EVIDENCE FOR THE PRESENCE OF ALKALIS AT HIGH TEMPERATURES IN TYPE II CHONDRULES IN ORDINARY CHONDRITES: Jeffrey N. Grossman[1] and Conel. M. O'D. Alexander[2], [1]U.S. Geological Survey, Reston, VA 20192, USA (jgrossman@usgs.gov), [2]DTM, Carnegie Institution of Washington, Washington D.C. 20015, USA (alexande@dtm.ciw.edu).

Introduction: Last year, we reported the initial results from our study of Na abundances in olivine phenocrysts from chondrules in Semarkona, and concluded that these grains generally have igneous zoning profiles, consistent with closed-system crystallization with Na concentrations similar to what is currently observed in the chondrules [1]. These data are inconsistent with condensation of Na into chondrules cooling and crystallizing under anything like canonical nebular conditions, which would result in steep zoning profiles and severe depletions in olivine cores. However, recent interpretations of chondrules conclude that they many not be simple igneous systems at all: in one radical model, olivine phenocrysts and surrounding material are interpreted to be unrelated, with most olivine being xenocrystic [2,3]. Consequently, we have extended our study to include a detailed examination of the crystallization history of chondrules, allowing us to explore relationships between minerals formed over a wide range of temperatures. We report here on our results for type II chondrules in Semarkona.

Experimental: Twenty-six type II chondrules from Semarkona were selected. Most were olivine-rich (IIA), and five contained enough low-Ca pyroxene to be classified as IIAB or IIB. We focus here on the type IIA group. The bulk compositions were measured by analyzing a grid of 100 points by electron microprobe, using the method of [4]. Zoning profiles across large olivine grains were done at high beam currents and long counting times to determine Na, as in [1]. Spot analyses of olivine rims and crystallites were done at the same conditions. Clinopyroxene (CPX) grains occurring as euhedral crystals, dendrites, and overgrowths were also analyzed. Finally, rastered-beam analyses of glassy areas as free from microlites as possible were done using the method of [5]. The crystallization history of each chondrule was modeled using the MELTS program [6], under both equilibrium and fractional crystallization conditions to determine the liquidus temperature and predict zoning relationships.

Results and discussion:

Are olivine phenocrysts related to each other? Relict grains are well-known in type IIA chondrules, usually recognized by anomalously low FeO contents in grain cores; these were observed in some of our samples. The majority of large olivines inside a single type IIA chondrule, however, generally appear similar to each other in BSE images. Zoning profiles of large olivines show similar features for many elements from grain to grain, including, in one case, an oscillatory pattern. In contrast, frequently there are large differences between olivine grains in different chondrules. We conclude that, with the exception of obvious relicts, most of the grains in a given chondrule formed together, under conditions that are often distinct from the grains in other chondrules.

Are olivine phenocrysts related to the surrounding melt? If chondrules are relatively simple igneous systems, then the cores of large olivine grains (excluding obvious relict grains) should have compositions that reflect partitioning between olivine and a melt with the chondrule bulk composition near the liquidus temperature. Although partition coefficients (Kd) are not well-known for compositions and conditions relevant to chondrule formation, a good correlation between core olivine and bulk composition for a minor or trace element can be taken as evidence for such partitioning and would provide an estimate of Kd. Several minor elements do show fairly strong correlations, establishing that phenocrysts and melt did, in fact, form an igneous system in most chondrules: as similarly shown by [7], the P_2O_5 content of olivine cores correlates with bulk P_2O_5; Al_2O_3 also shows such a correlation.

The phenocryst cores show a wide range of Na contents, from values similar to those observed in type I chondrules [1] to nearly 10× higher. The olivine-core Na does not correlate with bulk-chondrule Na in type IIs. We know from elements like P and Al that the olivine did form from something close to a total-chondrule melt, and that Na does not diffuse quickly in the olivine [1]. This lack of correlation between core olivine and bulk Na contents could result from (i) the presence of cores that do not reflect the first phase of crystallization, (ii) cores that are unrecognized relicts, and/or (iii) equilibration with melts having different Na contents at the time of core crystallization than is currently observed. Off-center, random sectioning would cause (i), although this was minimized by selection of large grains. (ii) cannot be ruled out for some grains, although the P and Al data would probably limit these to invisible relict grains from other type II chondrules. However, for the purposes of this abstract, establishing whether explanation (iii) occurred is the most important. If it did, we can use an olivine-melt Kd of ~0.005 [1] to calculate hypothetical initial chondrule bulk (parent melt) compositions from the olivine core compositions. The result would be that most type

IIA chondrules formed from melts with 1-2 wt% Na_2O. The mean hypothetical Na content is almost the same as the observed mean because some chondrules would have higher Na and some lower. So, even if type II chondrules no longer have their primary Na contents, they still must have started with 3-4× as much Na as type I chondrules. That Na contents may have changed is supported by the presence of low-Na glass inclusions in some Na-rich type II chondrules in Semarkona.

Was the Na content of type IIA chondrules constant during their entire cooling history? Using an olivine-liquid Na Kd of ~0.005, the MELTS program reproduces the zoning relationships in olivine phenocrysts reasonably well, indicating that Na was not changing dramatically during crystallization.

The Na contents of late-formed olivines, occurring as rims on large grains and small crystallites in the mesostasis, also do not correlate with those in chondrule glasses, although most olivine/glass Na ratios are consistent with a Kd of ~0.005. The lack of correlation might arise either because we did not analyze the final olivine compositions where rims are thin and crystallites small, or, again, because the Na content of the mesostasis has changed since olivine crystallization ceased.

Assuming that the preceding calculation of the bulk Na content of type IIA melts at the onset of olivine crystallization is meaningful, we can check whether the late-formed olivine was in equilibrium with a hypothetical residual liquid after the large olivines crystallized. We assumed that such a liquid would be enriched in Na relative to the calculated bulk composition to the same extent that the natural mesostasis was enriched over the natural bulk composition. Indeed, there is a strong correlation between Na in late-formed olivine and this hypothetical liquid, indicating that at least 70-80% of the Na was retained in the chondrules across the temperature range of olivine crystallization. Data from MELTS indicates liquidus temperatures of ~1600-1650°C, and that olivine continued to form down to temperatures near 1100-1200°C, when CPX is expected to start forming.

Sodium in CPX in type I chondrules correlates well with that in surrounding glass [8], and forms the best evidence for elevated Na in these chondrules at CPX crystallization temperatures. However, the Na content in CPX in the type IIA chondrules does not correlate with that in either the observed glass or the calculated residual liquid based on olivine cores. This is probably because CPX in type IIs crystallized over a lower range of temperatures than type Is where the Na Kd becomes much more temperature dependent [8].

When were chondrules open to Na loss or gain? One interpretation of our olivine data is that some chondrules had different Na contents above 1200°C than is presently observed. We confirm the observations of [9], that many Semarkona type II chondrules have non-solar K/Na, most commonly >1 and in some cases >2. This is also a strong indication that alkalis were once mobile in the chondrules, and led [9] to speculated that Na was lost from chondrule glass during parent-body metamorphism.

Our new data on type II chondrules is not adequate for evaluating whether the mobilization of alkalis occurred near the temperature of CPX crystallization in the presence of melt, or subsolidus as preferred by [9]. We do know that alkalis were well-behaved in type I chondrules at the time of CPX crystallization [8]. However, some type I chondrules exhibit alkali zonation in their mesostases and non-igneous CPX/mesostasis Na ratios in the zoned regions, suggesting that the Na entered the solid chondrules by inward diffusion. In light of this, we prefer the same mechanism for type II chondrules, which appear to have been significantly more open to alkali exchange than type I chondrules.

Conclusions: Aside from obvious relict grains of olivine, type IIA chondrules in Semarkona appear to be igneous systems, with olivine phenocrysts having grown from the chondrule melts, and crystallized under nearly closed-system conditions with respect to Na across hundreds of degrees of cooling. Initial type II chondrule compositions varied widely in Na content, and were generally much richer in Na than type I chondrules. Late-formed CPX also reflects high Na contents, but these data cannot be used to derive the compositions of coexisting melts as they can in type I chondrules. Type II chondrules were probably quite open to alkali exchange after solidification.

Models for chondrule formation must be able to accommodate high levels of Na, in the range of 1-2 wt% Na_2O, at near-liquidus temperatures, and keep them in the chondrule until solidification. The implications of this are explored in a companion abstract [10].

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