Chondrule precursor minerals as anhydrous phases

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Part of a series of papers dedicated to the memory of Paul Barringer)

Abstract—Chondrules might be generated from hydrous or anhydrous precursor minerals, but vesicles due to dehydration during melting are absent in natural chondrules. The occurrence of vesicles in experimental charges made from serpentine-rich starting material that was (a) flash heated and remelted several times, (b) melted for long durations and (c) melted in a vacuum has been studied in order to test whether vesicles could be eliminated in chondrules made from hydrous precursors. High percentages of vesicles in all experiments indicate that chondrules, whether melted once, multiple times, for a brief or extended period, at solar nebula or higher pressure, were made from anhydrous phases.

INTRODUCTION

Chondrules are millimeter-sized, igneous-textured spheres of mostly silicate composition (Grossman et al., 1988) that were melted in the solar nebula and are found in meteorites. The pervasive chondrule-forming event has, to a large extent, obscured the meteoritic record of earlier nebular events such as condensation and the event is itself poorly understood. Most proposed chondrule-forming mechanisms involve nebular processes, though parent-body collisions are still discussed (Boss, 1996; Hewins et al., 1996). Standard chondrule models (e.g., Grossman, 1988) usually assume melting of aggregates of anhydrous condensates in a flash-heating event of some kind (Nagasara, 1981; Rambaldi, 1981; Greenwood and Hess, 1996; Boss and Graham, 1993; Morfill et al., 1993; Hood and Horanyi, 1991), and such events apparently occurred so as to remelt chondrules (Kring, 1991; Rubin, 1984; Wasson et al., 1995; Rubin and Krot, 1996).

Uncertainties in the nature of chondrule precursors and of the heating event(s) compound the difficulty of deciphering their exact origin, but one question that can be addressed experimentally is whether the precursor phases could have been hydrated. The equilibrium condensation sequence culminates at low temperature in hydrous silicates such as serpentine, but their formation may well be kinetically inhibited (Fegley, 1988). However, some olivine chondrules were serpentinized before their emplacement in the chondrule host (Metzler et al., 1992), either in the nebula or in an earlier generation of parent bodies. Generation of chondrules by melting of hydrous condensates, recycling of hydrated chondrules, or collisions of hydrated parent bodies are models that can be tested (and possibly eliminated) by high-temperature experiments, as dehydration during melting may generate vesicles.

Natural chondrules are virtually vesicle free, although vesicles in some chondrules have been reported (Zbib and Lang, 1983). Ablation spherules generated from meteorites containing sheet silicates show numerous vesicles (Brownlee et al., 1983). The lack of vesicles in natural chondrules and their abundance in single-stage flash-heating runs at 1 atm (1.01325 bar) with serpentine-rich starting material (Maharaj and Hewins, 1994) suggests that the original precursor components of chondrules were anhydrous. However, since chondrules were probably produced in a low-pressure environment (Wood and Morfill, 1988; Boss, 1996) and possibly flash heated multiple times (Kring, 1991; Rubin, 1984; Wasson et al., 1995; Rubin and Krot, 1996), it is important to determine if these factors could eliminate vesicles produced from any hydrous precursor components. We have melted serpentine-rich starting materials to examine any dependence of vesicle abundance on (a) multiple melting events, (b) long-duration melting, and (c) vacuum melting. We have used peak temperatures, heating times and cooling rates that yield reasonable chondrule textures, mineral zoning, and concentrations of moderately volatile elements (Radomsky and Hewins, 1990; Yu and Hewins, 1996) and, in particular, examined whether vesicles could be eliminated in chondrules made from hydrous precursors.

EXPERIMENTAL TECHNIQUE

Starting Composition

The experiments were performed on a mixture of 50% type IIAB chondrule composition (Connolly and Hewins, 1995) and 50% serpentine. The Type IIAB starting material was prepared by mixing oxides that were fused, quenched to glass, and ground to a fine powder (Radomsky and Hewins, 1990). It has a liquidus temperature of 1504 ± 2 °C (Radomsky and Hewins, 1990). X-ray diffraction (XRD) analysis shows the serpentine is lizardite. The serpentine component consists of 95.6% lizardite and 4.4% magnetite. Therefore, total serpentine in the starting composition is 47.8%.

Subsolidus reactions for the dehydration of serpentine have been examined by Berman et al. (1986) as a function of water pressure. Lizardite will break down to successive talc and anthophyllite assemblages before total dehydration. The net reaction is:

\[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3 + 2\text{H}_2\text{O} \]

However, as these reactions take place at 400–600 °C at 1 atm (Berman et al., 1986), they will all be overstepped in our experiments at 1500 °C, where we have:

lizardite + IIAB glass → olivine + melt + H_2O

This reaction goes to completion within 5 s.

Vesicle percentages in our quenched samples were calculated from backscattered electron (BSE) images by point counting and weight integration. Values obtained by these methods differ by 0.5% or less. Photographs shown in this paper are BSE images.

Multiple Melting and Long-duration Experiments

Experiments involved melting at 1500 °C and IW-0.5 in a 1 atm Deltech (DT-31-VT-OS) vertical muffle-tube furnace. Temperature was monitored 2–3 mm above the sample by a Pt100/Pt90Rh10 type S thermocouple internal to the sample rod. The thermocouple was periodically calibrated against the melting points of Au (1064 °C) and Pd (1552 °C). Most experiments were duplicated in order to limit the error associated with looking at any one sample. Vesicle percentages
TABLE 1. Experimental conditions and results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time at 1500 °C</th>
<th>Cool rate (°C/h)</th>
<th>Quench T(°C)</th>
<th>Number of melting events</th>
<th>Vesicle %</th>
<th>Average vesicle %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP-5</td>
<td>5 s</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>87.0</td>
<td>87</td>
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<td>SRP-9</td>
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<td>500</td>
<td>1000</td>
<td>2</td>
<td>41.0</td>
<td></td>
</tr>
<tr>
<td>SRP-32</td>
<td>5 s</td>
<td>500</td>
<td>1000</td>
<td>2</td>
<td>40.1</td>
<td>41</td>
</tr>
<tr>
<td>SRP-33</td>
<td>5 s</td>
<td>500</td>
<td>1000</td>
<td>3</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>SRP-34</td>
<td>5 s</td>
<td>500</td>
<td>1000</td>
<td>3</td>
<td>29.5</td>
<td>25</td>
</tr>
<tr>
<td>SRP-28</td>
<td>5 s</td>
<td>p/a</td>
<td>1500</td>
<td>1</td>
<td>73.6</td>
<td></td>
</tr>
<tr>
<td>SRP-35</td>
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<td>p/a</td>
<td>1500</td>
<td>1</td>
<td>74.7</td>
<td></td>
</tr>
<tr>
<td>SRP-36</td>
<td>5 s</td>
<td>p/a</td>
<td>1500</td>
<td>1</td>
<td>61.4</td>
<td>70</td>
</tr>
<tr>
<td>SRP-29</td>
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<td>p/a</td>
<td>1500</td>
<td>5</td>
<td>38.5</td>
<td></td>
</tr>
<tr>
<td>SRP-30</td>
<td>5 s</td>
<td>p/a</td>
<td>1500</td>
<td>5</td>
<td>34.3</td>
<td>36</td>
</tr>
<tr>
<td>SRP-37</td>
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<td>p/a</td>
<td>1500</td>
<td>25</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>SRP-38</td>
<td>5 s</td>
<td>p/a</td>
<td>1500</td>
<td>25</td>
<td>29.2</td>
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<table>
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<th>Long duration</th>
<th>Time</th>
<th>Cool rate (°C/h)</th>
<th>Quench T(°C)</th>
<th>Number of melting events</th>
<th>Vesicle %</th>
<th>Average vesicle %</th>
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<tbody>
<tr>
<td>SRP-25</td>
<td>30 min</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>16.1</td>
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</tr>
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<td>SRP-26</td>
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<td>500</td>
<td>1000</td>
<td>1</td>
<td>16.0</td>
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</tr>
<tr>
<td>SRP-41</td>
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<td>500</td>
<td>1000</td>
<td>1</td>
<td>14.9</td>
<td></td>
</tr>
<tr>
<td>SRP-42</td>
<td>1 h</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>16.5</td>
<td>16</td>
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</table>

<table>
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<th>Vacuum Experiment</th>
<th>Time</th>
<th>Cool rate (°C/h)</th>
<th>Quench T(°C)</th>
<th>Number of melting events</th>
<th>Vesicle %</th>
<th>Average vesicle %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP-44</td>
<td>5 s</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>36.6</td>
<td></td>
</tr>
<tr>
<td>SRP-45</td>
<td>1 min</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>SRP-47</td>
<td>30 min</td>
<td>500</td>
<td>1000</td>
<td>1</td>
<td>34.7</td>
<td>37</td>
</tr>
</tbody>
</table>

p/a = pull/air quench

for duplicate runs (Table 1), in general, show good reproducibility, particularly considering the effects of sectioning.

In multiple flash melting experiments, samples were (a) melted 1x, 2x and 3x for 5 s each at 1500 °C, cooled at 500 °C/h, and then quenched each time at 1000 °C in distilled, deionized water; or (b) 1x, 5x and 25x for 5 s at 1500 °C, pulled and air quenched each time. In long-duration melting experiments, samples were melted once for 30 min or 1 h, cooled at 500°C/h, and quenched at 1000 °C in distilled, deionized water.

Maharaj and Hewins (1995) showed that charges typically heat up (and cool down) faster than indicated by the thermocouple. Geothermometry experiments with metal wires placed inside charges (Maharaj and Hewins, 1998, unpubl. data) indicate charges reach 1500 °C in ~5 s. We estimate the cooling rate of samples quenched in water to be ~500 °C/s. An inferred cooling path (temperature vs. time) for charges pulled and air quenched (Maharaj and Hewins, 1995) shows radiatively cooled charges reach room temperature in ~2.5 min. Subsolidus temperatures are reached in ~6 s, which corresponds to a cooling rate of ~86 °C/s.

Vacuum Experiments

Vacuum experiments were performed on the same composition in a vertical muffle-tube Deltech furnace (DT/31/VT/OS/C) fitted with a vacuum system (Yu and Hewins, 1997). Experiments were run in residual air at ~10⁻⁵ atm (~10⁻⁵ bar) (i.e., above the iron-wüstite buffer curve). Samples were melted at 1500 °C for 5 s, 1 min and 30 min, cooled at 500 °C/h and quenched at 1000 °C in vacuum. Samples experienced ~10⁻⁵ atm (~10⁻⁵ bar) conditions for the entire length of all vacuum experiments (i.e., from before being placed in the furnace hotspot to after quenching).

Yu and Hewins (1997) have shown that such conditions yield chondrule-like charges, with the extent of Na retained depending particularly on fO₂.

Fig. 1. Textures. (a) Sample (SRP-5), 500 °C/h cooled run, contains coarse-grained pyroxene poikilitically enclosing rounded olivine with minor zoning and zoned euhedral olivine (Fo₈₅₋₉₀). (b) Pulled and air quenched sample (SRP-28) contains fine euhedral olivine and very fine-grained bladed pyroxene.

ANALYTICAL METHODS

X-ray diffraction was performed on a Siemens D500 diffractometer in the Ceramic Engineering department at Rutgers University. The analysis used Ni-filtered CuKα radiation, a divergent slit of 1°, a receiving slit of 0.05°, an operating voltage of 40 kV and a current of 30 mA. The data for the full scan (10 to 80° 2θ) was collected by a DACO microprocessor using a stepwidth of 0.05° 2θ and a measuring time of 1 s. The data for the shorter scan (32 to 40° 2θ) was collected using a stepwidth of 0.02° 2θ and a measuring time of 20 s. The sample was rotated in the beam two rotations per second in order to improve counting statistics. Phase identification was performed by matching with standard patterns from the JCPDS card file.

Electron microprobe analyses were performed on a JEOL JXA-8600 Superprobe in the Department of Geological Sciences at Rutgers University. Operating conditions were 15 kV accelerating potential and 15 nA beam current. Natural and synthetic minerals and glasses were used as standards. A 10 s counting time was used for all elements. Analyses were calculated using the correction procedures of Bence and Albee (1968). Each reported analysis is an
average of ~8 points. A special routine was devised for glass analyses and included: (a) albite (SiO$_2$ = 68.60 wt%) as the Si standard, (b) a schedule counting Na, Si and K first and for 3 s each and (c) a rastering beam of ~5 μm. This routine improved glass totals by ~2 wt%, with Na$_2$O ~ 1.0–1.5 wt% higher.

RESULTS

Textures

All samples contain olivine, Ca-poor pyroxene and glass. Vacuum experiments also contain magnetite. Magnetite is not surprising in these experiments, as they were conducted slightly above the iron-wüstite buffer curve and magnetite is present in the starting material. There is no serpentine in experimental charges.

The two cooling techniques used produced different textures. Runs cooled at 500 °C/1 h contain coarsely-grained pyroxene and two types of olivine (Fig. 1a). Olivine poikilitically enclosed by pyroxene is ~10 μm, rounded in habit and relatively unzoned. Olivine occurring in the glass is ~20 μm, euhedral in habit and displays strong normal zoning (see Mineral Compositions). Samples pulled and air quenched contain very fine euhedral olivine and very fine-grained (~1 μm) bladed pyroxene in the glass interstitial to olivine (Fig. 1b). Skeletal pyroxene formed during quenching of melt. As charges are remelted, the olivine coarsens from ~10 μm (1 melt) to ~30 μm (25 melting events).

Modal Abundances

Flash-heating runs cooled at 500 °C/1 h contain 50–55% olivine, 40–45% pyroxene and ≤5% glass. Samples melted and air quenched once contain ~75% olivine, 5–10% pyroxene and ~15% glass. Samples melted and air quenched 5× contain 65–70% olivine, 15–20% pyroxene and 10–15% glass. Samples melted and air quenched 25×
contain ~65% olivine, ~25% pyroxene and 5-10% glass. Long-duration experiments contain 50-55% olivine, 40-45% pyroxene and ~5% glass. Vacuum runs contain ~55% olivine, ~40% pyroxene, ~2% glass and <4% magnetite. All samples cooled at 500 °C/h contain nearly identical percentages of olivine, pyroxene and glass. Experiments pulled and air quenched show an increasing pyroxene/olivine ratio and a decreasing glass percentage as the number of melting events rise.

Mineral Compositions

The chemical compositions of all major phases, as well as glass are listed in Table 2. All mineral analyses are core compositions. Pyroxene in samples pulled and air quenched is too fine grained for accurate probe analyses. Melt regions in these charges are filled furthermore with skeletal pyroxene and therefore not analyzed.

Olivine and pyroxene compositions and olivine zoning patterns are similar to those of type IIAB chondrules (Jones and Lofgren, 1993). Olivine in flash-heating runs cooled at 500 °C/h is zoned from Fo99 (core) to Fo77 (rim). Olivine in pulled and air quenched samples is typically zoned from Fo98 (core) to Fo97 (rim) only, with some cores as Mg-rich as Fo83. Olivine in long-duration experiments is zoned from Fo98 (core) to Fo78 (rim). Olivine in vacuum runs is typically zoned from Fo82 (core) to Fo78 (rim). Olivine is more ferroan in vacuum runs due to the higher FeO. Pyroxene is Ca-poor.

Anhydrous standard glasses analyzed with a special routine for glasses (see Analytical Methods section) total ~100 wt%. Glass totals in all serpentine runs are low (<92 wt%). Although we were unable to detect small bubbles in the SEM, we infer that the low totals are due to submicroscopic pores or water in the melt.

Vesicle Percentages

Experiments flash heated for 5 s and cooled at 500 °C/h contain an average of 87%, 41% and 25% vesicles when heated 1, 2 and 3×, respectively (Fig. 2a,b). Experiments flash heated for 5 s and pulled and air quenched contain an average of 70%, 36% and 21% vesicles when heated 1, 5 and 25×, respectively (Fig. 2c,d). Experiments heated for either 30 min or 1 h contain an average of 16% vesicles (Fig. 3). Vacuum experiments melted for 5 s, 1 min and 30 min contain 37%, 39% and 35% vesicles, respectively (Fig. 4). Charge volumes increase as vesicle percentages rise, as in some meteor ablation spherules (Brownlee et al., 1983).

**Fig. 2.** Experiments flash heated (a) 1× for 5 s (SRP-5) and (b) 3× for 5 s (SRP-34) and cooled at 500 °C/h contain ~87% and ~30% vesicles, respectively. Experiments flash heated (c) 1 (SRP-35) and (d) 25× (SRP-38) for 5 s and pulled and air quenched contain ~75% and ~29% vesicles, respectively.
Fig. 3. Experiments heated for (a) 30 min (SRP-26) or (b) 1 h (SRP-42) contain nearly the same amount of vesicles (i.e., ~16%).

Fig. 4. Vacuum experiments melted for (a) 5 s (SRP-44), (b) 1 min (SRP-45) and (c) 30 min (SRP-47) contain virtually no difference in the amount of vesicles (i.e., ~37%, ~39% and ~35%, respectively).
DISCUSSION

Multiple Melting and Long-duration Experiments

Theoretical studies of bubble formation in silicate melts (e.g., Sparks, 1978) emphasize the decreasing saturation level of water as magma rises towards a planetary surface, but pressure changes are not relevant to our experiments. Melting of serpentinite at 1 atm generates much more water vapor than can be dissolved in the melt, and it is partially retained in the charges within vesicles. Crystallization of the charges during cooling must generate supplementary bubbles, as water would otherwise become highly supersaturated in the residual melt.

Samples melted once and quenched from 1500 °C contain abundant vesicles (Table 1), showing that nearly all vesicles form immediately upon heating (i.e., in <5 s). However, if the charge was continually cooled down to 1000 °C instead of being quenched, more bubbles are present (Table 1). This suggests that escape is difficult after crystals are abundant and that vesicles continue to form due to crystallization as the residual melt saturation level was exceeded. Remelting charges results in a lower percentage of vesicles for both groups of flash-heating experiments (Table 1). This is a direct result of bubble escape when crystal abundance is reduced during remelting and of the inability of relatively dry residual melts to generate abundant new vesicles. The majority of vesicles are lost early on, and additional heating events are inefficient at eliminating bubbles, possibly because the melt is no longer supersaturated and does not generate new bubbles to move gas around within the relatively viscous olivine-melt mixture.

Vesicle contents are higher in runs quenched from the melting temperature than in those cooled to 1000 °C. Samples melted 3x and cooled at 500 °C/h contain an average of 25% vesicles, but samples melted 5x and pulled and air quenched contain 36% vesicles. Either escape of bubbles takes much longer than the 5 s melt time or the quenched melts are still supersaturated. We consider the former more likely. More bubbles would be expected to be liberated if samples are cooled over a longer period while solidifying. In any case, recycling of chondrules is unlikely to always totally eliminate vesicles, if any substantial fraction of their precursors were hydrous phases.

Charges melted for either 30 min or 1 h contain virtually the same amount of vesicles, which indicates that the serpentinite is destroyed and most water lost well before 30 min. The bubbles in these charges were probably generated during crystallization. The abundance (16%) corresponds to the difference in bubble contents of the quenched and "slow" cooled singly melted charges (Table 1). The percentage of vesicles (~16%) is rather high for samples heated for up to 1 h at the melting temperature and shows that even if chondrules were melted for long durations instead of being flash heated, we should see some evidence of vesicles if chondrule precursors were made of hydrous phases.

Vacuum Experiments

Virtually no difference in the amount of vesicles can be seen in vacuum experiments heated from 5 s to 30 min (Table 1). The analogous 5 s run at 1 atm contains a much higher percentage of vesicles (87%) than the vacuum run (37%), but the analogous 30 min runs at 1 atm contain less percentage of vesicles (16%). The low-pressure conditions probably allowed for the total escape of the bubbles produced immediately upon heating (i.e., in <5 s). Therefore, the low pressure probably caused very low equilibrium saturation levels and drove continuous production of water bubbles during crystallization to a higher level than in 1 atm experiments. In any case, melting under vacuum conditions clearly does not guarantee elimination of bubbles, and hydrous precursors of chondrules are unlikely.

CONCLUSIONS

High percentages of vesicles are retained in flash-heated, remelted charges (melted up to 25x), charges melted for long durations (up to 1 h) and charges run in a vacuum if they are assembled from hydrous precursor components. Therefore, chondrules—whether melted once, multiple times, for a brief or extended period, even at solar nebula pressure—were made of anhydrous phases.

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