the governing mechanism, the increase of average grain size \( d \) with time \( t \) can be described by the equation:

\[
\frac{d^n - d_0^n}{d_0^n} = k_0 \exp\left(-\frac{E_a}{RT}\right) t
\]

where \( d_0 \) is the starting grain size, \( d \) the grain size at time \( t \), \( n \) the growth exponent, \( k_0 \) a characteristic constant, \( E_a \) activation energy, \( R \) the gas constant, and \( T \) absolute temperature.

For normal grain growth of a single, pure phase, a growth exponent of \( n = 2 \) is predicted, while chemical exchange via other phases yields \( n > 2 \) (Atkinson, 1988). Ostwald ripening of solid particles may be rate-limited by diffusion of material from one grain to another through the matrix or by removal and precipitation of material from the crystal surface, defined as diffusion controlled and surface reaction controlled ripening (Martin et al., 1997). The growth exponent predicted for diffusion controlled Ostwald ripening is \( n = 3 \), while for surface reaction controlled Ostwald ripening it is \( n = 2 \).

The distribution of the relative size of grains forming an aggregate that underwent normalised grain growth or Ostwald ripening is time-invariant, though the average grain size increases with time. Hence, grain size distributions normalised by dividing the value of each size bin by the mean grain size \( d_m \) are characteristic for a specific growth process. The position of the distribution’s maximum frequency and the width of the grain size distribution scatter with respect to the mean grain size are potential diagnostic characteristics (Lifshitz and Slyozov, 1961; Hillert, 1965).

For grain growth controlled by diffusion-limited Ostwald ripening, Hillert (1965) defined a normalised grain size distribution having a cut-off at \( 1.5 \) \( d_m \) and the peak positioned at \( d > d_m \). First-order surface reaction controlled Ostwald ripening, governed by the movement of discrete growth units from one position to another along grain surfaces (Hanitzsch and Kalweit, 1969), has also a peak at \( d > d_m \) and a maximum grain size \( d_{max} \) of \( <1.7 \) \( d_m \). Second order surface reaction controlled growth, where new layers of atoms are continuously spread along faceted crystal surfaces (Bennema and van der Eerden, 1987), leads to a maximum at \( d < d_m \) and a tail extending to \( 2.5 \) \( d_m \). Finally, theoretical grain size distributions can be calculated for grain growth, where grain boundary motion is random (so-called Rayleigh distribution, Louat, 1974) and for a standard Log-normal distribution (Atkinson, 1988). Both distributions have a peak at \( d < d_m \) and a maximum grain size \( >3.0 \) \( d_m \), Rayleigh and Log-normal distributions can be adjusted by varying the parameters in their defining equations (Eqs. 4 and 5 in Faul and Scott, 2006).

### 3. RESULTS

#### 3.1. Composition of olivine and Fe–S melt

Olivine is compositionally homogeneous in each run, indicating that chemical equilibration is reached even for short experiments and relatively low temperatures (Table 1). With respect to the starting material, olivine Fe-contents increase in all experiments by about 2 wt% except for OFS-15 (Table 2), where annealing of a mixture containing 40 vol% of Fe–S yielded an olivine shifted towards a more Mg-rich composition. Olivine NiO-contents dropped to \( \leq 0.018 \) wt% (Table 2), starting from an average of 0.44 wt% (Galoisy et al., 1995). The melting temperature of the resulting Fe–S compositions is lower than run temperature in all experiments (Usselman, 1975; Fei et al., 1997), the presence of 1–2 wt% Ni in the iron-sulphide may have further reduced the melting temperature of the alloy. The texture of the Fe–S portion is indicative of exsolution during quench. In run OFS-15 features that might be related to the stability of two coexisting metallic phases are observed: one with a composition similar to FeS (with clear quench features) and one that is almost pure iron. The latter has triangular or pseudo-circular shapes (Fig. 2). Precise analysis of the Fe–S alloy is difficult, because melt pools are usually small (4–5 \( \mu \)m) but a beam size of \( \sim 10–15 \mu \)m would be needed to average across the quench heterogeneities. Nevertheless, the Fe–S matrix shows a decrease in iron content (by 5–9 wt%) with a concomitant increase of oxygen (0.2–1.2 wt%) and sulphur (4–9 wt%, Table 2). Analysis of the two quench phases with a focused beam (beam size 1 \( \mu \)m) revealed that the brighter phase has a composition with \( >80–90 \) wt% iron and contains up to 2.5 wt% Ni (run OFS-1), whereas the lightgrey phase composition is almost stoichiometric FeS (63.5 wt% Fe). The minute size of the Fe–Ni alloy (\( <3–4 \mu \)m), resulted in mixed analyses with the light grey phase as the excitation volume of the electron beam generally exceeds the dimension of the Fe–Ni phase. This results in a variation of the sulphur concentration measured in each spot (\( \sim 7–20 \) wt%).

Analyses of uncoated samples of runs FS-1, FS-2 and FS-3 (Table 1) showed a preservation of the starting composition (Fe\(_{90}\)S\(_{30}\) in wt%), with additional 0.3–0.8 wt% oxygen (Table 2). Carbon remained below detection limit (\( <0.5 \) wt% with EDS) and was not visible in elemental X-ray maps. This observation is consistent with the Fe–S–C ternary at 1 atm (Wang et al., 1991), indicating that Fe--S\(_{90}\) and graphite\(_{90}\) coexist at the experimental temperatures and Fe-S proportion of our starting mixture, with \( <0.5 \) wt% carbon dissolved in the Fe–S melt. The possible coexistence of immiscible sulphur- and carbon-rich liquids at run pressure appears unlikely when extrapolating the topology of the Fe–S–C system to 1 GPa on the basis of data at 2–6 GPa from Dasgupta et al. (2009).
Table 2
Composition of olivines and iron-sulphide alloys after annealing.

<table>
<thead>
<tr>
<th>Element (weight%)</th>
<th>OFS-1</th>
<th>OFS-2</th>
<th>OFS-3</th>
<th>OFS-4</th>
<th>OFS-nf-1</th>
<th>OFS-9</th>
<th>OFS-10</th>
<th>OFS-11</th>
<th>OFS-nf-14</th>
<th>OFS-15*</th>
<th>S. Carlos</th>
<th>Typical s.d. b</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>39.81</td>
<td>39.97</td>
<td>39.79</td>
<td>40.51</td>
<td>39.63</td>
<td>40.28</td>
<td>40.27</td>
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Element (weight%)

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<th>OFS-3</th>
<th>OFS-4</th>
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<td>36.77</td>
<td>36.60</td>
<td>36.13</td>
<td>39.34</td>
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<tr>
<td>O</td>
<td>0.53</td>
<td>0.71</td>
<td>0.77</td>
<td>0.75</td>
<td>0.76</td>
<td>0.61</td>
<td>0.37</td>
<td>0.19</td>
<td>0.78</td>
<td>1.17</td>
<td>0.28</td>
<td>0.19</td>
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<tr>
<td>Total</td>
<td>99.70</td>
<td>99.54</td>
<td>99.87</td>
<td>98.75</td>
<td>99.55</td>
<td>98.47</td>
<td>99.81</td>
<td>99.36</td>
<td>99.56</td>
<td>100.71</td>
<td>100.11</td>
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<tr>
<td>O (atomic%)</td>
<td>1.50</td>
<td>1.94</td>
<td>2.08</td>
<td>2.13</td>
<td>2.11</td>
<td>1.74</td>
<td>1.02</td>
<td>0.52</td>
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<td>9</td>
<td>8</td>
<td>4</td>
<td>10</td>
<td>9</td>
<td>12</td>
<td>9</td>
<td>7</td>
<td>11</td>
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</table>

Runs with iron-sulphide mix

<table>
<thead>
<tr>
<th>Element (weight%)</th>
<th>FS-1</th>
<th>FS-2</th>
<th>FS-3</th>
<th>s.d.</th>
</tr>
</thead>
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<tr>
<td>Fe</td>
<td>66.44</td>
<td>67.96</td>
<td>65.87</td>
<td>0.61</td>
</tr>
<tr>
<td>S</td>
<td>29.36</td>
<td>30.46</td>
<td>30.12</td>
<td>0.59</td>
</tr>
<tr>
<td>O</td>
<td>0.51</td>
<td>0.80</td>
<td>0.29</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>96.31*</td>
<td>99.22</td>
<td>96.28*</td>
<td></td>
</tr>
<tr>
<td># of analysis</td>
<td>18</td>
<td>12</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

Beam size for WDS analysis set to 50 μm.

* The iron-sulphide presents evidences of stability of two phases on top of quench exsolution features in the sulphur-rich phase. One phase has composition similar to FeS (see the composition in the table), and the other is almost pure iron with minor amount of nickel.

b s.d. means single standard deviation.

c Nickel signal acquisition time for EMPA analyses was set to 120 s in order to enhance the detection limit.
3.3. Olivine grain growth

The final olivine grain size is proportional to the annealing time at a given temperature (Eq. (1)), while for the same run duration grain growth rates increase with increasing annealing temperature (Table 3 and Fig. 3). Growth rates are also influenced by the olivine fraction with larger average grain sizes occurring in runs with higher olivine contents (Table 3).

A non-linear square fit of Eq. (1) to the data from the annealing experiments with an olivine/Fe–S ratio of 80/20 led to the following growth parameters: $n = 2.42(46)$, $k_0 = 9.43 \times 10^6 \text{mm}^n \text{s}^{-1}$, $E_a = 289(59) \text{kJ/mol}$, with a starting grain size, $d_0$, of 1.8(5) μm, where parentheses indicate uncertainties. The fit parameters were $n$, $E_a$, and $k_0$. The errors on temperature measurement, average sample grain size, and on $d_0$ were included in the sum of squared results minimisation. Olivine growth curves for temperatures of 1100, 1200 and 1300 °C are shown in Fig. 3a. The maximum and minimum values of $k_0$ are $8.53 \times 10^8 \text{mm}^{2.28} \text{s}^{-1}$ and $4.06 \times 10^7 \text{mm}^{1.96} \text{s}^{-1}$. The effect of the error propagation is displayed in Fig. 3b.

3.4. Normalised grain size distributions (GSD) of experimental and natural samples

To determine grain size distributions of experimental and natural samples, we follow the approach of Faul and Scott (2006) and define the width of the bins employed to classify grain dimensions such that no more than 1/5 of the bins have a frequency $<5$ for the smallest number of measured grains (experiment OFS-4, pallasite Seymchan; Table 3). This procedure results in normalised bin widths of 0.15 for normalised GSD. Normalisation is performed by dividing the frequency of each bin by the value of the maximum frequency, grain sizes are normalised by dividing by the mean grain size $d_{\text{mean}}$.

Normalised GSDs of experimental samples are invariant with annealing time and temperature. The maximum grain size $d_{\text{max}}$ is always $<3.0 d_{\text{mean}}$, more than 85% of the grains have a size between 0.5 and 2.0 $d_{\text{mean}}$, and the maximum frequency is at a grain size $\leq d_{\text{mean}}$ (within 1σ; Fig. 4). In fact, the normalised GSD maximum is at $\sim1.0 d_{\text{mean}}$ for all runs except OFS-11 (Fig. 4b) and OFS-5, supporting the conclusion that steady-state growth was reached even for the shortest and lowest temperature runs.

Pallasites with rounded olivine (Brenham, Seymchan, and Springwater) have normalised GSDs with $d_{\text{max}} \leq 2.5 d_{\text{mean}}$ and a peak frequency at $d < d_{\text{mean}}$ (Fig. 5a). More than 85% of the Brenham and Springwater olivines have sizes between 0.5 and 1.5 $d_{\text{mean}}$ while Seymchan has a broader normalised GSD and a double peak (Fig. 5a and c). Image analyses of the angular olivines of Seymchan and of the olivines of pallasite Brahin yields normalised GSDs with a peak frequency at $\sim0.2–0.3 d_{\text{mean}}$ and a long tail extending to about 3 $d_{\text{mean}}$ for Seymchan (Fig. 5c), and to about 7 $d_{\text{mean}}$ for Brahin. This type of normalised GSD is characteristic for shock-induced fragmentation (Jones et al., 1996).

The normalised GSDs of experimental and rounded olivine-bearing natural samples were compared with theoretical distributions calculated for diffusion and surface reaction controlled Ostwald ripening of cylindrical particles (Hanitzsch and Kalhweit, 1969), as well as with Rayleigh and Log-normal distributions. This comparison reveals that none of the above-listed mechanisms can unequivocally explain the olivine growth observed in the experimental and natural samples (Figs. 4 and 5b). Either the position of the maximum frequency does not fit or the width of the GSD is too broad or narrow.

To quantify the similarity between calculated and measured normalised GSDs we use a $\chi^2$ test:
### Table 3
Results of digital image and NGSD analyses.

<table>
<thead>
<tr>
<th>Run name</th>
<th>Annealing time (h)</th>
<th>Annealing T (°C)</th>
<th>Nominal metal fraction (vol%)</th>
<th>Average grain size (μm)</th>
<th>Number of grains</th>
<th>$\chi^2$ value</th>
<th>2nd Order S. Diff.</th>
<th>1st Ordered S. Diff.</th>
<th>Rayleigh</th>
<th>Log-normal</th>
<th>Roundness$^a$</th>
<th>Perim/CircEqDiam$^b$</th>
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</thead>
<tbody>
<tr>
<td>OFS-1</td>
<td>72</td>
<td>1100</td>
<td>20</td>
<td>3.2 (8)</td>
<td>731</td>
<td>0.48</td>
<td>0.48</td>
<td>1.33</td>
<td>13.63</td>
<td>0.74 (13)</td>
<td>1.24 (11)</td>
<td></td>
</tr>
<tr>
<td>OFS-nf-1</td>
<td>150</td>
<td>1100</td>
<td>20</td>
<td>6.1 (8)</td>
<td>1303</td>
<td>0.48</td>
<td>0.59</td>
<td>0.57</td>
<td>12.02</td>
<td>0.73 (12)</td>
<td>1.13 (6)</td>
<td></td>
</tr>
<tr>
<td>OFS-11</td>
<td>300</td>
<td>1100</td>
<td>20</td>
<td>7.3 (12)</td>
<td>621</td>
<td>0.61</td>
<td>1.44</td>
<td>0.50</td>
<td>35.80</td>
<td>0.74 (12)</td>
<td>1.11 (4)</td>
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<tr>
<td>OFS-9</td>
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<td>1300</td>
<td>20</td>
<td>10.6 (5)</td>
<td>658</td>
<td>0.47</td>
<td>0.68</td>
<td>2.41</td>
<td>18.66</td>
<td>0.76 (11)</td>
<td>1.16 (5)</td>
<td></td>
</tr>
<tr>
<td>OFS-3</td>
<td>72</td>
<td>1300</td>
<td>20</td>
<td>16.3 (4)</td>
<td>383</td>
<td>0.47</td>
<td>0.51</td>
<td>0.89</td>
<td>22.70</td>
<td>0.78 (11)</td>
<td>1.19 (10)</td>
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</tr>
<tr>
<td>OFS-10</td>
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<td>20</td>
<td>18.6 (9)</td>
<td>303</td>
<td>0.48</td>
<td>0.49</td>
<td>0.78</td>
<td>47.73</td>
<td>0.76 (10)</td>
<td>1.13 (4)</td>
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<td>40</td>
<td>9.0 (10)</td>
<td>1308</td>
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<td>0.65</td>
<td>0.78</td>
<td>13.40</td>
<td>0.73 (12)</td>
<td>1.10 (3)</td>
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</tr>
<tr>
<td>OFS-3</td>
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<td>1300</td>
<td>20</td>
<td>16.3 (4)</td>
<td>383</td>
<td>0.47</td>
<td>0.51</td>
<td>0.89</td>
<td>22.70</td>
<td>0.78 (12)</td>
<td>1.19 (10)</td>
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<td>OFS-5$^d$</td>
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<td>18.6 (4)</td>
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<td>3.25</td>
<td>9.17</td>
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<td>1.19 (8)</td>
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<td>0.66</td>
<td>23.38</td>
<td>0.73 (13)</td>
<td>1.51 (22)</td>
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<td>OFS-2</td>
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<td>1200</td>
<td>20</td>
<td>7.1 (6)</td>
<td>604</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>OFS-nf-14</td>
<td>8</td>
<td>1430</td>
<td>20</td>
<td>8.9 (5)</td>
<td>554</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.75 (12)</td>
<td>1.13 (6)</td>
</tr>
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</table>

**Pallasite name**

<table>
<thead>
<tr>
<th>Average grain size (mm)</th>
<th>2nd Order S. Diff.</th>
<th>1st Ordered S. Diff.</th>
<th>Rayleigh</th>
<th>Log-normal</th>
<th>Roundness$^a$</th>
<th>Perim/CircEqDiam$^b$</th>
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</thead>
<tbody>
<tr>
<td>Brenham</td>
<td>4.88 (16)</td>
<td>654</td>
<td>0.61</td>
<td>24.52</td>
<td>0.57</td>
<td>1.08</td>
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<tr>
<td>Seymour</td>
<td>3.80 (17)</td>
<td>153</td>
<td>1.11</td>
<td>5.71</td>
<td>0.69</td>
<td>0.67</td>
</tr>
<tr>
<td>Springwater</td>
<td>6.21 (15)</td>
<td>303</td>
<td>0.75</td>
<td>11.99</td>
<td>4.62</td>
<td>1.04</td>
</tr>
<tr>
<td>Brahmin</td>
<td>1.24 (13)</td>
<td>277$^f$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Seymour breccia</td>
<td>1.96 (19)</td>
<td>599$^f$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Roundness: $4 \times [\text{Area}/\pi] \times [\text{Major Axis}]^2$; a regular hexagon has a roundness of 0.99, an idiomorphic olivine cross section with an aspect ratio of 1.5 or 2.0 has a roundness of 0.70 or 0.52, respectively.

$^b$ Perim/CircEqDiam: $([\text{Perimeter}]/2 \times [\text{Area}/\pi]^{1/2})/\pi$.

$^c$ Olv/Fe–S = 60/40.

$^d$ Olv/Fe–S = 85/15.

$^e$ Olv/Fe–S = 90/10.

$^f$ Number of fragments.
v_{2/4}^{1/n} b

where \( n_b \) is the total number of bins, \( f_c \) the theoretical normalised frequency and \( f_m \) the measured normalised frequency of each bin (Table 3). Rayleigh and Log-normal distribution fits to each measured GSD were optimised by adjusting the parameter(s) in their defining equations (Faul and Scott, 2006). The theoretical distributions for diffusion and surface reaction controlled Ostwald ripening are not adjustable. The quality of the fit with Ostwald ripening and Rayleigh theoretical distributions held similar results, whereas the fit with Log-normal distribution is always poor (Table 3).
The results for the normalised GSD of Brenham, Springwater, and the rounded olivine-bearing slice of Seymchan are more difficult to interpret, since maximum grain size and maximum frequency give contrasting indications (Fig. 5b). The \( \chi^2 \) test indicates that first order surface reaction controlled growth is the least favourable mechanism to interpret olivine growth in these samples.

4. DISCUSSION

4.1. Chemical equilibration of olivine and Fe–S

The almost constant olivine composition in experiments performed at different temperatures and annealing times at identical olivine/Fe–S proportions (Tables 1 and 2), indicates that chemical equilibration is readily reached at our experimental conditions. Attaining the equilibrium olivine composition involves redox reactions such as

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4 + 6\text{FeS} + 4\text{O}_2 & = \text{Fe}_2\text{SiO}_4 + 2\text{MgFe}_2\text{O}_4 + 3\text{S}_2 \\
\text{Fe}_2\text{SiO}_4 + \frac{1}{2} \text{S}_2 & = \text{FeS} + \text{FeSiO}_3 + \frac{1}{2} \text{O}_2
\end{align*}
\]

(Gaetani and Grove, 1999). Such reactions necessarily involve a second oxide or silicate phase, i.e. Mg-ferrite or ferrosilite, which were not observed in our runs, but could have gone unnoticed. An alternative would be the oxidation of graphite to CO\(_2\) which could reside in the porosity of the graphite capsule, but this would constrain oxygen fugacity to the graphite–CO–CO\(_2\) (CCO) buffer, which is inconsistent with the oxygen fugacities calculated for the experiments. Righter et al. (1990) developed an equation to relate \( \text{fO}_2 \) and olivine forsterite content in pallasites. The forsterite contents observed in our runs (Table 2) imply an equilibrium \( \text{fO}_2 \), expressed as difference to the iron–wüstite (IW) oxygen buffer, of \( \Delta\text{IW} = 0.55 \) to \( \Delta\text{IW} = 0.85 \) (in log units). These values are 4–5 log units below the CCO buffer at 1 GPa. This is consistent with Holloway et al. (1992) suggesting that graphite only imposes a maximum \( \text{fO}_2 \) and in fact the fairly reduced Fe–S in our experiments leads to reduced \( \text{fO}_2 \)-values. In principle, Mg-contents of olivine should increase with Fe–S fraction while oxygen fugacity decreases. This is clear for experiment OFS-14 with 40 vol% Fe–S, but less so for experiments with 10–20 vol% Fe–S (Tables 1 and 2).

Fig. 5. Normalised grain size distributions of pallasites and comparison with calculated normalised GSDs for rounded olivines. Vertical dashed lines correspond to average grain size. (a) Normalised GSDs of three pallasites bearing rounded olivine grains; (b) normalised GSD of Springwater pallasite compared with theoretical distributions for Rayleigh, Log-normal, and 2nd order surface reaction controlled growth. Rayleigh and Log-normal normalised GSD were optimised for best fit with the observed curve; (c) normalised GSDs of two different areas of Seymchan pallasite, one bearing mainly rounded olivine, and the other mainly fragmented crystals (Fig. 6); (d) normalised GSD of the fragmental pallasite Brahin, highlighting the extremely long tail characteristic of mechanically induced fragmentation, followed by little annealing.
The average NiO content of San Carlos olivine is 0.44 wt% (Galoisy et al., 1995), but almost no Ni was present after annealing (Table 2). Analyses of the iron-sulphide phase revealed that Ni partitioned into the metal alloy, as expected for the reduced FeO of our experiments, although quantification was difficult due to the quench exsolution textures of the metal. If Ni migrated entirely into the iron-sulphide melt, Ni contents would result to 0.35–1.56 wt% for olivine volume fractions of 60–90%.

4.2. Grain growth of olivine in molten Fe–S

Grain growth theory predicts grain growth exponents for Ostwald ripening or normal grain growth of 2–3. For olivine \( n = 2 \) was measured exclusively in experiments with nominally pore-free pure olivine aggregates (Karato, 1989). Experiments with olivine plus abundant basalt melt gave \( n = 3 \) (Cabane et al., 2005; Schmidt et al., 2012), whereas Faul and Scott (2006) obtained \( n = 4.3 \) for olivine + 2–4 wt% basalt. In studies involving olivine + pores or olivine + nickel values of \( n \geq 3.5–5 \) were computed (Nichols and Mackwell, 1991; Guignard et al., 2012). For a normal grain growth process growth exponents \( n > 3 \) are obtained by modelling the coarsening of the dominant phase for grain growth limited by grain boundary diffusion in the matrix phase (\( n = 4 \), Ardell, 1972) or by diffusion via one-dimensional pathways (\( n = 5 \), Johnson et al., 1999), both implying a low solubility of olivine in the matrix phase. In both cases the fraction of the matrix phase should not effect the growth rate and hence \( n \).

In our experiments an increase of the Fe–S fraction reduces the olivine growth rate (Table 3), and the growth exponent, computed for the experiments with 20 vol% Fe–S, is \( n < 3 \). This seems to preclude the possibility that olivine growth is controlled by normal grain growth in presence of a second phase and favours Ostwald ripening. On the other hand, Ostwald ripening is viable only when the solubility of the growing phase in the surrounding matrix is non-negligible (Lifshitz and Slyozov, 1961; Wagner, 1961). Whether the solubility of Mg, Si, and O in the iron-sulphide melt at the experimental conditions satisfies this condition cannot be ascertained from our current experiments and data available in the literature.

It should be noted that for anisotropic phases the distinction between normal grain growth and Ostwald ripening might not be relevant (Uli Faul, personal communication), and a more complex, intermediate grain growth mechanism might be envisaged. Fan and Chen (1997) modelled the grain growth of a two-phase system, where both phases were anisotropic, and verified that a change of the volume fraction of the second phase and/or of the interfacial (grain boundary) energy does not modify the growth mechanism leaving the growth exponent unchanged. Fan and Chen (1997) noted that grain growth of the dominant phase was controlled by volume diffusion (normal grain growth, \( n = 3 \)), whereas for the second phase long distance diffusion prevails (Ostwald ripening, \( n = 2 \)).

The activation energy of 289 kJ computed for our experiments is similar to those of oxygen and silicon lattice diffusion in olivine given by Houlier et al. (1988, 1990) and Gerald and Jaoul (1989). This may indicate that the process responsible for the grain growth requires diffusion or lattice scale reorganisation in the olivine, such as for volume reaction-controlled coarsening. The apparent change in the GSD for the longest runs may be taken as indication that steady-state grain growth was not achieved in all experiments. However, the impracticality of unequivocally defining the dominant grain growth mechanism precludes further discussion.

4.2.1. Comparison with previous studies

Our experiments aim at quantifying the growth process of olivine grains in pallasite-like material. Other studies on annealing of olivine + metal at high temperature used olivine + Fe–Ni (Saiki et al., 2003) and forsterite + Ni (Guignard et al., 2012) at subsolidus conditions. For an olivine:Ni ratio of 80:20, Guignard et al. (2012) determined a growth exponent \( n = 3.5 \) (or 4.8 if the shortest annealing experiment was not considered), i.e. a much slower coarsening rate than in our experiments. Guignard et al. (2012) compared their result with data on olivine rounding from Saiki et al. (2003), concluding that annealing in Fe–Ni renders a faster growth process. Iron in the matrix phase was proposed to promote faster diffusion leading to the conclusion that the nature of the matrix phase influences the ripening rate of the dominant phase. Our experiments yield much faster growth rates for a metal matrix with high S-contents in line with an enhanced diffusivity or mobility of chemical species.

Oxygen fugacity may affect olivine annealing in Fe–S. In order to diffuse in the Fe–S melt, Mg would probably be complexated as S-species, which would be stabilized by reducing conditions. Oxygen fugacity in the experiments of Saiki et al. (2003) was buffered to Ni–NiO (NNO) and in the case of Guignard et al. (2012) was NNO-3, i.e. 5 and 2 log units above the oxygen fugacity of our samples. Moreover, chemical diffusion in a liquid phase is orders of magnitude faster than in a crystalline medium (Bhat, 1973; Bakker et al., 1990). The combined effect of our lower oxygen fugacity, the S-rich metal composition and the liquid vs. solid state of the matrix phase results in the observed faster growth rate of olivine in this study.

4.2.2. Comparison with natural pallasites containing rounded olivines

The main difference between the natural and experimental samples is the composition of their metal-sulphide fraction. Brenham and Springwater contain 5.8 and 5.3 wt% of FeS (troilite) and 28.4 and 27.9 wt% Fe–Ni, respectively (Buseck, 1977). The phase proportions of Seymchan are not reported, but a dominance of Fe–Ni over FeS is apparent in the available slices and slabs. In comparison, our experimental metal alloy corresponds to a mixture of 80 wt% FeS and 20 wt% Fe.

In the pallasite slices FeS amounts to \( >15\% \) of the area of Brenham, 10–15% of Seymchan and <7–10% of Springwater (Fig. 6a–c). The texture of the pallasite slices is remarkably similar to that of our run products in terms of the degree of rounding of olivine, the morphology of
the contacts between Fe–S and olivine, and olivine grains being almost always in mutual contact, even in 2D sections (Figs. 1, 2 and 6a–c).

4.2.3. Rounding of olivine fragments

Rounding of olivine fragments at our experimental conditions seems to occur during the earliest stages of annealing and does not increase with run duration (Table 3). This observation confirms the suggestion of Saiki et al. (2003) that the presence of sulphur might catalyse the rounding process. The olivine fraction seems to affect the degree of roundness of grains, quantified by the ratio between grain perimeter and circle equivalent diameter, but only at olivine volume fractions beyond 85% (Table 3). Guignard et al. (2012) observed that olivine grains were more faceted in experiments with the largest olivine fraction in olivine–nickel mixtures. This effect could be related to different grain boundary energies between olivine–olivine and olivine–Fe–S (or olivine–Ni) boundaries.

4.3. Olivine grain growth in pallasites

The width of normalised GSDs measured for the three selected pallasites extends from a minimum normalised grain size between 0.0 and 0.5 \( d_m \) to a maximum size between 2.5 and 3.0 \( d_m \), which is fundamentally similar to the experimentally determined ones.

Unlike the experimental samples, for natural pallasites many factors may have reduced the olivine grain growth (and rounding) rate and potentially changed the dominant grain growth mechanism. One possible factor is the composition and volume proportion of the metal–sulphide alloy. We observe that an increase in the metal fraction drastically reduces the grain growth rate (Table 3). Moreover, the average sulphur amount measured in the metal matrix of pallasites (0.4–1.0 wt%; Buseck, 1977) is much smaller than in the experiments (36 wt% S). Possibly our experimentally determined growth rate for olivine fragments in molten Fe–Ni–S is faster than for lower Fe- (i.e. highest Ni) and S-contents. Even if composition and fraction of the metal alloy could influence the growth and rounding rate and mechanism, only a weak correlation was found between the type of olivine present in the pallasite samples and the sulphur and/or nickel amounts (Buseck, 1977; Boesenberg et al., 2012).

4.4. A comparison of boundary conditions of the experiments and pallasite formation

In order to assess the representativeness of the experimentally determined grain growth parameters for olivine coarsening in pallasites, we compare the experimental conditions with \( P, T, fO_2 \), and composition of the interior of terrestrial planetesimals. The experiments were performed at 1 GPa, equivalent to \( \sim 35 \) km depth in the Earth, but in a body with \( r \lesssim 600 \) km, 1 GPa exceeds the maximum pressure. The topology of the Fe–FeS system does not change significantly for pressures of 0–1 GPa (Brett and Bell, 1969; Usselman, 1975; Fei et al., 1997), any deduction relative to the eutectic melting temperature of the alloy and the fraction of molten Fe–S at a given temperature remains hence valid for planetesimals. Parameters controlling grain growth, such as surface energy and grain boundary migration rate are not pressure sensitive (Saiki et al., 2003 and

Fig. 6. Photographs of pallasite slices. Images (a–f) are slices of the pallasites Springwater, Brenham, Seymchan (rounded portion), Brahin, Seymchan (fragmental), and again Seymchan (fragmental). White and yellow arrows point at agglomerates of FeS. The white rectangle represents a scale bar of 10 mm length.
Based on olivine compositions, redox conditions in the parent body of pallasites were estimated to range from ΔIW = −0.5 to +0.5 (Righter et al., 1990), similar to the ΔIW = −0.9 to −0.6 of the experiments. For \( f_O^2 > 1 \), wüstit could stabilize as an additional phase, but was not observed in pallasites. Instead, for moderate to high sulphur activities, FeS or FeS\(_2\) is formed (Naldrett, 1969). Hence, phase stability is not much influenced by the small difference in the experimental and natural \( f_O^2 \). On the other hand, oxygen fugacity plays a key role for interconnection of the melt as explained below.

Estimated compositions of the metallic portion of terrestrial planets and planetesimals have 2–15 wt% S (Dreibus and Palme, 1996), much less than the Fe\(_{30}\)S\(_{80}\) used in the experiments. Furthermore, the cosmogenic Fe:Ni ratio is ~19.5 (Grossmann, 1972) and pallasites have 3–8 wt% Ni (Buseck, 1977), leading to minor amounts of pentlandite and pyrrhotite, and the formation of kamacite–taenite and plessite in the crystallized metal fraction. At 1 atm pressure Ni depresses the eutectic temperature of the Fe–Ni–S eutectic to ≤800 °C (Clark and Kullerud, 1963; Waldner and Pelton, 2004) while that of the Fe–S binary is 990 °C (Brett and Bell, 1969; Usselman, 1975; Fei et al., 1997).

The smaller S-content of planetesimals should reduce the fraction of molten Fe–(Ni)–S at a given temperature with respect to our experiments, but Ni counterbalances this effect. Moreover, it has been suggested that S-loss during meteorite formation is a common process affecting irons and pallasites (Brett and Bell, 1969; Usselman, 1975; Fei et al., 1997). Our experiments simulate the scenario where the Fe–Ni–S could form an interconnected network if molten Fe–(Ni)–S is present at relatively oxidising conditions. Thus, with an average S-content of ~4 wt% in pallasites with rounded olivine (Buseck, 1977), the metal matrix would contain ~2 wt% eutectic melt (Usselman, 1975; Waldner and Pelton, 2004) and an interconnected melt network could be present down to almost the temperature of the Fe–Ni–S eutectic at 820–840 °C (Usselman, 1975). For the 20 vol% Fe–S experimental series, the interconnectivity threshold is overcome (Yoshino et al., 2003; Bagdassarov et al., 2009) and we conclude that grain growth was governed by the same mechanism in the experiments and in natural pallasites.

### 4.5. Formation of mixed-type pallasites

Pallasites that contain both rounded and angular fragmented olivines (Fig. 6c–e) cannot be simply explained with a different burial depth or localisation of the olivine + Fe–(Ni)–S mixture in the planetesimal mantile. The maximum olivine size observed in Seymchan, i.e. ~9 mm (Fig. 6c), could be reached after ~30 ka (Fig. 7). A possible scenario is that aggregates of rounded olivines, formed during initial cooling at greater depth were displaced from their original depth and mixed with shallower, angular olivine-bearing portions. Such mixing could be triggered by a smaller and later impact. Refraction of shock waves may preserve domains of rounded olivines, and the sudden temperature increase following the later impact may allow localised melting of the Fe–(Ni)–S alloy and hence may promote the displacement of slurries containing rounded olivines. In this scenario, the maximum temperature reached after the later impact is just above the Fe-Ni-S eutectic. Further annealing of the material, rapidly cooling to the solid state, would then be limited.

### 5. MODELLING OLIVINE GRAIN GROWTH IN A PLANETESIMAL INTERIOR

To model the growth history of olivines, an initial fragment size and a temperature–time evolution are needed. We employ the 1D finite-difference conduction model of Tarduno et al. (2012) to calculate the temperature evolution at different depths (Fig. 7) in bodies with a radius up to 600 km. In our model, the growth of an olivine grain with an initial diameter \( d_0 \) of 100 μm is calculated in steps of 1000 years using Eq. (1) and assuming constant temperature for each time step. In comparison, Saiki et al. (2003)

- Bagdassarov et al., 2009
- Rose and Brenan, 2001
- Terasaki et al., 2005
and Guignard et al. (2012) calculated the grain size evolution or the degree of rounding of olivine assuming a constant temperature, an approach that overestimates olivine growth and degree of rounding.

5.1. Model setup

As argued above, olivine growth becomes negligible when temperature decreases to that of the Fe–Ni–S ternary eutectic, i.e. 820 °C (Clark and Kullerud, 1963), since olivine coarsening in a solid metal matrix is orders of magnitude slower than in molten metal.

Growth parameters employed in Eq. (1) are those computed for our experiments with an olivine/Fe–S volume ratio of 80/20, i.e.: \( n = 2.42 \), \( k_0 = 9.43 \times 10^7 \mu \text{m}^3 \text{s}^{-1} \), and \( E_a = 289 \text{ KJ/mol} \). We also calculated the grain size evolution of olivine fragments with a set of values computed by fitting the forsterite:Ni = 80:20 data of Guignard et al. (2012) using their reported grain size at \( t = 0 \) for the value of \( d_0 \). The least square fit to Eq. (1) yields \( n = 4.45 \), \( k_0 = 9.10 \times 10^7 \mu \text{m}^3 \text{s}^{-1} \), and \( E_a = 320 \text{ KJ/mol} \).

The starting grain size in the numerical model, i.e. 100 μm, is an approximation derived from the smallest and least rounded olivine fragments observed in highly fragmented pallasites (Buseck, 1977; Scott, 1977a) believed to represent those annealed for the shortest time. These pallasites are thought to originate from the shallowest depth in the target body mantle preserving a fragment size distribution representative for the onset of the annealing process.

The scenario of pallasite formation encompasses the impact of a smaller body onto an already differentiated one, followed by almost instantaneous vigorous mixing of the impactor metal with the now fragmented mantle of the target body. The mixed olivine + metal cools down to the local mantle temperature over less than a few years (Tarduno et al., 2012), accompanied by almost no olivine growth. Afterwards, the temperature decrease follows the cooling rate of the local mantle. It should be noted that

![Fig. 7. Olivine grain growth and temperature evolution in the pallasite parent body based on 1D finite-difference conduction modelling (Tarduno et al., 2012). The time on the x-axis starts at the onset of cooling of the planetesimal. D is the depth of the olivine + Fe–S aggregate in the body. The starting grain size (d0) is 100 micrometres. The impact time is t = 0 for all curves except in (d) where impact times are indicated in the upper left corner. (a) and (b): Solid curves represent olivine grain size calculated employing Eq. (1), whereas dot-dash-dot curves are olivine grain sizes calculated employing the grain growth law fit to the data of Guignard et al. (2012). Dashed curves indicate that the selected D lies within the megaregolith in the case of olivine grain size computed with Eq. (1). (c) Temperature evolution at various depths inside a 200 km body based on a 1D finite-difference conduction model. (d) Olivine grain size for a depth of the metal intrusion D = 40 km in a body with a 200 km radius, calculated with Eq. (1) considering different impact times, t.](image-url)
in the 1D finite difference model employed for our calculations, the cooling rate of the planetesimal is reduced by the presence of a megaregolith layer (Tarduno et al., 2012).

In the impact scenario, annealing is effectively only achieved due to heat stored in the parent body. The duration of annealing and the cooling rate depend on the body radius, the depth where mixed olivine + metal are located, and on the time of impact relative to planetesimal formation (Fig. 7). The timing of the impact cannot be directly constrained (Tarduno et al., 2012 and references therein). Nevertheless, the impact happened at a time such that subsequent olivine grain growth of the fragments yields a final grain size in the range observed in rounded olivine-bearing pallasites, i.e. ~1–20 mm (Buseck, 1977; Scott, 1977a and references therein), and the impact derived olivine + Fe–S mix must have been located at a depth which is consistent with the metallographic cooling rates of the Fe–Ni portion. These are 2.5–18 °C/Ma, corresponding to the temperature window of kamacite–taenite exsolution lamellae formation, i.e. ~700–500 °C (Yang et al., 2010).

5.2. Model results

Fig. 7 shows the results of our calculations for two hypothetical parent bodies with radii of 200 and 600 km. The calculations start at the time corresponding to the onset of cooling of the parent body. Since olivine growth rates decrease exponentially with temperature, olivine grain size curves flatten during cooling of the parent body and the maximum grain sizes that can be reached depend on the depth of the olivine + Fe–S aggregate.

Employing the olivine grain growth law based on the data of Guignard et al. (2012) yields a maximum grain size <1 mm for any of the bodies even for an impact right at the onset of cooling (t = 0; Fig. 7a and b). Thus, the rate of olivine coarsening for an exponential growth with n = 4.45 is insufficient to yield the grain sizes observed in pallasites with rounded olivine even for a large parent body with r = 600 km (larger than Ceres, the largest body in the present-day asteroid belt) (Fig. 7b).

For a 200 km radius body metallographic cooling rates of Fe–Ni are satisfied at depths (D) between 8 and 73 km. Tarduno et al. (2012) and Bryson et al. (2015) argue that a depth of 40 km or shallower inside such a parent body allows the recording of the remnant magnetisation observed. Therefore, we focused our attention on the grain growth near D = 40 km. The numerical models show that olivine coarsening at the depth range of interest is possible during the first 73.5 Ma after model start (Fig. 7d). Grain growth calculations show that the largest olivine grains observed in pallasites can be reproduced even for collisions occurring more than 43 Ma after the model start i.e. into an already significantly cooler target body mantle (Fig. 7d).

6. FINAL REMARKS

We have addressed compositional effects on grain growth, the rounding kinetics of olivine plus metal mixtures and olivine grain size distributions. These allow deciphering of the formation conditions of pallasites with rounded olivines. We derive a likely formation scenario, which, despite some limitations (e.g., determination of a fast olivine growth rate, Section 4.3), supplies an explanation of how pallasites could be formed after an impact into the pallasite parent body. This scenario does not include any singular or unlikely events, hence pallasites could stem from several parent bodies, which in turn could be an explanation for the different pallasite groups.

Two key points emerge from this study:

1. Olivine grain growth in molten and/or sulphur-bearing metal is orders of magnitude faster than coarsening in a solid metal matrix;
2. Impact-induced olivine fragmentation followed by annealing in (partially) molten Fe-(Ni)–S in the mantle of a small planetesimal (r < 600 km) can yield rounded grains in the range observed in pallasites.

For a 200 km radius body, annealing can occur at ~40 km depth as required for the explanation of remnant magnetisation observed by Tarduno et al. (2012) and Bryson et al. (2015).

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