

MINERALOGICAL AND ISOTOPIC EFFECTS OF SHOCK WAVE THERMAL HISTORIES ON CHONDRULE PRECURSORS. A. V. Fedkin¹, L. Grossman^{1,2}, F. J. Ciesla¹ and S. B. Simon¹, ¹Dept. of the Geophysical Sciences, Univ. of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 (avf@uchicago.edu), ² Enrico Fermi Institute, Univ. of Chicago.

Introduction: Nebular shock waves are a suggested heat source for chondrule formation, as they are calculated to produce peak Ts and cooling rates like those in experiments that yield chondrule textures [1, 2, 3]. Shock wave thermal histories show a near-linear heating rate ending at a pre-shock T, followed by a sharp T spike to a peak T, then a sharp drop to a post-shock T, and finally a near-linear cooling rate. Because of lack of isotopic evidence for evaporation, chondrules are thought to have formed at high dust enrichments. All else being equal, these lead to shock wave thermal histories with higher heating and cooling rates, and higher pre-shock and peak Ts. To stabilize the relatively high FeO contents of Type II chondrules, high water enrichments are needed. These lead to higher peak Ts and lower cooling rates [4]. A kinetic model for evaporation and recondensation, based on metal-silicate, liquid-crystal phase relations of MELTS [5], was applied to the chemical and isotopic evolution of chondrule precursors subjected to passage of nebular shock waves through dust- and water-enriched systems in [6]. Subsequent work [4] used input thermal histories from shock wave models at higher spatial resolution, and a modified Hertz-Knudsen equation [7] that accounts for thermal disequilibrium between condensed and vapor phases occurring in such models.

Technique: The present work builds upon these earlier studies and incorporates several additional, important improvements. Kinetics of melting were treated as in [8], using the partial molar Gibbs free energy of each silicate and oxide in the multicomponent liquid to substitute for the free energy of fusion of the respective solid phases. Olivine composition histograms were measured in the run products obtained at 10 and 100 K/hr on a Type II chondrule composition in [9]. These were used to derive calibration curves for the fraction of the total olivine sequestered as a function of T that can be used with MELTS to model fractional crystallization, and were interpolated and extrapolated to other cooling rates. Activity-composition relations from MELTS were spliced with those from CMAS [10] such that evolution of chondrule precursors could be tracked continuously before and after complete evaporation of iron and alkalies, and before and after the beginning of their recondensation. Shock wave thermal histories computed for this work are for systems enriched 600x in dust and 550x in water relative to solar composition, yielding $\log f_{O_2} \sim IW-1$ to $\sim IW-1.5$ in the ambient gas. Profiles are shown in Fig.

1, together with approximate liquidus Ts for these compositions. Pre-shock, peak and post-shock Ts are labeled as well as heating and cooling rates in K/hr. These are referred to as the high-T, slow- and fast-heating (and cooling) cases. Computational runs begin at 1400K, where 75% of the solid, non-metallic fraction is assumed to be sequestered from the remaining, equilibrated fraction of the droplet. As T increases, the amounts of sequestered and equilibrated silicates and oxides decrease and the amount of liquid increases at rates governed by melting kinetics, evaporation occurs into a closed system at rates governed by experimentally determined evaporation coefficients and the liquid surface area, and metallic Fe disappears both by evaporation and by oxidation by the surrounding water-rich gas on a time-scale assumed to be comparable to the chondrule evolution time. Although the peak T may be superliquidus, the T spike generally lasts for no more than 1 or 2 minutes, so all solid olivine present at the pre-shock T is assumed to survive melting. As T falls, recondensation occurs, and fractional crystallization is assumed to start at the post-shock T. Orthopyroxene crystallization is suppressed during cooling. Histograms of XFa and the isotopic composition of olivine are composed of relics that survived heating, olivine that fractionally crystallized during cooling and the olivine in equilibrium with liquid at the end of the run, 800K. Two types of models were used to try to account for the Fe/Si depletion in Type II chondrules relative to CI chondrites [11], both employing precursor solids initially equilibrated at 1400K and $\log f_{O_2} = IW-2.6$: a high-Fe case, using a chondritic precursor (29.7 wt% FeNi; 2.3% FeO), and physical removal of metallic NiFe during recondensation; and a low-Fe case, with a chondritic precursor except for $Fe/Si = 0.33 \times CI$ (11.2% FeNi; 2.8% FeO).

Results: In all runs, a large fraction of the droplet is solid olivine at the pre-shock T, ~15 wt% in the high-T runs and 20-25% in the others. It being unlikely that such large amounts of olivine would melt in the short times spent above these Ts, such physico-chemical conditions are favorable for forming porphyritic, rather than barred, textures. In all cases, alkalies are the first to evaporate totally and the last to recondense. Fe and Ni are the next to totally evaporate, prior to the pre-shock T in all cases. The bulk of Mg and Si evaporation occurs at the highest Ts, from liquids in the CMAS system. In all cases, a much greater fraction of the Si evaporates than the Mg because the SiO₂ con-

tents of the liquids at this point are much higher (~55 wt%) than their MgO contents (~25 wt%). Before recondensation, ~63% of the Si and ~38% of the Mg evaporate in the high-T runs, ~25% and ~1%, resp., in the fast-heating runs and ~8% and ~1%, resp., in the slow-heating cases. Fig. 2 shows olivine composition histograms for the model droplets. Because pre-shock olivine equilibrated with, and the first post-shock olivine crystallized from, FeO-free liquids, all histograms have a large peak at pure Fo. In the high-T, low-Fe case, olivine crystallization is 65% complete before Fe recondensation starts. Histograms for fast- and slow-heating, high-Fe runs have a second peak at Fa11 and Fa17, resp., but those for all other runs have long, low tails out to Fa30-35. Mean X_{Fa} in the high-Fe, slow-heating case is 0.134, but in all other runs is 0.048-0.086, similar to Type I chondrules. The model droplets, however, are not as low in Fe/Si as Type I chondrules. To obtain mean X_{Fa} as high as in Type II chondrules requires even greater water enrichments than used here. When metallic NiFe beads are physically separated from the droplet in the high-Fe cases, recondensation of Fe continues, as metal and FeO into the droplet and metal into the beads. For this separation to result in the desired Fe/Si ratio for the bulk droplet, the T where it occurs is such that the bulk of the Fe that condenses into the beads has positive $\delta^{56}\text{Fe}$, leaving the droplet with a negative bulk $\delta^{56}\text{Fe}$ of -2 to -7%. This is avoided in low-Fe models by postulating metal separation from the starting material prior to chondrule formation. Because Fe isotopic anomalies of this size are not found in chondrules [12], low-Fe models are preferred. Even when all Fe recondenses into the droplet, yielding near-normal Fe isotopic composition for the bulk droplet, as in the low-Fe models, a record of the Fe evaporation stage is still preserved as internal Fe isotopic heterogeneity. In the low-Fe, fast-heating case, e.g., the first Fe to recondense into the droplet has $\delta^{56}\text{Fe}$ ~ -18‰, and ~15% of the total olivine (~1.8% of the total Fe) has this composition due to fractional crystallization. Later olivine, isolated after more complete Fe recondensation, has $\delta^{56}\text{Fe}$ from -4 to -11‰, but $\delta^{56}\text{Fe}$ of metal (59% of the total Fe) and glass (16%), both assumed to stay in contact with the gas, is +2.5‰. As seen here, dust enrichment, invoked to retard evaporation, actually promotes evaporation in shock wave models by causing increased Ts.

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