

A condensation model for the formation of chondrules in enstatite chondrites

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Abstract—It is proposed that the chondrules in enstatite chondrites formed near the Sun from rain-like supercooled liquid silicate droplets and condensed Fe-Ni alloys in thermodynamic equilibrium with a slowly cooling nebula. FeO formed and dissolved in the droplets in an initial stage when the nucleation of iron was blocked, and was later mostly reduced to unalloyed Fe. At high temperatures, the silicate droplets contained high concentrations of the less volatile components CaO and Al₂O₃. At somewhat lower temperatures the equilibrium MgO content of the droplets was relatively high. As cooling progressed, some droplets gravitated toward the Sun, and moved in other directions, depleting the region in CaO, Al₂O₃, and MgO and accounting for the relatively low observed CaO/SiO₂, Al₂O₃/SiO₂, and MgO/SiO₂ ratios in enstatite chondrites. At approximately 1400 K, the remaining supercooled silicate droplets crystallized to form MgSiO₃ (enstatite) with small amounts of olivine and a high-SiO₂ liquid phase which became the mesostases. The high enstatite content is the result of the supercooled chondrules crystallizing at a relatively low temperature and relatively high total pressure. Finally, FeS formed at temperatures below 680 K by reaction of the condensed Fe with H₂S. All calculations were performed with the evaluated optimized thermodynamic databases of the FactSage thermodynamic computer system. The thermodynamic properties of compounds and solutions in these databases were optimized completely independently of any meteoritic data. Agreement of the model with observed bulk and phase compositions of enstatite chondrules is very good and is generally within experimental error limits for all components and phases.

INTRODUCTION

It is generally agreed that chondrules originated in the early solar nebula. Their spherical or ellipsoidal shapes, smooth surfaces and dendritic textures, along with the presence of glassy mesostases, clearly indicate that chondrules formed by solidification from a liquid state. However, there is disagreement as to whether they formed by direct condensation as liquids from the nebula, or by melting of pre-existing solids during transient localized heating events. The former model of direct condensation was first proposed and promoted by Wood (1962, 1963), Blander and co-workers (Blander and Katz [1967], Blander and Abdel-Gawad [1969]), Wood and McSween (1977), Blander (1983) and Blander et al. (2001), while the latter model was advanced by Cameron (1966), Whipple (1966), Larimer (1967), Larimer and Anders (1967), and Gooding et al. (1980). It is the model of melting of pre-existing dust aggregates which is favored by the majority of researchers in the field today.

In order to explain the melting of pre-existing solid aggregates, a heat source for the melting is required. There is still no consensus on the nature of such a heat source, as recently summarized by Engler et al. (2007). Several heating mechanisms have been suggested, such as lightning (electrical discharge heating) in a turbulent or stratified nebula (e.g., Cameron 1966; Whipple 1966; Rasmussen and Wasson 1982; Wasson 1992; Phillip et al. 1998; Desch and Cuzzi 2000) or frictional heating of dust clumps falling into the nebular mid-plane (Wood 1983, 1984) as well as nebular flares (Sonett 1979; Levy and Araki 1989). More recently, FU Orionis outbursts or gamma-ray bursts, bipolar outflows, and especially nebular shock waves (Liffman and Brown 1996; Weidenschilling et al. 1998; McBreen and Hanlon 1999; Desch and Connolly 2002; Ciesla and Hood 2002, 2003) are the most popular proposed heating mechanisms for chondrule formation (Boss 1996). In the X-wind model of Shu et al. (1996, 2001), chondrules are melted near the proto-Sun by radiation related to flares. Additional models suggest that chondrules were formed in interstellar space (Skinner 1990;

Cameron 1995). However, there is no firm evidence for any of these mechanisms as the source of the putative melting. Furthermore, no simple convincing unified hypothesis has been advanced to explain how precursor dust aggregates were formed of sufficient size and of sufficient chemical diversity to account for the observed wide chemical diversity of chondrules. The model of chondrule formation by melting of precursor dust aggregates remains speculative.

The model of direct condensation of liquids from the solar nebula is currently in disfavor mainly for the following reasons. First, liquids are thermodynamically stable in a gas of solar composition only over very restricted ranges of temperature and pressure. Equilibrium thermodynamic calculations frequently predict condensation of solids directly from the gas, with no intermediate liquid state and, in any case, whether or not an equilibrium intermediate liquid state is predicted by the calculations, the elemental and mineralogical compositions of the final solidified chondrules, calculated assuming thermodynamic equilibrium, do not correspond well with observed chondrule compositions. Opponents of the model further claim that the observed wide diversity of elemental and mineralogical compositions of chondrules could not result from condensation from a homogeneous nebula. In order to overcome this problem, a dust-enriched solar nebular environment was proposed in recent works of Yoneda and Grossman (1995), Ebel and Grossman (2000), Alexander (2004), and Ebel (2005). They showed that in regions of high dust enrichment, or high total gas pressure, olivine-rich silicate liquids can exist as stable equilibrium phases. Ebel et al. (2003) also applied the same approach for pyroxene-rich liquid compositions, which become stable in Mg-depleted systems, although in a highly restricted pressure-temperature-composition field. Although liquid condensation based on the dust-enriched solar nebular hypothesis is theoretically possible, it still remains speculative and qualitative. Petaev and Wood (1998) proposed the condensation with partial isolation (CWPI) model. The model assumes that as condensation proceeds a specified fraction (called the isolation degree) of the existing condensate is steadily withdrawn from reactive contact with the residual nebular gas while the remaining condensates remain in equilibrium with the gas.

Yet another objection to the model of direct condensation of liquids is that the microstructure (texture) of chondrules clearly indicates very rapid cooling, with temperature decreasing by several hundreds of degrees over a period of seconds or minutes. This is inconsistent with a model of liquid droplets slowly cooling and eventually solidifying at equilibrium. Yet another objection is the presence, in some chondrules, of small “relict” grains with chemical and isotopic properties different from the chondrules.

We believe that we can counter these objections to a direct condensation model using the Constrained Equilibrium Theory of Blander and Katz (1967). This model postulates two nucleation constraints. The first constraint is the blocking

of Fe and other gaseous metal atoms from condensing to form solid or liquid metallic phases because of the very high surface free energies of solid and liquid metals. Thermodynamically, if Fe metal were to condense, the chondrules at thermodynamic equilibrium would contain virtually no FeO because of the very reducing nature of the solar nebula, whereas the observed FeO content of the chondrules is not negligible. The second constraint is the blocking of the solidification of solid oxides with the resultant formation of metastable supercooled liquid oxide droplets several hundred degrees below their liquidus temperatures, as is consistent with laboratory experiments in which supercooling of 400 K or more occurs (Blander et al. 2004) as well as with the microgravity experiments of Nagashima et al. (2002, 2003, 2003b, 2005) and Tsukamoto et al. (2001), who observed undercooling of liquid forsterite and enstatite droplets of 400–500 K. This evidence shows that equilibrium between metastable supercooled liquid and the solar nebula could have occurred over a wide temperature range, and thus counters the aforementioned objection to the model of direct condensation of liquids from the solar nebula.

In the present model, we assume that the supercooled liquid droplets were in thermodynamic equilibrium with the nebula. As the nebula cooled, the compositions of the supercooled oxide droplets changed. At higher temperatures, they were richer in the less volatile oxides such as CaO and Al_2O_3 . As the temperature of the nebula decreased over time, the droplets became richer in more volatile components such as MgO and SiO_2 and, at even lower temperatures, in FeO. As the cooling progressed, some of these droplets gravitated towards the Sun, and moved in other directions, thereby depleting the region in CaO, Al_2O_3 and MgO and accounting for the relatively low observed CaO/ SiO_2 , Al_2O_3 / SiO_2 and MgO/ SiO_2 ratios in enstatite chondrites. As the nebula cooled, the undercooled droplets solidified stochastically, those solidifying at higher temperatures becoming CaO- and Al_2O_3 -rich chondrules, those solidifying at lower temperatures producing chondrules richer in MgO and SiO_2 , and those solidifying at even lower temperatures forming chondrules with high FeO contents. In this way, the model provides an alternative mechanism for the wide range of observed chondrule compositions. This counters the second aforementioned objection that direct condensation from a homogeneous nebula cannot explain the observed wide diversity of elemental and mineralogical compositions of chondrules.

As will be shown by the calculations, our model can account quantitatively not only for the observed bulk compositions of chondrules, but also for the compositions of the individual phases, including the glassy or very finely crystalline mesostases.

When a supercooled droplet solidifies, it does so very rapidly, thereby accounting for the observation that the microstructures of chondrules are consistent with rapid solidification and countering the third aforementioned

objection. This rapid exothermic crystallization resulted in an initial rapid temperature rise of 100–400 degrees over a period of a few seconds, followed by a slightly less rapid decrease in temperature. The crystallization thus occurred over a range of temperatures, resulting in composition gradients in the chondrule. Such very rapid crystallization of highly undercooled enstatite droplets was observed in the microgravity experiments of Nagashima et al. (2002, 2003) who also observed that this gave rise to the formation of the typical radial pyroxene and barred olivine morphology. Recent studies of Varela et al. (2005, 2006) show that the assumption of supercooled liquid droplet in equilibrium with solar nebular can explain the origin of barred olivine and porphyritic olivine textures based on the experimental evidence. Thus, the objection regarding the microstructure (texture) of the chondrules can be well countered in the model.

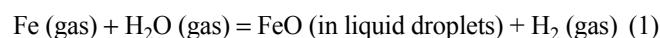
The crystallization of the droplets would frequently have been initiated by collision with small relict dust particles which acted as nucleation sites. Due to the speed of the exothermic solidification, the relict particles would most likely have melted only partially, retaining their original compositions to a large extent, as also observed in the microgravity experiments of Tsukamoto et al. (2001). Hence the presence of relict grains is not inconsistent with the present model. Note that collisions with relict particles is not the only mechanism for initiating nucleation which can also occur homogeneously at high degrees of undercooling or by shock.

The present model is not inconsistent with the observation of rims on chondrules. Although the bulk of the crystalline phases of a chondrule would no longer react with the nebula once solidification had occurred, its surface would continue to be modified through interactions with its surroundings.

In their recent study, Engler et al. (2007) also provide experimental evidence in support of a model of direct condensation. Major elemental and trace elemental analysis resulted in unfractionated (solar-like) ratios of $\text{CaO}/\text{Al}_2\text{O}_3$, Yb/Ce and Sc/Yb , and mostly unfractionated refractory lithophile trace element abundance patterns in several pyroxene and pyroxene/olivine micro-objects in a number of different unequilibrated ordinary chondrites. The authors show that these results support a direct condensation model.

With our development in recent years of large accurate evaluated optimized thermodynamic databases for oxide compounds and solutions (Pelton et al. 2008), it has become possible to test the Constrained Equilibrium model quantitatively. In a recent publication (Blander et al. 2004) we successfully applied the theory to calculate quantitatively the compositions of chondrules of types IA, IAB, IB, IIA, IIB, and CC (cryptocrystalline) in the LL3.0 ordinary Semarkona chondrite. It was postulated that each type of chondrule was formed by the rapid crystallization of supercooled liquid oxide droplets, in equilibrium with the gaseous nebula, but at different temperatures, with the IA chondrules crystallizing at

the highest temperatures and the CC chondrules at the lowest. Since the nucleation of metallic Fe was blocked, the partial pressure of Fe in the gas was much higher than it would be if Fe were condensed. This drove the following reaction to the right:



thereby resulting in much higher FeO contents in the oxide droplets than would have been the case if metallic Fe had condensed. The FeO content of the supercooled droplets increased with decreasing temperature, and became frozen in when the droplets crystallized. Hence, from the observed FeO contents of each type of chondrule, the temperature at which they crystallized could be calculated, and this in turn permitted the calculation of their elemental and mineralogical (phase) compositions, in very good quantitative agreement with the observed elemental and mineralogical compositions of all the chondrule types.

The model showed that the compositions of the CC chondrules can be explained by their being the last to crystallize at the lowest temperatures, as is also consistent with their fine cryptocrystalline texture and large fraction of mesostases. This correlation between composition and texture supports the model.

In this paper, we show that the same direct condensation model with the Constrained Equilibrium Theory can be applied to explain the formation of the chondrules observed in enstatite chondrites as well as those in ordinary chondrites, by assuming that the enstatite chondrites formed closer to the proto-Sun where the gas pressure was higher. Very recent reports (McClintock et al. 2008; Solomon et al. 2008) on the Messenger Mercury flyby, show that Mercury has a large metallic iron-rich core, being over 60% Fe by weight. In contrast, the average ferrous ion abundance of Mercury's surface materials, and by inference its crust and mantle, is less than 2 or 3 wt%, which is significantly lower than that of the other inner planets. That is to say, the composition of Mercury is similar to that of E-chondrites. This is consistent with a model of E-chondrites forming close to the Sun (and later coalescing to form Mercury).

In future work we shall show that the same unified concepts can also be applied to explain the formation of carbonaceous chondrites, including the formation of CAIs, ARCs, etc., if it is assumed that they formed further from the proto-Sun where the pressure was lower.

BASIC POSTULATES OF THE MODEL AS APPLIED TO ENSTATITE CHONDRULES INCLUDING THE TRANSITION FROM FeO-FORMATION TO METAL FORMATION

In extending the theory to the formation of enstatite chondrules, we note that enstatite chondrules are characterized by large amounts of metallic Fe and FeS. That is, the nucleation and condensation of metallic Fe occurred at

some stage during their formation, unlike the case for Semarkona. Consequently, the FeO content of the oxide phases is much lower in the enstatite chondrules, thereby resulting in the stabilization of enstatite (pyroxene) relative to olivine (since FeO preferentially dissolves in olivine and stabilizes the olivine phase). Although the observation that the enstatite chondrules consist mainly of enstatite, MgSiO_3 , with small amounts of olivine (mainly Mg_2SiO_4) is due primarily to their relatively low MgO/SiO_2 ratios compared to other chondrules, our thermodynamic calculations show that a low MgO/SiO_2 ratio alone is insufficient to stabilize enstatite relative to olivine unless the FeO content is also very low.

The fact that metallic Fe condensed during the formation of enstatite chondrules indicates that these chondrules were formed at higher pressures than Semarkona since higher pressure favors condensation thermodynamically. An increase in total gas pressure by a factor of ten increases the dew point of Fe by approximately 300 K. Consequently, the temperature at which Fe-Ni alloy first condenses from a supersaturated gas is also increased by approximately 300 K when the total pressure is increased by a factor of approximately ten. Furthermore, because temperatures are higher than those in Semarkona, the kinetic barrier to forming metal is much lower, and it requires much less chemical potential driving force to form Fe-Ni alloyed metal. This leads to a transition from the formation of FeO in the early high temperature stages of formation of enstatite chondrules to the formation of Fe-Ni alloys in the later lower temperature stages. Our calculations for Semarkona (Blander et al. 2004) showed that the observed compositions are consistent with formation in a region of the nebula where the total pressure was approximately 0.001 to 0.1 bar. We are thus led to postulate that enstatite chondrites formed in a region where the total pressure was of the order of 0.01 to 1.0 bar. That is, enstatite chondrites most probably formed very close to the Sun, closer than most other types of chondrites. As will be shown, our model is consistent with the formation of enstatite chondrules at pressures greater than about 0.01 bar. For purposes of calculation, we have assumed a pressure of 1.0 bar.

If the enstatite chondrules formed at equilibrium with condensed Fe in the reducing atmosphere of the solar nebula, their calculated FeO content would be approximately 0.1 wt%, whereas the measurements of Schneider et al. (2002) show an average FeO content of 0.85 wt% in EH chondrites and 0.75 wt% in EL chondrites, in accordance with our postulate that the nucleation and condensation of metallic Fe was initially blocked. The average temperature at which metallic Fe first nucleated and condensed might then be calculated as the temperature at which the FeO content of the chondrules in equilibrium with the nebula was 0.85 or 0.75%. However, it would be expected that during subsequent cooling, some of the FeO in the oxide droplets would be reduced to Fe in the reducing atmosphere of the nebula. This

is supported by the observation (Schneider et al. 2002) of fine Fe particles distributed within the silicates and attributed to *in situ* reduction of dissolved FeO. This reduction began when the Fe nucleation barrier was broken, continued as the chondrules subsequently cooled, and was still incomplete when the chondrules solidified. Hence, at the time when the FeO nucleation barrier was broken, the FeO content of the droplets was higher than 0.85 or 0.75 wt%. A rough estimate of how much of the total metallic Fe content is due to FeO reduction can be made as follows. Because the reduced Fe is very fine grained, it may have been missed in the early microphase measurements of total Fe from modal and mineral composition (Keil 1968) and would only be detected in the measurements of total Fe content by overall chemical analysis. Recently, Zhang et al. (1995) also performed modal analyses of enstatite chondrules; their results agree well with the data of Keil (1968). Hence, the amount of Fe from FeO reduction can be deduced from the difference between these two measurements. In this way we calculate the loss of FeO by reduction to be an average of 7.85 wt% in EH chondrules and 1.03 wt% in EL chondrules. Adding these values to the observed average residual FeO content of the chondrules (0.85 and 0.75 wt% respectively), we calculate that the average FeO content of the oxide droplets at the time and temperature when the Fe nucleation barrier was broken was 8.70 wt% in the case of EH chondrules and 1.78 wt% in the case of EL chondrules. From these FeO contents, in turn, the average temperature of first nucleation of Fe can be calculated for a given assumed total pressure. As will be shown in a later section, this temperature is approximately 1582 K in the case of EL chondrules and 1510 K in the case of EH chondrules when the pressure is 1.0 bar. However, these are clearly only rough estimates.

Our calculations and observations explain the observations by Weisberg et al. (1994) in which the environment leads to a relatively high FeO content in the precursor droplets, stage 1. Stage 2 is a transition when Fe-Ni alloys precipitate directly from the nebula and FeO is reduced to unalloyed Fe. In our work, this is not a change in oxidation but a change from forming supersaturated iron which leads to metastable FeO to a condensation of Fe-Ni rich alloys and a reduction of a large fraction of the FeO to unalloyed iron.

Transition in a CB Carbonaceous Chondrite from FeO to Metallic Fe

As an aside, it may be noted that the fact that formation of metallic iron is thermodynamically favored by high pressures and kinetically favored by high temperatures can also be invoked to explain the observed high metallic contents of the two CB chondrites Queen Alexandra Range (QUE) 9411 (Meibom et al. 2005) for which a relatively large amount of data are available. Most carbonaceous chondrites contain very low contents of metallic iron. However, in the

case of the CB chondrites QUE 9411 there was a shock stage which flattened the chondrule crystals (Bischoff and Stöffler 1992; Rubin et al. 2003) and which raised the temperature and pressure of the gas which moved with the condensed materials, which probably re-melted to a large extent. The shock effects could be similar to a powerful wind or explosive shock. Before the compression, FeO formed according to Equation 1. As the pressure and temperature increased, the barrier to nucleation was lifted as discussed in the previous section. Fe-Ni alloy then condensed from the nebula, while at the same time some of the FeO in the remelted silicate was reduced back to Fe metal, nucleating on the Fe-Ni alloy. The driving force for condensation of metal and for reduction of Fe was stronger than in the case of enstatite chondrites. The CB chondrites QUE 9411 have very high contents of Fe-Ni metal at 65–80 volume % (Meibom et al. 2005). The average composition of the Fe particles is 82.4% Fe, 2.12% S, 5.89% Ni, 0.31% Co, 0.17% Cr, and 0.16% P. Some of the silicate regions (unknown total amount), which probably crystallized before the transformation and remained as a solid, contain an average of 34.1% FeO. Because these regions did not remelt, the FeO was not reduced because of the relatively slow kinetics of gas/solid reactions. There were also relict silicate grains, which contained 3.48% FeO, which might be mesostases which contained enough liquids to transport out some of the FeO. These are probably regions which did not remelt during the shock phase. Some of the silicate grains might also be relict dust.

OBSERVED ENSTATITE CHONDRULE COMPOSITIONS

Overall compositions (including oxide, metallic, and sulfide phases) of three of the four enstatite chondrites analyzed by Jarosewich (1990) are listed in Table 1. The composition of the fourth, the Happy Canyon chondrite, appears to be anomalous and was not considered. The small amounts of K_2O , P_2O_5 , H_2O , Co, and C reported by Jarosewich were not included in Table 1, and the compositions shown were renormalized to sum to 100%. Analyses of 59 chondrules in six enstatite chondrites were performed by Schneider et al. (2002). The reported bulk compositions of the oxide phases are reported in Table 2A as the renormalized average contents of each component (averaged over 59 chondrules) as well as the maximum and minimum reported values (highest and lowest of the 59 chondrules). It can be seen that there are significant variations among the reported compositions of the different chondrules. As well, for any given chondrule Schneider et al. (2002) report quite large error limits for the major components of the order of ± 5 wt%, while compositions of minor components are generally reported as $x \pm x\%$. Compositions of the enstatite, olivine, and mesostases constituents of the chondrules were also measured by Schneider et al. Their

results are shown in Tables 2B, 2C, and 2D. The chondrules were observed to consist mainly of enstatite with small amounts of mesostases and olivine. Our calculations in these tables are much closer to the data of Schneider et al. than to those of Jarosewich, probably because Schneider et al. examined Type 3 chondrules which are relatively pristine.

The observed weight ratios MgO/SiO_2 , CaO/SiO_2 , and Al_2O_3/SiO_2 are also shown in Tables 1 and 2. Agreement between the results of Jarosewich (Table 1) and Schneider et al. (Table 2A) is good for the Al_2O_3/SiO_2 ratio, while the CaO/SiO_2 and MgO/SiO_2 ratios reported by Schneider et al., are respectively somewhat lower and somewhat higher than those of Jarosewich. However, all three ratios as reported by either author are significantly lower than those calculated under the assumption that all the Mg, Ca, Si, and Al in the solar nebula of solar composition (Table 3) precipitated and was incorporated in the chondrules. Were this the case, it can be calculated from Table 3 that the weight ratios would be $MgO/SiO_2 = 0.72$, $CaO/SiO_2 = 0.057$, and $Al_2O_3/SiO_2 = 0.072$ (Note that in stoichiometric enstatite, $MgSiO_3$, the weight ratio is $MgO/SiO_2 = 0.671$). By contrast, the observed values of all three ratios in ordinary chondrites like Semarkona (averaged over all types of chondrules) appear to be close to (although still somewhat lower than) those calculated from the expected solar composition (Blander et al. 2004).

Since virtually all the Mg, Si, Ca, and Al must eventually condense as the nebula cools, there must have been a process by which some of the condensed material was removed from the region at various stages of the formation of the chondrules as will be explained in detail in a later section.

THE “FACT” THERMODYNAMIC COMPUTER DATABASES

The calculations require accurate databases of the thermodynamic properties of multicomponent solutions (most importantly, of solid and liquid oxide solutions) as functions of temperature and compositions.

All thermodynamic calculations were performed with the FactSage thermodynamic computer system of which one of the present authors is a principal developer (Pelton et al. 2008), coupled with the large evaluated FACT databases which contain data for over 5000 pure substances and hundreds of multicomponent solutions (Pelton et al. 2008). FactSage consists of a suite of programs that use these data to perform chemical equilibrium calculations by means of a general Gibbs energy minimization algorithm (Eriksson 1975). The FACT solution databases give the thermodynamic properties (chemical potentials) as functions of temperature and composition for liquid and solid multicomponent solutions of oxides (including silicates), salts, sulfides, metals, etc.

These solution databases are prepared by first developing an appropriate mathematical model, based upon the structure

Table 1. Overall composition of enstatite chondrites (weight %).

Oxide phases										Metallic phases				Sulfide		Weight ratios		
SiO ₂	⁶⁶ TiO ₂ ^{****}	Al ₂ O ₃	⁵⁴ Cr ₂ O ₃ ^{****}	MnO	MgO	CaO	Na ₂ O	FeO	NiO	Fe	Ni	Cr	Si	Mn	FeS	$\frac{\text{MgO}}{\text{SiO}_2}$	$\frac{\text{CaO}}{\text{SiO}_2}$	$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$
Measured*																		
(Jarosewich 1990)																		
Eagle	43.46	0.10	2.12	0.32	0.28	24.07	0.76	0.84	—	18.48	1.39	—	—	—	8.16	0.55	0.017	0.049
ALMA 77295	37.19	0.11	1.86	0.42	0.28	19.10	1.31	0.81	—	22.95	1.91	—	—	—	14.05	0.51	0.035	0.050
Phillister	40.92	—	2.23	0.22	<0.02	21.51	0.64	0.82	—	22.65	1.73	—	—	—	9.27	0.53	0.016	0.055
Calculated	33.4	0.06	1.4	0.01	0.5	22.5	1.1	0.74	0.03	10 ⁻⁶	27.7	2.0	0.5	0.1	10.00****	0.67	0.034	0.043
from model																		

* Renormalized to 100% ignoring K₂O, H₂O, P₂O₅, Co and C.** TiO₂ + Ti₂O₃ recalculated as TiO₂.*** CrO + Cr₂O₃ recalculated as Cr₂O₃.

**** Amount of sulfide chosen arbitrarily to reproduce observed FeS contents.

Table 2. Measured (Schneider et al. 2002) and calculated compositions of oxide phases in enstatite chondrules (weight %).

Oxide phases													Metallic phases				Sulfide		Weight ratios		
SiO ₂	⁴⁸ TiO ₂ ^{***}	Al ₂ O ₃	⁵⁴ Cr ₂ O ₃ ^{****}	MnO	MgO	CaO	Na ₂ O	FeO	$\frac{\text{MgO}}{\text{SiO}_2}$	$\frac{\text{CaO}}{\text{SiO}_2}$	$\frac{\text{Al}_2\text{O}_3}{\text{SiO}_2}$										
A—Bulk composition																					
Measured :																					
Min.	51	~0	0.09	0.01	29	0.2	0.3	0.7	0.57	0.0039	0.0137										
Max.	60	0.12	0.7	0.20	40	2	2	5	0.67	0.0333	0.100										
Average***	56.6	0.1	0.3	0.10	35.8	0.8	0.9	2.3	0.63	0.0142	0.055										
Calculated :																					
	55.8	0.10	0.02	0.9	37.6	1.9	1.2	0.05	0.67	0.034	0.043										
B—Composition of protopyroxene phase																					
Measured :																					
Min.	55	0	0	0	35	0	0	0.2													
Max.	61	0.14	0.62	0.19	40.3	2	0.3	7													
Average***	59.2	0.03	0.2	0.08	38.7	0.4	0.03	0.9													
Calculated :																					
	59.4	0.02			39.5	0.42		~0													
C—Composition of olivine phase																					
Measured :																					
Min.	42.7	0	0	0	55	0	0	0.04													
Max.	44	0	0.33	0.15	57.6	0.46	0	0.51													
Average***	42.8	0	0.17	0.09	56.3	0.26	0	0.32													
Calculated :																					
	42.1			2.9	54.6	0.20		0.18													
D—Composition of mesostases																					
Measured :																					
Min.	60	0	0	0	0.06	0.15	0.11	0.08													
Max.	76	0.13	0.15	0.13	9	10	9.5	2.2													
Average***	68.2	0.3	0.07	0.01	3.1	2.6	3.4	0.44													
Calculated :																					
	65.45	0.62	0.09	0.82	2.5	10.1	7.4	0.02													

Calculated masses of protopyroxene phase, olivine phase and mesostases are respectively, 58%, 26%, and 16% of the total mass of the chondrules.

* TiO₂ + Ti₂O₃ recalculated as TiO₂.** CrO + Cr₂O₃ recalculated as Cr₂O₃.

*** Renormalized.

Table 3. Nebular gas composition (moles per mole of Si) (Anders and Grevesse 1989).

Element	Composition	Element	Composition
H	27900	Ca	0.0611
C	10.1	Al	0.0849
O	23.8	Mg	1.074
Si	1.00	Cr	0.0135
S	0.515	Mn	0.00955
Fe	0.90	Ti	0.0024
Na	0.0574	Ni	0.0501

of the solution, giving the thermodynamic properties as functions of composition and temperature. Next, all available thermodynamic and phase diagram data from the literature are simultaneously “optimized” to obtain one set of critically evaluated self consistent parameters of the model for all phases in 2 component, 3 component, and, if available, higher order sub systems. Finally, the models are used to estimate the thermodynamic properties of N component solutions from the database of parameters for lower order sub systems.

It must be stressed that the FACT databases were all developed and optimized completely independently of the present work. That is, no thermodynamic properties were adjusted in order to fit the meteoritic data.

For molten oxide solutions, we used the modified quasi chemical model for short range ordering, which was developed by the present authors (Blander and Pelton 1983, 1984, 1987; Pelton and Blander 1984, 1986; Pelton and Chartrand 2001). The olivine and pyroxene solutions are described using a model (Degterov et al. 2001) based on the compound energy formalism (Hillert et al. 1988), which correctly takes account of the distribution of the cations among the various sites in the crystal structure. Other ceramic solid solutions, such as spinels and melilites, are modeled similarly. For all these models, the references cited above describe how the lower-order parameters are combined to estimate the thermodynamic properties of higher-order systems. A database for molten and solid phases in the Fe-Ni-Co-Cr-S system has been developed using the modified quasi chemical model, which is applicable for all compositions from pure metal to pure sulfide.

All data of all types (phase diagrams as functions of T, composition and oxygen potential, activity measurements, calorimetric data, cation distribution data, etc.) from hundreds of original references have simultaneously been taken into account in developing the optimized FACT databases for oxide systems over the past 25 years (Eriksson and Pelton 1993; Eriksson et al. 1998a, 1993b, 1994; Wu et al. 1993a, 1993b; Degterov and Pelton 1996a, 1996b, 1997; Chartrand and Pelton 1999; Degterov et al. 2001, 2002; Jung et al. 2004a, 2004b, 2004c, 2004d, 2005; Kang et al. 2004a, 2004b). With the present databases in particular, all available data of all types are reproduced within experimental error limits for the $\text{SiO}_2\text{-MgO-FeO-Fe}_2\text{O}_3\text{-CaO-}$

$\text{Al}_2\text{O}_3\text{-(TiO}_2\text{-Ti}_2\text{O}_3\text{-CrO-Cr}_2\text{O}_3\text{-MnO-Na}_2\text{O-S)}$ system, where the components in parentheses are minor constituents. Furthermore, the models permit good estimations to be made in ranges of temperature, composition, and oxygen potential where data have not been measured. Many more components, such as CoO , B_2O_3 , ZnO , and PbO , are included in the FACT databases for oxides. Those listed here are only those relevant to the present article.

For the gas phase (solar nebula), ideal gas behavior has been assumed with data taken from the FACT databases for over 150 possible gaseous species, such as H_2 , H_2O , CO , Fe , H , H_2S , SiO , Na , Mg , SiS , Mn , HS , Cr , CO_2 , CH_4 , FeS , and AlOH .

THE DETAILED MODEL

From their spherical shapes, it is generally accepted that chondrules formed from liquid droplets, while their morphologies indicate that the crystallization was rapid. Rather than postulate that liquid droplets were produced by re-melting during energetic events, it is simpler to assume that the chondrules were formed by solidification of supercooled liquid rain-like droplets in equilibrium with the solar nebula. Our experimental studies (Blander et al. 2004) with levitated droplets have shown that liquid silicate droplets can exist at temperatures more than 400 K (with some close to 600 K) below their liquidus temperatures (which are in the range from 1800 to 2000 K). Nagashima et al. (2002, 2003, 2003b, 2005) and Tsukamoto et al. (2001) also observed undercooling of liquid forsterite and enstatite droplets of 400–500 K in microgravity experiments. This is the essence of the Constrained Equilibrium Theory (Blander and Katz 1967; Blander et al. 2001).

Figure 1 shows the calculated composition of supercooled liquid silicate droplets in equilibrium with a gas initially of the solar composition (Table 3) at a total pressure of 1.0 bar. At high temperatures the droplets can be seen to consist mainly of the less volatile components Al_2O_3 and CaO . At lower temperatures, the more volatile components MgO and SiO_2 predominate. The total calculated relative mass of the droplets at equilibrium is also shown on Fig. 1. Below about 1550 K the mass and composition of the droplets are nearly constant, since below this temperature virtually all the Mg, Si, Ca and Al in the nebula has condensed and is present in the droplets.

For other assumed total pressures over the range from $\sim 10^{-4}$ to ~ 10 bar, curves can be calculated which are virtually identical to those in Fig. 1, except that all the curves are displaced to the right or the left by about 50 degrees per order of magnitude change in pressure. For example, at $P = 0.1$ bar, the curves are all nearly equally displaced about 50 degrees to the left of their positions in Fig. 1. That is, even if we assumed that the total pressure was 0.1 or 0.01 bar, virtually the same calculated results can be obtained by simply shifting all

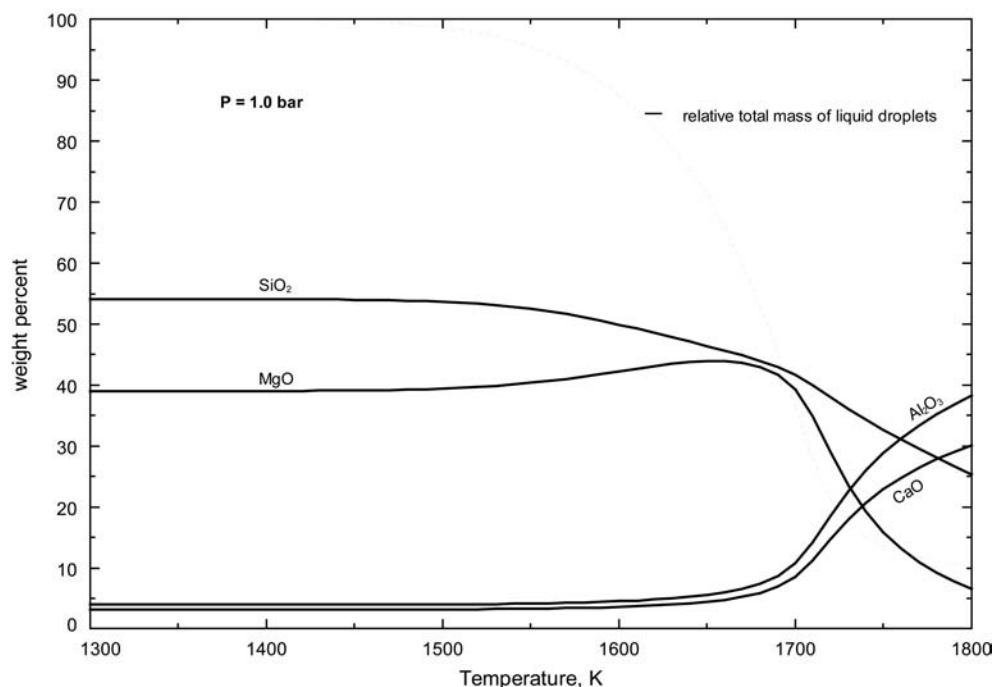


Fig. 1. Composition of supercooled liquid droplets in equilibrium with the solar nebula (and with metallic Fe if present at equilibrium) at $P = 1.0$ bar.

temperatures by 50 or 100 degrees lower than the calculated results at 1 bar.

The calculations also show that, at thermodynamic equilibrium, in addition to the supercooled liquid droplets, metallic Fe precipitates from the nebula as an Fe-Ni alloy. In the reducing atmosphere of the nebula, iron condenses as a metal rather than as FeO; the calculated concentration of FeO dissolved in the silicate droplets at thermodynamic equilibrium is less than 0.1 wt%. However, if the nucleation of metallic Fe is blocked, the FeO content of the droplets is significantly larger.

As mentioned above, at temperatures below about 1450 K essentially all the Mg, Ca, Al, and Si in the nebula has essentially condensed into the droplets. Therefore, chondrules formed by solidification of these droplets would have MgO/SiO₂, CaO/SiO₂, and Al₂O₃/SiO₂ ratios calculable from the solar nebula composition (0.72, 0.057, and 0.072, respectively) which, as discussed above, are higher than the observed ratios. We are thus led to propose the model shown schematically in Fig. 2 and described as follows.

We propose that enstatite chondrites were formed in a region of the solar nebula near the Sun, where the pressure was relatively high. We have assumed a pressure of 1.0 bar for calculations. We propose that the nebula cooled gradually from an initial temperature of the order of 1900 K or higher. This cooling may have occurred by radiation or because of the adiabatic expansion which would be expected to occur at a late stage during the formation of the Sun.

The cooling nebula was at thermodynamic equilibrium

with a "cloud" of liquid silicate droplets and, at lower temperatures, condensed iron droplets, whose quantity and composition changed as the temperature decreased. As time progressed some of these were moved in many directions because of the complex interactions of the Sun and other forces (Cassen 1994) so that some droplets left their birthplace, falling towards the Sun and moving in other directions as well. Although this process occurred continuously as the temperature decreased, for the sake of calculational simplicity we have modeled it as taking place in three isolated "events" at 1780, 1650, and 1507 K as shown in Fig. 2. If we assume that the initial temperature is about 1900 K, then the three removal "events" occur at intervals of approximately 130°, with approximately 30 to 50% of the droplets being removed at each "event." That is, about 0.3% of the droplets are removed from the region for each degree of cooling. Although removal events can continue below 1507 K, by this point the precipitation from the gas is essentially complete. Hence, such removals will no longer have any effect on the chemistry of the chondrules.

The first removal event is assumed to occur at 1780 K. We first assume that 30% of the silicate droplets present at 1780 K were removed from the region. This corresponds to 4.2 g of silicate droplets being removed per 100 g of enstatite chondrules which finally formed. As can be seen from Fig. 1, these droplets had relatively high CaO and Al₂O₃ contents. Therefore, this process led to a reduction of the CaO/SiO₂ and Al₂O₃/SiO₂ ratios in the region.

At 1650 K, the second "event" is assumed to have

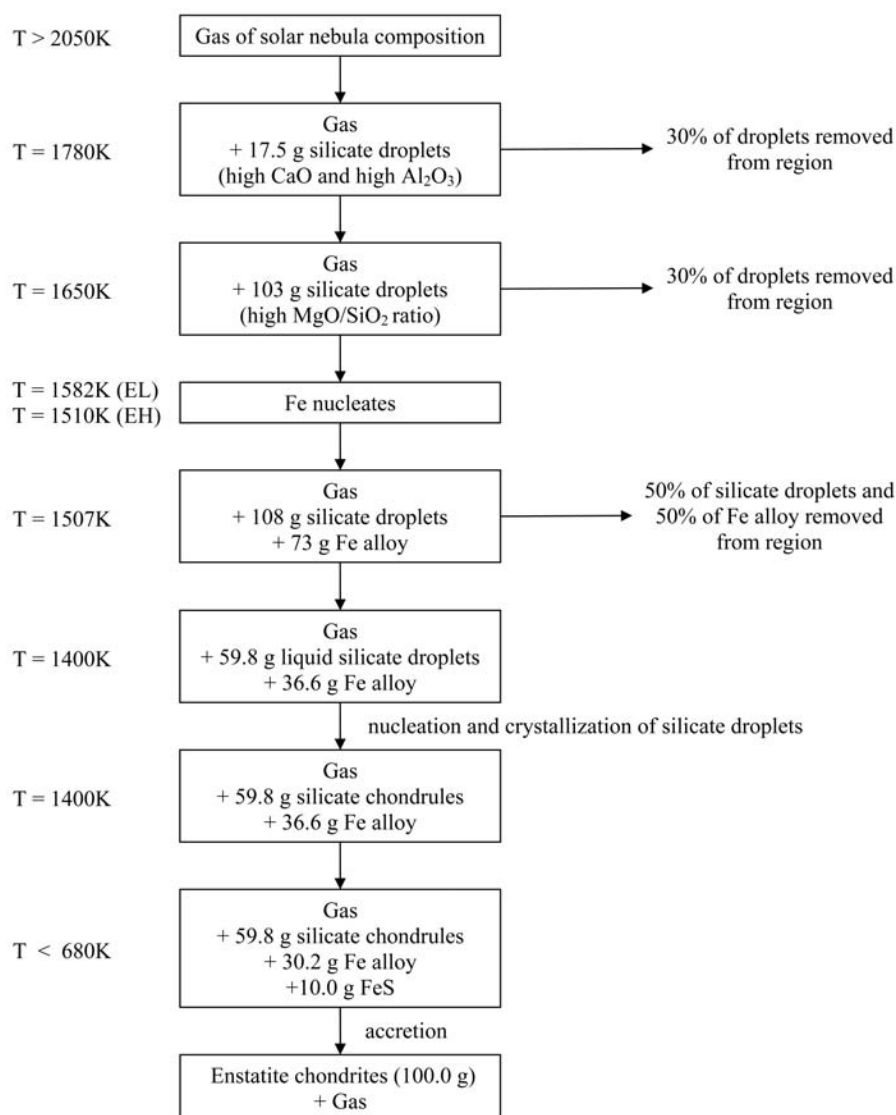


Fig. 2. Schematic of model of enstatite chondrule formation (per 100 g of final chondrules). $P = 1.0$ bar.

occurred, with 30% of the equilibrium condensed silicate droplets present being removed from the enstatite chondrite birth region. This corresponds to the removal of 31 g of silicate droplets per hundred g of final enstatite chondrules. As can be seen in Fig. 1, the MgO/SiO_2 ratio in the equilibrium droplets was equal to 0.9 at 1650 K, which is greater than the ratio in the nebula. Hence, the removal of these droplets led to a reduction of the MgO/SiO_2 ratio in the region.

As the temperature continued to decrease, iron began to nucleate and precipitate from the supersaturated nebula as a metallic phase. This process occurred continuously as the temperature decreased over a range from about 1600 K to 1500 K. However, again for the sake of computational simplicity, we have modeled it as occurring at 1582 K in the case of EL chondrules when, according the calculations, the FeO content of the silicate droplets was 1.78 wt%, and at 1510 K in the case of EH chondrules when the FeO content

was 8.7 wt%. As explained in a previous section, this accounts for the observed concentrations of unalloyed Fe and residual FeO in the chondrules.

Although we have proposed, for the sake of simplicity, that the nucleation of Fe in the case of EL and EH chondrules occurred at different temperatures at the same total pressure, it is probably more likely that the nucleation actually occurred at approximately the same temperatures in the two cases but at slightly different total pressures; this would account equally well for the different FeO contents of the EL and EH chondrules.

The third “event” is assumed to have occurred at 1507 K with 50% of the equilibrium condensed iron and silicate droplets present either being gravitated toward the Sun or being displaced in other directions. This corresponds to the removal of 54 g of silicate droplets and 36.5 g of Fe per hundred grams of final enstatite chondrules.

The temperature continued to decrease to ~1400 K. At this temperature, virtually all the remaining Ca, Al, Si, and Mg in the nebula had condensed and was present in the silicate droplets. Nucleation then occurred in the supercooled silicate droplets which solidified rapidly after nucleation (over a period of seconds) to produce solid enstatite chondrules of virtually the same overall composition as the droplets. Of course the solidification did not occur at a single temperature, but continuously over a temperature range around 1400 K as the nebula cooled. However, for simplicity we have modeled it as occurring as a single event at 1400 K. The calculated overall composition of the chondrites (including oxide, metallic, and sulfide phases) is shown in Table 1. The calculated bulk composition of the oxide phases is shown in Table 2A. This is also the composition of the equilibrium silicate droplets at 1400 K. The calculations show that after solidification, the chondrules consist of 58% by weight of protopyroxene (enstatite) which is mainly MgSiO_3 , 26% olivine (mainly Mg_2SiO_4) and 16% of a silica-rich liquid phase. The calculated compositions of these phases are shown in Tables 2B, 2C, and 2D. As the temperature decreased further, the liquid phase transformed to a glass and eventually crystallized partially to become mesostases.

As the temperature decreased further, FeS began to form only below 680 K by reaction of H_2S with the Fe-rich particles in the reducing atmosphere of the nebula. The amount of FeS present at equilibrium increased as the temperature decreased; however thermodynamic equilibrium would not be expected at such low temperatures. Hence, the amount of FeS shown in Table 1 was chosen arbitrarily so as to reproduce the observed FeS contents (Jarosewich 1990). Lauretta et al. (1997) observed the formation of sulfide in the laboratory by reaction of meteoritic Fe with $\text{H}_2/\text{H}_2\text{S}$ mixtures in the range of 558–643 K. Our calculations show that FeS-NiS solid solutions (as opposed to pure FeS) are formed, in agreement with the observations of Lauretta et al. However, since the system is not in equilibrium at these temperatures we cannot calculate the NiS content exactly and so have shown only pure FeS as being formed.

DISCUSSION

A comparison of the calculated and measured compositions in Tables 1 and 2 shows that agreement is generally within or nearly within the experimental error limits. The calculated MgO/SiO_2 ratio is at the upper range of the measurements of Schneider et al. (2002) (Table 2). The calculated ratio could be decreased by assuming that more droplets were swept out of the region at higher temperatures.

The observations of Schneider et al. that the amount of olivine varied among the chondrites which they studied is explained by the fact that the crystallization of the droplets actually occurred not at the one single temperature of 1400 K but over a range of temperatures near 1400 K. Calculations

show that droplets that crystallized at higher temperatures contain relatively more olivine than those which crystallized at lower temperatures. This results from the nature of the reaction:



(where the SiO_2 is dissolved in the liquid silicate which becomes the mesostases). The enthalpy change of this peritectic reaction is positive so that the equilibrium is shifted to the right at higher temperatures. From the observed large relative amount of pyroxene in enstatite chondrules, it must be concluded that they tended to crystallize below 1450 K; otherwise the calculated olivine content exceeds the calculated pyroxene content. With further reference to reaction [2] it may be noted that CaO and Al_2O_3 dissolve in the liquid phase, thereby causing a lowering of the activity of SiO_2 and hence causing reaction [2] to be displaced to the right. Had we not removed some CaO and Al_2O_3 , their presence in the chondrules would have resulted in a calculated olivine content higher than observed.

Crystallization of chondrules in enstatite chondrules thus takes place at ~1400 K, which is somewhat lower than our calculated temperatures of crystallization of the chondrules in Semarkona (Blander et al. 2004). It is commonly assumed that turbulence in the solar nebula led to early solids crashing into each other to form dust particles which became nucleation sites for chondrules. Possibly in the region where enstatite chondrites formed, a large amount of such materials were “wanderers” so that the probability of crystallization of the enstatite chondrules was lower than in the case of ordinary chondrites.

Effect of Pressure

A pressure of 1.0 bar was selected for the calculations. As discussed in a previous section, the curves in Fig. 1 are displaced by about 50° for each order of magnitude change in pressure. In order that the enstatite chondrules consist principally of enstatite, it is necessary that their crystallization occur at a temperature where the MgO and SiO_2 contents are near their maximum values; that is on the flat part of the curves below 1550 K on Fig. 1. For pressures lower than 1 bar the present model can thus still reproduce the observations provided that a lower crystallization temperature is assumed. For example, at $P = 0.001$ bar, we must assume solidification at 1300 K. However, such a large supercooling is probably unrealistic. Furthermore, at such low pressures, Fe rich alloys would not be expected to nucleate. At assumed pressures higher than 1.0 bar, the model can also reproduce the observations as well as at 1.0 bar. The use of a higher pressure does not lower the amount of undercooling which is required however. We must still assume that the supercooled droplets solidify at about 1400 K because of Reaction 2 which is independent of pressure and which is displaced too far to the right at temperatures above 1400 K. Hence, in order to

reproduce the observations, a pressure equal to or greater than about 0.1 bar is required. Unpublished calculations based upon a model (Bell et al. 1997) for solar-type nebula formation, indicate pressures greater than 0.1 bar at distances approximately 0.3 AU from the Sun; that is, near the present orbit of Mercury. As mentioned in the Introduction, the composition of Mercury is similar to that of E chondrites. This is consistent with the model of E chondrites forming close to the Sun (and later coalescing to form Mercury.) Hence pressures equal to or greater than 0.1 bar are consistent with the formation of enstatite chondrites in a region close to the Sun.

CONCLUSIONS

We have proposed a model for the formation of enstatite chondrules which includes a transition from blocking iron condensation to condensation of Fe-Ni alloys. It is proposed that their formation occurred in a region near the Sun in a slowly cooling nebula in thermodynamic equilibrium with rain-like supercooled liquid silicate droplets and condensed Fe-Ni rich alloys. FeO formed in stage 1 when iron condensation was blocked and was later mostly reduced to unalloyed Fe. This conclusion is supported by the fact that most observed chondrules have FeO contents higher than the equilibrium contents. At high temperatures, the silicate droplets contained high concentrations of the less volatile components CaO and Al_2O_3 . At somewhat lower temperatures, the equilibrium MgO content of the droplets was relatively high. As the cooling progressed, some of these droplets were gravitated to the Sun and moved in other directions (approximately 0.3% of droplets removed from the region per degree of cooling), thereby depleting the region in CaO, Al_2O_3 , and MgO and accounting for the observed relatively low CaO/SiO₂, Al_2O_3 /SiO₂, and MgO/SiO₂ ratios in enstatite chondrites.

Around 1400 K the remaining supercooled silicate droplets crystallized to form mainly MgSiO₃ (enstatite) with small amounts of olivine and a high-SiO₂ liquid phase which, upon further cooling, became the mesostases. The solidification occurred over a period of seconds. During solidification the temperature of the droplets may have increased about 50 degrees due to the heat of solidification, and then the droplets cooled back to the ambient temperature. The crystallization must have occurred at temperatures close to 1400 K because at higher temperatures Reaction 2 would be thermodynamically displaced too far to the right to be consistent with the observed very high enstatite content of enstatite chondrites. For assumed pressures less than 0.1 bar, the model can still reproduce the observations. However, it is then necessary to postulate that crystallization of the droplets occurred at temperatures below 1400 K. It is unlikely that liquid droplets could reach such low temperatures before

crystallizing. Finally, FeS formed at temperatures below 680 K by reaction of the condensed Fe particles with H₂S.

All calculations were performed with the evaluated optimized FACT thermodynamic databases of the FactSage system (Pelton et al. [2008]). Agreement of the model with the observed compositions of enstatite chondrules is very good, and generally within the experimental error limits for all components and phases.

In an earlier publication (Blander et al. 2004), we applied the Constrained Equilibrium Theory to explain the compositions of the various chondrules in ordinary chondrites. Here we have shown that the same theory can be applied to explain the formation of enstatite chondrules. In future work we shall show how the same unified concepts can be applied to the formation of carbonaceous chondrites, including the formation of CAIs, ARCs etc.

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