

CONSTRAINING THE NATURE OF TYPE-I CHONDRULES: I. CHEMICAL MODELS. H. Barcena^{1,2} and H. C. Connolly Jr.^{1,2,3,4}. ¹Dept. Physical Sciences, Kingsborough Community College of the City University of New York, 2001 Oriental Blvd., Brooklyn N.Y. 100235, USA; ²Dept. Earth and Planetary Sciences, AMNH, Central Park West, New York, NY 10024, USA; ³Dept. of Earth and Environmental Sciences, The Graduate Center of CUNY, 365 5th Ave., New York, New York, 10016, USA; ⁴University of Arizona, Lunar and Planetary Laboratory, Tucson, AZ 85721, USA (homar.barcena@kbcc.cuny.edu).

Introduction: Chondrules are spherical igneous rocks that are the major structural component of chondritic meteorites [1]. Their existence attests to high-temperature transient heating events within the early stages of the protoplanetary disk. The mechanism that produced these objects is unknown and it is not intuitive to science that planetary materials should be thermally processed before the accretion stage of asteroids and hence planets [2,3]. Furthermore, chondrules can be classified into petrographic and geochemical groups, with the major group being the ferromagnesian chondrules. Chondrules thus preserve a record of variations in composition of their precursors and of the redox conditions they experienced before and during their melting [1,4,5]. The two major types of ferromagnesian chondrules are type-I or FeO-poor, and type-II or FeO-rich, with an arbitrary cut-off of 10% Fa (fayalite, FeO) [6,7].

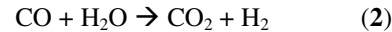
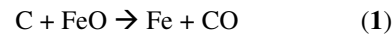
A major task in the investigation of chondrules is constraining the processes that controlled the redox conditions (oxygen fugacity or fO_2) they experienced and thus their mineral chemistry and bulk composition. Five hypotheses are proposed that may have controlled or influenced the redox conditions that chondrules experienced: First, the precursors of chondrules are a mixture of only silicates and the redox conditions they experienced were controlled by the surrounding nebular gas of a specific fO_2 . Second, chondrule precursors contained a mixture of silicates and reduced carbon. Alternatively, the precursors of chondrules were a mixture of silicates and H_2O ice. Fourth, chondrule precursors were a mixture of silicates, reduced carbon, and H_2O ice. Lastly, any combination of the above scenarios. Herein we focus our discussion to the modeling of the second hypothesis and predict the chemical reactions while the chondrules were molten.

Modeling: We explore the likely chemical reactions that took place during the melt synthesis of ferromagnesian chondrules, the expected molecular species that are released to the ambient environment during melting, and the heterogeneous reactions that occurred with the surrounding gas. To explain the processes that lead to the formation of the variations in ferromagnesian ratios and the range of oxygen isotopic anomalies found in chondrules, we deduced the redox

conditions capable of producing the ferromagnesian content empirically observed.

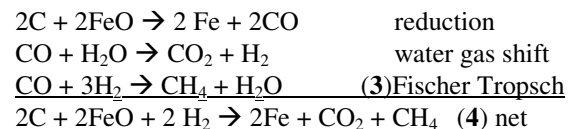
Discussion: For this abstract we focus our discussion to the second hypothesis. Assuming that the precursors are a combination of silicates and reduced carbon, we show below a series of reactions that involve and subsequently influence the fO_2 the melt experiences. This in turn governs the ferromagnesian ratio in the major silicate phases. Highly volatile products will escape from the melt, which react with the surrounding nebular gas. The net result is a change of the fO_2 of the ambient gas in the chondrules' microenvironment.

Starting with a mixture of Fa_{10} and carbon dust, we infer the production of CO upon reduction of FeO in the olivine melt (1&2). Carbon has been experimentally shown to buffer the formation of iron metal in chondrule melts [4,8].



The CO escapes from the melt and subsequently reacts with water vapor at the surface of the hot refractory chondrule to produce CO_2 and H_2 . The hydrogen gas produced reinforces the reducing environment under which chondrules are formed. We note that this water-gas shift reaction (2) can only occur at high water vapor concentrations and is less favorable at high temperatures.

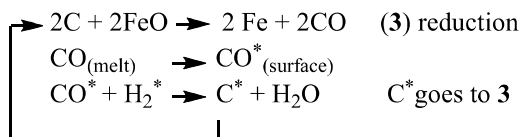
Under low fO_2 and high temperatures, an alternate mechanism is the Fischer-Tropsch (F-T) reaction 3. Metallic Fe species are active catalysts for the F-T, and while the F-T can produce higher hydrocarbons, at high temperatures, methane is the favored product. At low fO_2 , the net reaction of the sequence is 4:



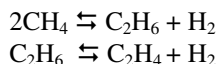
It has been calculated that the F-T catalysis by Fe and FeNi metal is a feasible process for the thermally-driven pathway to convert CO into other forms of carbon in the solar nebula, particularly at low temperatures [9]. At higher temperatures, formation of a graph-

itic layer on the catalyst surface poisons the conversion of CO to CH₄. Specifically, CO dissociates into carbon and oxygen atoms at the surface of the catalyst, with each reacting with adsorbed hydrogen to form water and methane. The limitation of the F-T is the poisoning of the catalyst surface from the graphitic carbon by-product, which retards the adsorption of H₂ and the subsequent formation of methane and higher hydrocarbons. At higher temperature, the adsorbed hydrogen is limited, and carbon does not get reduced to methane [9]. The discrepancy is that at temperatures where the F-T is favorable, the chondrules are cooling.

In our hypothesis, the heterogeneous F-T reaction could have occurred not only on isolated metal grains within the chondrule forming region but also on chondrule surfaces where exposed metal grains are in contact with nebular gas. By recycling the CO produced from reaction 3, we can remove the limitations imposed by catalyst poisoning of graphitic carbon buildup and propose a high F-T catalytic activity even at elevated temperature. We propose that the graphitic carbon C* formed on the surface could re-enter the melt and react with FeO in a catalytic fashion, producing a feed-back loop during reduction. The following sequence may occur at high temperatures and at low H₂ surface adsorption rate:



We deduce further heterogeneous reactions that occur between the gas and the melt in congruence with our hypothesis. At temperatures above 1470K, a highly endothermic methane pyrolysis could occur to produce ethane, and then subsequently ethylene [10]:



This process can further produce acetylene, C₂H₂, which, along with ethylene and benzene, were detected in a planetary nebula [11]. Methane pyrolysis produces organic radicals, ethylene, and higher hydrocarbons [12]. These are the precursors to more complex organic molecules found in carbonaceous chondrites [13].

Implications: By linking the F-T reaction with chondrules, formation of methane and other organics becomes favorable at high temperatures. Interestingly, the synthesis organics proposed here may not be related to a photochemical event; the processes can occur from chondrule formation. This is significant because

chondrules formed from repeated heating and cooling events [3]. Consequently, given only silicate dust, iron oxide, carbon, and water, a chemical feedstock is available for organic reactions to occur anywhere in the nebula, provided there is a heat source. Organic reactions distal from the protosun could have occurred, and the products would not have undergone photochemical UV degradation.

Furthermore, our hypothesis couples the formation of FeO-poor olivines in type-I chondrules from more FeO-rich olivines with the synthesis of organics. Meteoritic organic materials are enriched in ^{17/18}O [14]. This could have two different implications to the oxygen isotope anomalies found in meteorites. First, the reaction series described above, which recycles C back into the chondrules after interacting with the ambient nebular gas, produces ^{17/18}O enrichment in the chondrules. Alternatively, the enrichment of ^{17/18}O in organics could have resulted from a mass-dependent fractionation of oxygen from the FeO reduction in the chondrule melt. We believe the latter to be the case. The partitioning of heavy isotopes to the organics could mean that the lighter oxygen-16 isotope remain with the chondrule. We predict that melt-grown forsterites will be relatively ¹⁶O-enriched, as compared to dusty olivines within the same chondrule. One caveat to this prediction, however, is that chondrules have been recycled and this may blur isotopic and petrographic signatures of the prediction.

Chondrules synthesized in the same microenvironment are likely to be found within the same chondrite, and should have relatively similar isotope anomalies, although their size will play a significant role in determining the oxygen isotope compositions if mass dependent fractionation occurred within them and C was the reducing agent of the reactions. We thus infer that type-I chondrules showing ¹⁶O enrichments will be larger than those that do not.

References: [1] Laurette et al., 2006 *MESS II*; [2] Connolly, H. C. and Desch, S. J. (2004) *Chemie der Erde*, 64, 95-125. [3] Connolly et al., 2006, *MESS II*; [4] Zanda B. et al. (1994) *Science* 265, 1846-1849. [5] Connolly et al., 1994, *Science*; [6] Jones & Scott, 1988, *Proc. LPSC*; [7] Jones, 1990, *GCA*; [8] Connolly et al., 2001, *GCA*; [9] Kress, M. E. et al., 2001, *MPS*, 36, 75-91. [10] Cho, Y.-G., et al. (2008) *Bull. Kor. Chem. Soc.*, 29, 1609-1612. [11] Bernard-Salas, J., et al. (2006) *Astrophys. J.*, 652, L29-L32. [12] Storch, H. H., et al. (1933) *Ind. Eng. Chem.* 25, 768-771. [13] Sephton, M. A. (2002) *Nat. Prod. Rep.* 19, 292-311. [14] Hashizume, K. et al., (2011) *Nature Geo.* 4, 165-168. Supported by NASA grant # Grant NNX10AG46G (HCCJr, PI).