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Comment on "On the lower limit of chondrule cooling rates: The significance of iron loss in dynamic crystallization experiments" by S. Weinbruch, et al.

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INTRODUCTION

It is unlikely that the presence of chondrules, and thus their formation, within the protoplanetary nebula would be predicted if it were not for their ubiquitous presence in most chondritic meteorites. The study of these enigmatic, igneous objects has a direct influence on how meteoritic and solar system researchers model the processes operating and the materials present within our protoplanetary nebula. Key to understanding chondrule formation is a determination of constraints on their thermal histories. The three important variables in this history are (1) their peak melting temperatures, (2) the duration of their melting at peak temperatures, and (3) the rate at which these object cool. Although these three variables are interdependent, it is cooling rate that provides the most powerful constraint. Cooling rate has a direct affect on the development of both crystal morphology and the elemental distributions within these grains. To date, experiments have indicated that chondrule cooling rates are in the range of 10's to 100's of degrees per hour for porphyritic chondrules (the most abundant type). The cooling rate for radial and barred chondrules is thought to be more rapid. To generate these cooling rates (rapid relative to the cooling of the nebula as a whole, but slow compared to simple black body radiation) the environment of chondrule formation must have been localized, and the abundance of solid materials must have been greatly enhanced above a gas of solar composition. Thus accurate determinations of chondrule cooling rates is critical in understanding both their formation and the nebular environment in which they formed.

Constraining the cooling rates experienced by chondrules is achieved through comparisons between their textures and fractionated mineral chemistries to their experimentally synthesized analogs. The dynamic crystallization experiments of Lofgren and Russell (1986), Lofgren (1989) and the further analysis of Lofgren's 1989 experiments by Jones and Lofgren (1993) established that cooling rates as slow as 5°C/hr produced analog textures and major and minor element zoning profiles in minerals, implying that a lower limit on chondrule cooling rates may be approximately 5°C/hr. These results, however, are in conflict with those reported by Radomsky and Hewins (1990). In their paper, Radomsky and Hewins (1990) established a lower limit on chondrule cooling rates of 100°C/hr, a factor of 20 higher than that suggested by Jones and Lofgren (1993). The higher cooling rates suggested by Radomsky and Hewins (1990) have gained considerable favor within the meteoritic community largely because it appears more consistent with the preservation of Na in chondrules, which tends to volatilize at the slower cooling rates. In their study, however, Radomsky and Hewins (1990) did not use Pt hang wires that were coated or saturated with Fe. The lack of such techniques likely facilitated Fe loss from their experimental chondrules to the hang wire during formation (Jones and Lofgren, 1993). The effect of Fe loss could produce an inaccurate determination of cooling rates since these rates are largely determined by the Mg-Fe distributions in individual crystals.

In a quest to more accurately determine the lower limit on cooling rates and to determine in more detail the effects of Fe loss from a molten sample to Pt wire loops, Weinbruch et al. (1998) have explored this issue experimentally and reevaluated the findings of Radomsky and Hewins (1990) in light of their new results. We applaud Weinbruch et al. (1998) for undertaking this issue and for asserting that the lower limit for chondrule cooling rates is ambiguous. The basic conclusions of their paper are an important contribution to our understanding of how experimental techniques can affect established constraints on chondrule formation and are thus of interest to a wide audience. We do believe, however, that their methodology produces results that provide inappropriate impressions of the applicability of their study to chondrule formation and nebular processes. Furthermore, the extensive body of previous experimental work on chondrule bulk compositions cannot be invalidated, as they suggest, by the results of Weinbruch et al. (1998). It is for these reasons that within this comment we address the applicability of the results presented by Weinbruch et al. (1998) to previous studies and illustrate how the experimental conditions chosen for their series of experiments introduced a significant bias in their results.

EXPERIMENTAL CONDITIONS

The problem of Fe-loss to Pt containers and hang wires is not new to the experimental community. Researchers have both quantified the extent of the problem and determined various methods to minimize the effects of Fe-loss on experimental results. Johannes and Bode (1978) showed that increasing hydrogen fugacity, temperature, or run duration all increased the amount of iron lost from the sample. Johannes and Bode (1978) plated the Pt capsule with an Fe film and saw no decrease in the Fe content of the sample material. Similarly, Lofgren et al. (1979) compared Fe-capsule experiments to Fe-saturated, Pt and Fe loop experiments. Lofgren (1989) plated Pt wire loops with 12-15 wt. % Fe, but still found a loss of up to 20 % FeO depending on the run conditions. This is not surprising, since the melt temperatures were quite high (1550 to 1600°C) and the melt duration was 2 hours. Jones and Lofgren (1993) used similar experimental techniques on the same bulk composition, but with lower melt temperatures (1525 to 1550°C). Radomsky and Hewins (1990) did not make any attempt to mitigate Fe-loss in their experiments, but did examine the amount of Fe and Na loss in isothermal experiments at 1601°C for 0.5 hr and

4 hr experiments. The Fe loss was significantly greater for the 4 hr experiment (23%) compared to the 0.5 hr experiment (6%).

The experimental protocol used by Weinbruch et al. (1998) is significantly different from that employed in previous studies. These variances have the potential for increasing the amount of Fe loss to Pt compared to the standard experimental protocol used in other laboratories. In particular, we will address the following issues: (1) diameter of the Pt hanging wire, (2) sample size, and (3) heating and cooling profile.

Diameter of the Pt hanging wire. Weinbruch et al. (1998) state that "Two wires (0.35 mm in diameter) were twisted together and formed into a loop." We will give them the benefit of the doubt and assume that they twisted two wires together, then separated them at the ends and formed a loop, so that the hanging wire in contact with the sample consisted of a single loop of 0.35 mm Pt wire. If, however, Weinbruch et al. (1998) actually fashioned their loop out of twisted wire it would effectively double the volume of Pt adjacent to the sample, further enhancing Fe loss.

The diameter of their wire is significantly thicker than that used in previous work. Radomsky and Hewins (1990), Lofgren and Russell (1986), Lofgren (1989), and Jones and Lofgren (1993) used 0.20 mm diameter Pt wire. The cross-sectional area of 0.35 mm Pt wire is more than three times greater than that of a 0.20 mm Pt wire (0. 0962 mm^2 vs. 0. 0314 mm^2). The larger surface area in contact with the sample facilitates greater Fe loss from the sample at a more rapid rate than experiments utilizing smaller diameter Pt wire (Presnall and Brenner, 1974; Donaldson et al., 1975). We believe that Weinbruch et al. (1998) should have used a single strand of 0.20 mm diameter Pt wire if their goal was to compare the effect of Fe loss on the results of previous studies such as Radomsky and Hewins (1990).

Sample size. Weinbruch et al. (1998) used a sample size of 10 mg, compared to the 100 mg used in the experiments of Radomsky and Hewins (1990). The majority of chondrule experiments have been performed with sample sizes in the range of 40 - 100 mg. The volume of a 4 mm diameter sphere (100 mg sample) is 33.5 mm^3, while that of a 10 mg sample is 3.35 mm^3, which translates to a sphere with a diameter of ~1.85 mm. Sample size has been shown to have an effect on the resulting chondrule texture for experimental charges of 1, 2, and 4 mm diameter (Connolly and Hewins, 1991). Therefore, sample size needs to be considered in the interpretation of experimental results.

The amount of Fe that will diffuse into the Pt wire is dependent on many factors, including the wt. % of Fe in the sample and the total weight of the sample (this is the available reservoir of Fe that is available), the surface area of the Pt in contact with the sample, and the diffusion rate of Fe in the sample (will vary depending on temperature and proportion of crystal vs. liquid). Since Weinbruch et al. (1998) state that the glass is homogeneous in runs of 10°C/hr, we can probably assume that diffusion of Fe in the liquid is not the rate limiting factor for the loss of Fe into the Pt. Since Radomsky and Hewins (1990) used the same starting composition as Weinbruch et al. (1998) the difference in the available reservoir of Fe is a function of the volume of the sample.

If we assume that the Pt wire is shaped into a loop the diameter of the sample, and that only one half of the Pt wire is in contact with the sample during the experiment, we can calculate the surface area of the Pt wire covered with melt. For a 0.35 mm diameter Pt wire shaped into a 1.85 mm diameter loop the available surface area is 3.29 mm^2 (the experimental conditions of Weinbruch et al., 1998). For a 0.20 mm diameter Pt wire shaped into a 4 mm diameter loop the available surface area is 3.98 mm^2 (standard experimental conditions used for chondrule experiments). Dividing the volume of the sample (the reservoir of Fe) by the surface area of the

Pt (the size of the "pipeline") shows that the Weinbruch et al. (1998) experiments have approximately one mm^3 of sample per mm^2 of Pt compared to 8.4 mm^3 sample per mm^2 of Pt for Radomsky and Hewins (1990) and others.

Heating and cooling profile. Both an increased amount of time and an increase in temperature will increase the diffusion rate of Fe in both the melt and the Pt wire (e.g., Johannes and Bode, 1978). Experimental runs by Lofgren, Hewins, and co-workers are generally performed by bringing the furnace to the maximum run temperature for the experiment before inserting the room temperature sample into the hot furnace. The sample is held at the maximum run temperature for a specified period of time before commencing cooling. Thus the factors that affect the Fe loss to the Pt wire include the amount of time it takes for the cold sample assembly to reach the maximum temperature, the length of time the sample is held at maximum temperature, and the absolute value of the maximum temperature. Fe loss to the Pt wire increases when any of these values is increased.

In addition, the lower the quench temperature and the slower the cooling rate, the longer the sample remains at a temperature where there is a potential for Fe loss to the Pt wire. Therefore, decreasing the quench temperature and/or cooling rate will increase Fe loss. This effect is likely to be minor compared to other factors, and will diminish as temperature decreases and the amount of crystallization in the sample increases.

Instead of placing the sample in the furnace at the maximum run temperature, Weinbruch et al. (1998) placed the sample in the furnace at 800°C and heated at 20°C/min (1200°C/hr) to 1450°C followed by heating at 5°C/min (300°C/hr) to the run temperature of 1500°C. These experimental conditions were chosen to follow the heating path as closely as possible to the calorimeter experiments. The samples were held at 1500°C for 30 minutes and then cooled at 10 or 100°C/hr to 1000°C. Although not clearly stated, the implication from Radomsky and Hewins (1990) is that they also held their samples at maximum temperature for 30 min. In addition, the quench temperature for the Radomsky and Hewins (1990) experiments was 1250°C, compared to 1000°C for Weinbruch et al. (1998). For a 10°C/hr experiment it means that the Weinbruch et al. (1998) samples would remain in the furnace at temperatures above the solidus for an additional 25 hours, during which Fe loss to the Pt would likely occur. Therefore, a direct comparison between the results of Weinbruch et al. (1998) and Radomsky and Hewins (1990) is questionable based on the residence time of the sample in the furnace.

The total sum of the experimental conditions selected by Weinbruch et al. (1990) results in enhancement of Fe loss to the Pt compared to the experimental conditions of Radomsky and Hewins (1990) and other workers. An increase in the diameter of the Pt wire, a decrease in the sample size, and an increase in the residence time of the sample at temperatures above the solidus all contribute to increased Fe loss to the Pt wire.

ANALYSIS OF RESULTS

In order to fully understand the effects of Fe loss to Pt wire it is critical to have at least a semi-quantitative understanding of the amount of iron lost from the starting material. This information could have easily been obtained by analyzing the Pt wire for Fe, preferably along a traverse covering the cross section of the wire. With this information, along with the analyses of the glass, pyroxene, and olivine, it would be possible to do a simple mass balance calculation to determine how much of the iron was lost from the starting material. Ideally this exercise would be completed for both the experimental conditions used by Weinbruch et al. (1998), along with the more standard experimental conditions used in previous studies. It is only with this information that a definitive statement about the effects of Fe loss on the conclusions reached by previous authors can be made.

Weinbruch et al. (1998) found different results depending on whether the Fe crucible, Pt wire, or presaturated Pt wire was used to hold the sample. Similar results were found by Lofgren et al. (1979) for a lunar basalt composition, with additional quantification of the effects of the sample holding technique on nucleation and phase chemistry. These authors confirmed by INAA analysis that no Fe was lost to presaturated Pt loops in experiments cooled at 4°C/hr. A small amount of Fe loss was found in the 2°C/hr experiment.

The loss of Fe to the wire, severe using the pure Pt, but still significant with the pre-saturated Fe-Pt alloy wire loop, has the potential to significantly change the liquidus of the melt and therefore its crystallization behavior. Fe loss increases the SiO_2 content of the remaining melt relative to MgO + FeO and therefore stabilizes pyroxene relative to olivine. Furthermore, because the Fe content of the melts in each of the different kinds of experiments is changing, it cannot be assumed that the melt temperature is the same for each experiment because the liquidus of the starting material changes as the Fe content changes. The number of nuclei in a sample is the main factor controlling the texture. A change in the liquidus temperature can cause a significant change in the number of nucleation sites present for a specified run temperature.

Since the proportion of the iron in the samples of Weinbruch et al. (1998) is greater than in previous experiments it would follow that the change in mineralogy (as is evident by the stabilization of tridymite in some experiments) after accounting for Fe loss, would also be greater. Tridymite formed in experiments using the presaturated Pt loops, suggesting that the presaturation step (22 hr at 1462°C with an fO_2 of IW - 0.16) was not adequate for the final run conditions, which were at a higher temperature, lower fO_2, and, for the 10°C/hr experiments, were in the furnace above the solidus longer. Further evidence that the presaturation step was insufficient to mitigate Fe loss includes the fact that pyroxene rather than olivine is the first crystallizing and dominant phase in the presaturated Pt loop experiments. Since no attempt was made by Weinbruch et al. (1998) to quantify the Fe loss, or lack thereof, in any of their experiments, as was done by Lofgren et al. (1979), this is the extent of the conclusions that can be drawn based on the experimental results presented.

IMPLICATIONS FOR CHONDRULE COOLING RATES

The lower limit of chondrule cooling has not been firmly established. Placing constraints on the cooling rate of chondrules is complicated by many factors, including the bulk composition under discussion and the texture of the chondrule. Cooling rate can only be defined for the temperature range of crystallization for the phase(s) being examined, and most experiments to date have examined linear cooling profiles, which are probably not likely to exist for the chondrule forming event.

Since maximum temperature and time at maximum temperature are the dominant controls on the nucleation characteristics of any bulk composition, these values vary significantly from study to study. If all other experimental conditions are kept constant, a variation in cooling rate will generally result in a variation in the phase chemistry, due to changes in the growth rate of crystals and diffusion in the crystal and liquid. At rapid cooling rates there is insufficient time for olivine crystals to equilibrate completely with the liquid and they show zoning from core to rim. Hence, comparison of olivine zoning profiles in experiments and chondrules can be used as an indicator of cooling rate during formation. Weinbruch et al. (1998) claim that "discrepancies of the published values for the lower limit of chondrule cooling rates can be explained by the use of different receptacle materials." These authors are referring to Hewins (1988) and Radomsky and Hewins (1990) who concluded that chondrules formed at cooling rates of 100°C/hr or faster. However, as Weinbruch et al. (1998) note, the experiments of Jones and Lofgren (1993) yielded a cooling rates as low as 2 to 5°C/hr for porphyritic olivine chondrules. It should be stressed that Jones and Lofgren (1993) did mitigate Fe loss to the Pt wire by plating the loops with Fe prior to the experiment.

Weinbruch et al. (1998) state: "If cooling rates are to be derived from comparison of synthetic analogues and natural chondrules, Fe loss during the experiment has to be avoided completely." The bulk compositions of natural chondrules, however, have an extremely wide range of FeO content, ranging from nearly Fe free in the enstatite chondrites to ~53 wt. % FeO rich chondrules from ordinary chondrites (Connolly et al., in press; Hewins and Radomsky, 1990).

Given these factors, the conclusion of Weinbruch et al. (1988) that "chondrule cooling rates cannot be constrained precisely from such experiments" is not reflective of the complete body of experimental data on chondrule cooling rates currently available and should only include those experiments that did not account for Fe loss to Pt.

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