THE CHEMICAL ENVIRONMENT EXPERIENCED BY CHONDRULES FORMED IN PLANETARY EMBRYO BOW SHOCKS.

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Introduction: Chondrules are some of the oldest solids in the Solar System [1-6]. As such, their properties can be used to gain insight into conditions in the early solar nebula. The meteoritic record provides numerous constraints on the formation of chondrules [7]. The formation model most consistent with these constraints is the nebular shock model [8,9,7]. The most plausible sources of shocks are gravitational instabilities in the disk, leading to large-scale shocks [10,11], and bow shocks around small ($<$ 1000 km diameter) planetesimals on eccentric orbits [12-15]. The planetesimal bow shock model has not been generally accepted because the cooling rates of chondrules it produces are too rapid to match meteoritic constraints [13,16,17]. Chondrule thermal histories require very large planetesimals ($\gg$ 1000 km diameter), and substantial concentrations of chondrules by factors 30-200 above background nebular values [16,17].

More recently [18] have investigated the formation of chondrules in bow shocks around much larger ($\approx$ 5000 km diameter) planetary embryos on eccentric orbits. Chondrule formation in planetary embryo bow shocks (Fig. 1), differs fundamentally from the planetesimal case. Chondrules remain dynamically coupled to the gas and flow around the embryo. In contrast, chondrules are generally accreted by planetesimals. The chondrule formation region around the planetary embryo is optically thick and chondrule cooling rates are $< 100\,\mathrm{K\,hr^{-1}}$. In contrast, the region is optically thin around a planetesimal, and cooling rates are too rapid. Finally, the planetary embryo develops a primary atmosphere acquired from nebular gas and is likely to develop and retain a secondary, outgassed atmosphere that is rich in volatiles. Chondrules are seen to pass through gas stripped from the embryo's atmosphere. Here we investigate these effects on the chemical environment of chondrule formation. We find many aspects of chondrule formation are explained by interaction of chondrules with the volatiles outgassed from a magma ocean.

FeO and Na in chondrules: Chondrules appear to have been exposed to anomalously high partial pressures of volatiles. [19] reported high mass fractions, $\approx 0.010 - 0.015$ wt%, of Na_2O in the cores of olivine phenocrysts of Semarkona chondrules. This strongly implies that the melt contained Na throughout olivine crystallization, and that the partial pressures of Na vapor were high enough to prevent evaporation of Na from the melt. Using the values quoted in [19] we calculate the required partial pressures of Na at $\approx 2 \times 10^{-5}$ bar, many orders of magnitude higher than expected for a solar composition gas unless chondrules are concentrated by factors $\sim 10^6$. Potassium in chondrules exhibits a lack of isotopic fractionation [20], implying evaporation of K was likewise suppressed.

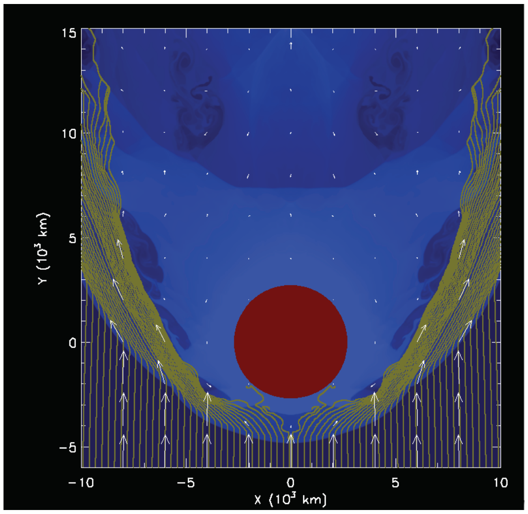

Figure 1: Gas density (blue contours), velocities (white arrows), and trajectories of chondrule precursors / chondrules (gold streamlines), in the vicinity of the bow shock surrounding a 2720-km radius planetary embryo (i.e., half a Mars mass). Velocities are measured in the frame of the planetesimal, moving at $8\,\mathrm{km\,s^{-1}}$ with respect to the local gas. Chondrules with impact parameters $>$ 400 km are *not* accreted.

Although Type I chondrules are considered low-FeO and Type II considered high-FeO [21], both have FeO contents that imply oxygen fucacities f_{O_2} well above gas of solar composition [22-24]. The FeO content of chondrules requires log $f_{O_2} \sim$ IW-1 to IW-2, 5-6 log units higher than the solar value of $\sim$ IW-7 [22-24]. This implies formation in a gas with distinctly non-solar composition [25,26]. [27] found that water enrichments of factors $>$ 550 were needed for Type II chondrules, and [24] found enrichments of $\sim$ 240-820 were needed. Increases in f_{O_2} due to enrichment of dust or water via settling or radial migration of icy bodies [28,29] were investigated by [23,24], who concluded that maximum water enrichments were only a factor $\approx$ 10 above background levels, and dust enrichments even less. It is thus a mystery how the high partial pressure of water vapor required to explain FeO content was attained. Based on the work of [22], we estimate this value at $P_{\mathrm{H2O}} > 4 \times 10^{-5}\,\mathrm{atm}$.

Outgassed Atmosphere: Chondrules formed in a planetary bow shock will be exposed to volatiles outgassed from the protoplanet's magma ocean. Any protoplanets formed by the time of chondrule formation, ~ 2 Myr after CAIs [4,6], likely possess a magma ocean due to melting by $^{26}\mathrm{Al}$ [30,31]. This magma ocean would rapidly outgas volatiles, developing an atmosphere that is in chemical equilibrium with the magma in $< 10^3\,\mathrm{yr}$. This outgassed atmosphere would be maintained for several Myr before the protoplanet solidifies [32], and would primarily consist of H_2O, CO_2, and N_2, as well as moderately volatile species such as S, Na, Zn, Cl, and K [33,34]. This atmosphere would be continuously stripped by Kelvin-Helmoholtz (KH) instabilities at the interface between the atmosphere and the post-shock gas streaming by the planet (Fig. 1). [18] estimate the atmosphere is stripped at a rate $\approx 2 \times 10^{12}\,\mathrm{g\,s^{-1}}$, sufficient to remove the atmosphere in ~ 250 yr. However, further outgassing will replenish the atmosphere.

Analyses of Martian meteorites have led to estimates of Mars's bulk water content ranging from $\sim$ 140-250 ppm [35] to $\approx 0.5 - 1.8\mathrm{wt}\%$ [36-39]. We assume a mass fraction $x_{\mathrm{H2O}} = 0.2\mathrm{wt}\%$ as a representative value for the planetary embryo. Using mass balance, chemical equilibrium, and the formula of [40] for the mass fraction of water dissolved in the magma, $x_{\mathrm{H2O}} = 10^{-3}\,(P_{\mathrm{H2O}}/1\,\mathrm{atm})^{0.54}$, we estimate a partial pressure of water vapor of 3.3 bar at the surface. The mass of water vapor in the atmosphere ($\approx 10^{22}\,\mathrm{g}$) is a small fraction of the total water content. We conduct a similar calculation for CO_2, based on the solubility of carbon dioxide in magma of [41], $x_{\mathrm{CO2}} = 4.4 \times 10^{-7}\,(P_{\mathrm{CO2}}/1\,\mathrm{bar})$, and assume the total mass fraction of C is the same as on Earth, resulting in $P_{\mathrm{CO2}} \approx 10\,\mathrm{bar}$. We estimate $P_{\mathrm{N2}} \sim 0.1\,\mathrm{bar}$. Finally, the outgassing of Na vapor is calculated assuming Na is dissolved as NaOH and follows the formula of [42], $P_{\mathrm{NaOH}} = 1.2 \times 10^{-3}\,(P_{\mathrm{H2O}}/1\,\mathrm{bar})^{1/2}$. We find $P_{\mathrm{NaOH}} \approx 2 \times 10^{-3}\,\mathrm{bar}$ at the protoplanet's surface.

The trajectories of chondrules take them through the KH rolls that are stripping the upper reaches of the protoplanet's atmosphere, about 850 km above the surface. Given the scale height of the atmosphere, ~ 185 km, we estimate that gas pressures will be $\sim 1\%$ of their values at the surface. We accordingly propose that chondrules melted in planetary embryo bow shocks will be exposed to partial pressures $P_{\mathrm{H2O}} \sim 3 \times 10^{-2}\,\mathrm{bar}$ and $P_{\mathrm{NaOH}} \sim 2 \times 10^{-5}\,\mathrm{bar}$. These are sufficient to explain the lack of evaporation of Na from olivine melts and the high FeO content of chondrules.

Mars is likely only one of many planetary embryos present at the time of chondrule formation [30]. Some models of its origin [43,44] indicate it may have been scattered onto an eccentric orbit. Chondrule formation by planetary embryo bow shocks appears to match known constraints on cooling rates, etc. [18]. Additionally, we find that exposure to the protoplanet's atmosphere outgassed from its magma ocean may explain outstanding mysteries of chondrule formation.

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