A multi-step model for the origin of E3 (enstatite) chondrites

MELINDA HUTSON1* AND ALEX RUZICKA1,2
1Portland Community College, P.O. Box 19000, SYL ST312, Portland, Oregon 97219, USA
2Department of Geology, Portland State University, Portland, Oregon 97207-0751, USA
*Correspondence author's e-mail address: m hutson@pcc.edu
(Received 1999 August 3; accepted in revised form 2000 February 12)

Abstract—It appears that the mineralogy and chemical properties of type 3 enstatite chondrites could have been established by fractionation processes (removal of a refractory component, and depletion of water) in the solar nebula, and by equilibration with nebular gas at low-to-intermediate temperatures (approximately 700–950 K). We describe a model for the origin of type 3 enstatite chondrites that for the first time can simultaneously account for the mineral abundances, bulk-chemistry, and phase compositions of these chondrites by the operation of plausible processes in the solar nebula. This model, which assumes a representative nebular gas pressure of 10^-5 bar, entails three steps: (1) initial removal of 56% of the equilibrium condensed phases in a system of solar composition at 1270 K; (2) an average loss of 80–85% water vapor in the remaining gas; and (3) two different closure temperatures for the condensed phases. The first step involves a "refractory element fractionation" and is needed to account for the overall major element composition of enstatite chondrites, assuming an initial system with a solar composition. The second step, water-vapor depletion, is needed to stabilize Si-bearing metal, oldhamite, and n在一个serite, which are characteristic minerals of the enstatite chondrites. Variations in closure temperatures are suggested by the way in which the bulk chemistry and mineral assemblages of predicted condensates change with temperature, and how these parameters correlate with the observations of enstatite chondrites. In general, most phases in type 3 enstatite chondrites appear to have ceased equilibrating with nebular gas at approximately 900–950 K, except for Fe-metal, which continued to partially react with nebular gas to temperatures as low as ∼700 K.

INTRODUCTION

The enstatite chondrites are a unique class of meteorites that consist of highly reduced phase assemblages. The silicates contain almost no FeO, and the Fe-metal contains significant amounts of Si (up to 4.9 wt% in EH3 chondrites; Weisberg et al., 1995). The enstatite chondrites also contain a variety of unusual minerals, such as ningenite (MgS) and oldhamite (CaS), which are not commonly found in ordinary or carbonaceous chondrites (Mason, 1966; Petaev and Khodakovsky, 1986).

Several models to account for the origin of the enstatite chondrites have been proposed, including: (1) condensation with slow nucleation kinetics (Blander, 1971); (2) condensation at high pressures (>1 bar) (Herndon and Suess, 1976; Sears, 1980); (3) formation in a region of the nebula with low H2O/H2 ratio (Buechecker and Wasson, 1975) or high C/O ratio (Larimer and Bartholomay, 1979; Lodders and Fegley, 1993, 1997); (4) increasing the amount of a "tar" component in the nebula (Wood and Hashimoto, 1993); and (5) condensation with partial isolation of solids (Petaev and Wood, 1998). None of these models have successfully replicated the observed modal mineralogy and bulk compositions of type 3 enstatite chondrites. For example, Si2N2O (sinonite) has been observed only in the EL enstatite chondrites. On the other hand, ningenite (MgS) never occurs in EL meteorites. Thus, these two minerals, which formed together in the model of Larimer and Bartholomay (1979), have never been seen to coexist in enstatite chondrites. In this paper, attention is focused on the type 3 chondrites, because these are the most likely to reflect the mineralogy and bulk composition of the original (premetamorphic) assemblage.

We considered chemical perturbations of the solar composition (Anders and Grevesse, 1989) as a possible way to explain the unusual mineralogy of the enstatite chondrites. Chemical perturbations in the nebula can occur at condensation fronts where there is both excess condensate (on the antisunward side of the front) and a sunward depletion of the vapor phase involved in the condensation reaction (Morrill, 1985; Stevenson and Lunine, 1988; Cyr et al., 1998). Three types of plausible models involving chemical perturbations were considered: (1) water depletion, (2) refractory element fractionation, and (3) combinations of water depletion and refractory element fractionation.

The mineralogy and bulk composition of condensed phases were determined by using the PHEQ program (Wood and Hashimoto, 1993), which searches for the minimum free-energy configuration of a system with a particular bulk-elemental composition at a particular temperature and gas pressure. The program includes 93 possible gas species and 148 possible solid species. The elements included in the model are H, O, C, Mg, Si, Fe, S, Al, Ca, and Na. All of the calculations were done at a gas pressure of 10^-5 bars, because this is considered a plausible pressure for the inner part of the solar nebula (e.g. Wood and Morrill, 1988; Wood and Hashimoto, 1993). Output is expressed in terms of the relative molar abundance of a phase. The PHEQ program assumes ideal mixing for solid solutions (Wood and Hashimoto, 1993).

The model results for a system of solar composition (Anders and Grevesse, 1989) are shown in Fig. 1. Wood and Hashimoto (1993) demonstrated that these results are similar to those obtained by others who used somewhat different calculation procedures (Grossman, 1975; Saxena and Eriksson, 1983a,b). As is evident from Fig. 1, some of the diagnostic minerals of enstatite chondrites, such as oldhamite (CaS), ningenite (MgS), and silica polymorph, are not stable at any temperature for the solar composition. Moreover, this model predicts too much forsterite and negligible amounts of Si dissolved in the Fe-metal phase, compared to that observed in enstatite chondrites. This demonstrates the widely recognized conclusion that the enstatite chondrites do not correspond to equilibrium condensates in a gas of solar composition.
RESULTS

Water Depletion

Depleting the water content of a gas, as might be expected sunward of the water condensation front (Morrill, 1985; Stevenson and Lunine, 1988; Cyr et al., 1998), has the effect of increasing the C/O ratio of the gas (e.g., Baedecker and Wasson, 1975). An increase in the C/O ratio has been proposed as the most likely way to create minerals such as CaS and MgS in the solar nebula (e.g., Larimer and Bartholomay, 1979; Lodders and Fegley, 1993). That water-vapor depletion in a nebular gas may have been important for enstatite chondrites is suggested by the work of Baedecker and Wasson (1975), who calculated that the Si content observed in E4 metal could be obtained at a pressure of $10^{-4}$ atm if the H$_2$O/H$_2$ ratio of the gas was 5x lower than solar. However, these authors did not determine the modal mineralogy that resulted from such a water depletion.

For the present work, we investigated the effect of various degrees of depletion of "cosmic water". Cosmic water is defined as the maximum relative molar abundance of water vapor in a solar-composition nebula, at a temperature just above that in which species start to condense (corresponding to temperatures of approximately 1700–1800 K in a solar-composition system at a pressure of $10^{-5}$ bar). Calculations were done for 0–100% water depletion (in 5% increments) relative to cosmic water. For 0–80% water depletion, the mineralogy is identical to that of the solar case, and the only effect is a lowering of the condensation temperature for silicate phases. This is consistent with the work of Larimer and Bartholomay (1979), who showed the same effect with increasing C/O ratio.

However, the modal mineralogy changes significantly with 85% water depletion, as shown in Fig. 2. Differences from the solar case include: (1) a decrease in the proportion of enstatite produced at high ($\geq 1000$ K) temperatures; (2) an increase in the proportion of enstatite at the expense of forsterite at $\sim 900$ K; (3) the stable appearance of oldhamite and nijingerite at $\sim 900$ K; (4) the stable appearance of graphite at $\sim 850$ K; and (5) the occurrence of an Si-bearing metal component. The assemblage at 900 K and 85% water depletion resembles that of enstatite chondrites, except that it lacks silica minerals and albite and contains too much graphite. Additional water depletion causes a greater mismatch with type 3 enstatite chondrites. Consequently, water depletion alone does not explain the observed mineralogy of type 3 enstatite chondrites. However, some aspects of the mineralogy of enstatite chondrites are obtained with a water-depleted composition, which suggests that this model has some merit. We will return to this point in a later section.

Refractory Element Fractionation

The model discussed above does not match the observed bulk chemistry of the enstatite chondrites. Larimer and Wasson (1988) concluded that the enstatite chondrites (EH and EL combined) had lost $\sim 58\%$ of their solar complement of Al and Ca, $51\%$ of their solar Mg, and $33\%$ of their solar Si in a "refractory element" fractionation. Petaev and Wood (1998) reported that partial isolation of a refractory component over a range of temperatures produced minerals such as silica polymorph, oldhamite, Na-sulfides, metal, troilite, and enstatite, most of which are found in enstatite chondrites. Modal abundances were not given, but Petaev and Wood (1998) stated that "the matches between calculated and real mineralogy... are not perfect."

Our trial-and-error calculations show that the removal of $\sim 56\%$ of the condensed phases in equilibrium with a solar-composition gas at 1270 K can produce approximately the correct bulk composition of the enstatite chondrites for these four elements. To simulate the effects of this refractory element fractionation, condensation calculations were performed at temperatures between 1600–500 K for an initial gas composition in which all elements had solar composition except those elements (Mg, Al, Ca, and Si) that were involved in the refractory element fractionation. Refractory element fractionation could have occurred by the removal of a high-temperature condensate during fractional condensation. Alternatively, it could have occurred during fractional vaporization, by the separation of the highest temperature residues from the gas phase.
Figure 2. Equilibrium relative molar abundances of condensed phases for a model investigating the effects of water depletion alone, assuming a system of solar composition from which 85% of the water has been removed. Other conditions and symbols are the same as in Fig. 1.

Figure 3. Equilibrium relative molar abundances of condensed phases for a model investigating the effect of a refractory element fractionation, assuming the removal of 56% of a refractory component from a system with solar composition. This refractory component corresponds to the equilibrium condensate-residue at a temperature of 1270 K and a gas pressure of 10^-5 bar. Other symbols and conditions are the same as in Fig. 1.

Figure 3 shows the equilibrium assemblages predicted for partial (56%) removal of the refractory component at 1270 K. For completeness and ease of comparison with the other models discussed here, results are shown both above and below the temperature at which the refractory component is believed to have been fractionated (1270 K), because these equilibrium models do not discriminate between scenarios in which temperature either increases or decreases subsequent to the refractory element fractionation. Removing the refractory component from the system changes the subsequent equilibrium mineral assemblage considerably (Fig. 3). Differences from the solar case include: (1) the presence of silica minerals at the expense of forsterite over a broad range of temperatures; (2) an increase in the abundance of enstatite over a larger range of temperatures; (3) the appearance of Na₂SiO₃, and (4) a decrease in the abundance of plagioclase (albite–anorthite solid-solution) and diopside. Although the coexistence of abundant enstatite with a silica polymorph is reminiscent of enstatite chondrite mineralogy, the presence of Na₂SiO₃, and the absence of oldhamite, niningrite, and an Si-metal component suggests that refractory element fractionation alone cannot produce a mineral assemblage similar to that in enstatite chondrites.

Preferred Model

A preferred model can be constructed for enstatite chondrites that combines some of the best attributes of the models discussed above. There is general agreement (Dodd, 1981; Wasson, 1985; Larimer and Wasson, 1988) that chondritic meteorites experienced various types of refractory element fractionations, and this is a requirement for any model of enstatite chondrite formation that assumes an initial solar composition. However, the presence of
oldhamite and niningerite in enstatite chondrites, as well as the Si content of the metal, require more reducing conditions, such as are obtained with water depletion or an increase in the C/O ratio. Quantitative models of water transport in a turbulent nebula (Stevenson and Lunine, 1988; Cyr et al., 1998) suggest that the amount and spatial extent of water-vapor depletion, occurring sunward of the water condensation front, increase as a function of time. Consequently, we examined cases in which the refractory element fractionation (as described in the previous section) was followed by water depletion.

For a model in which refractory element fractionation is followed by up to 80% depletion of cosmic water (Fig. 4a), the assemblages are similar to those produced for the case involving refractory element fractionation alone (Fig. 3). The major differences are that the silicate condensation temperatures are lowered, and the abundance of forsterite at high temperatures is increased as the abundance of water vapor decreases.

With a further decrease of water abundance, the condensate assemblage changes significantly. For 85% removal of cosmic water (Fig. 4b), the differences from the 80% water-loss case include: (1) the absence of silica minerals, and the presence of additional forsterite, for temperatures down to \(\sim 900\) K; (2) the appearance of graphite at temperatures between \(\sim 700\) and \(950\) K, with a large abundance maximum at \(\sim 850\) K; (3) the appearance of a Si-metal component at temperatures between approximately 900–1050 K; and (4) the presence of oldhamite and niningerite over a narrow temperature range, with an abundance maximum at \(\sim 900\) K.

Lodders and Fegley (1993) modelled equilibrium condensation of rare earth elements (REE) in oldhamite for conditions somewhat different than ours (10^{-3} atm, solar composition, except C/O = 1.2) and found that relatively flat REE patterns and REE abundances of approximately 60–100 \(\times\) CI in oldhamite are produced at a temperature of approximately 1200–1360 K. This compares with oldhamite grains in EH3 and EH4 chondrites that have REE abundances of approximately 40–90 \(\times\) CI, and which typically show either monotonic light-REE (LREE)-enriched patterns or LREE-enriched patterns with positive Eu anomalies, Yb anomalies, or both. Based on their model results, Lodders and Fegley (1993) suggested that oldhamite condensed from the solar nebula at a significantly higher temperature than for our preferred model. It is unclear whether the observed REE abundances for oldhamite are consistent with our model; further work is needed to track the

© Meteoritical Society • Provided by the NASA Astrophysics Data System
distribution of the REE in mineral assemblages as a function of pressure, temperature, and gas composition.

Features that are reminiscent of the mineralogy of enstatite chondrites occur in models that combine refractory element fractionation with subsequent 80 or 85% water loss. These include: (1) the coexistence of silica polymorph and enstatite between ~850 and 1100 K in the 80% water-depletion case (Fig. 4a); (2) the presence of olivine and enstatite between ~850 and 1000 K in the 85% water-depletion case (Fig. 4b); and (3) the presence of Si-bearing metal between approximately 900–1050 K in the 85% water-depletion case (Fig. 4b). Graphite, which occurs as a minor phase in enstatite chondrites, is present in the 85% water-depletion case below 950 K (Fig. 4b). Thus, the minerals observed in enstatite chondrites are present in the combination refractory element loss and 80 or 85% water-depletion models between approximately 900–950 K, but no model by itself has the complete, appropriate assemblage for enstatite chondrites.

In type 3 enstatite chondrites, both forsterite and silica polymorph are present, although in equilibrium these phases should not coexist. Thus, a single equilibrium model should not be able to fully reproduce the observed mineralogy of the enstatite chondrites. Possibly, materials from different formation locations were mixed together to form the enstatite chondrites. The 80 and 85% water-depletion models are in some sense complementary, and the optimal model is a 50/50 mixture of these two. Such a mixture could arise as the result of a small amount of radial mixing in the nebula brought on by turbulence or by the mixing of materials formed at slightly different times in an evolving nebular system.

As discussed above, the mineralogy of the predicted condensates closely approximates that of the enstatite chondrites at equilibrium temperatures between 900 and 950 K. Similarly, the bulk chemistry of the predicted condensates most closely approaches that of the enstatite chondrites for the same temperature range. This is illustrated by Fig. 5, which shows the Si-normalized major element abundances in the condensed assemblage for the preferred model (50/50 mix of 80 and 85% water loss) as a function of temperature, compared to the ranges observed in enstatite chondrites (Hutson, 1996). With the exception of S/Si, all the model elemental ratios match those observed in the enstatite chondrites between approximately 900–950 K (Fig. 5). Thus, both the bulk chemistry of the model assemblage, with the exception of S, as well as the mineralogy of the assemblage, compare favorably to enstatite chondrites in the approximately 900–950 K temperature interval. This suggests that the enstatite chondrites could represent a mixture of mineral assemblages that largely equilibrated with nebular gas at a temperature of approximately 900–950 K.

The S/Si abundance ratio of the predicted condensate assemblage increases sharply at lower temperatures (Fig. 5), corresponding to the formation of Fe-sulfide (troilite–pyrrhotite solid-solution) by reaction with H₂S vapor, resulting in the "sulfidation" of metal (Fig. 4). The S/Si abundance ratio of the model assemblage matches that of enstatite chondrites at a temperature of ~700 K (Fig. 5). This implies that metal could have continued to react with nebular gas down to a temperature of ~700 K, roughly 200–250 K lower than the apparent closure temperature needed for other phases. This type of difference in closure temperature is reasonable. Fegley (1988) suggested that different minerals ceased equilibrating with the solar nebula at different temperatures because of kinetic effects. Reactions involving extensive solid-state diffusion, such as those involving silicates, are unlikely to reach completion at low temperatures (Fegley, 1988), whereas the formation of troilite by sulfurization of metal is a rapid process, even at low temperatures (e.g., Lauretta et al., 1996a, 1998). In experimental studies of the sulfidation of metal, diffusion rates in troilite are typically the rate-limiting step to troilite formation (e.g., Lauretta et al., 1996a, 1998), but this diffusion occurs so rapidly that it probably would not have significantly prevented the conversion of metal to troilite in the nebula even at temperatures as low as 400 K (Lauretta et al., 1996a). Instead, the breakdown of metal to troilite may have ceased when metal grains became effectively isolated from the remaining system (Lauretta et al., 1996a), perhaps by the sequestering of metal grains in a parent body.

As noted above, except for the special case of troilite and metal, both the mineralogy and bulk-chemistry of the condensates produced at a temperature of approximately 900–950 K resemble those of enstatite chondrites. This implies that the modal composition of the condensates from this temperature interval should match those of enstatite chondrites. Figure 6 and Table 1 compare the modal mineralogy of the condensates produced by the...
is true also for the metal phase, despite the indication that it may have been partly sulfidized at lower temperatures.

In detail, there are differences between the predicted phase compositions and those observed in E3 chondrites. Although orthopyroxene and olivine grain compositions in E3 chondrites are typically highly magnesian similar to those predicted by the model, orthopyroxene and olivine grains as ferrous as En$_{78}$ and Fo$_{91}$ are found in E3 chondrites, respectively (Weisberg et al., 1995). Likewise, although Si contents as high as 4.9 wt% are found in kamacite grains in E3 chondrites, most metal grains in E3 chondrites have lower Si contents (1.6–3.6 wt% in EH3, 0.3–0.8 wt% in EL3) (Weisberg et al., 1995) than that predicted. Clearly, E3 chondrites were derived from materials that formed under conditions more diverse than those assumed in the preferred model. In particular, the discrepancies could be explained if some of the orthopyroxene, olivine, and kamacite grains in E3 chondrites equilibrated at temperatures less than 900–950 K, as silicates become more ferrous and metal becomes less silicic at lower equilibrium temperatures. As argued above, metal sulfidation may have occurred at temperatures less than that at which most other phases ceased equilibrating. Such a failure to attain complete equilibrium could explain how E3 metal could become partially sulfidized (which implies low temperatures) while still retaining an elevated Si content (which implies higher temperatures).

**DISCUSSION**

The mineralogy, bulk chemistry, and phase chemistry of the principal phases of E3 chondrites can be explained surprisingly well by a model that involves plausible processes operating in a low-pressure, gaseous environment with an original solar composition. These processes include: (1) the partial removal of a refractory-element-enriched component at high temperatures, involving a gas–solid fractionation during condensation or vaporization processes; (2) the subsequent depletion of water vapor, similar to what one would expect on the sunward side of a water-condensation front in the solar nebula; and (3) the partial equilibration of condensed phases with the remaining vapor, at temperatures ranging from 900–950 K (most phases) to ~700 K (Fe-metal and Fe-sulfide), corresponding in both cases to temperatures at which reactions become kinetically inhibited, or to a situation where solids are sequestered from the remaining gas, possibly by their accretion in a parent body. The success of the model in explaining the mineralogy and chemistry of E3 chondrites implies that the components of enstatite chondrules could have originated and largely equilibrated in a nebular (gas-rich) setting, sunward but possibly close to the water-condensation front.

Texturally, the E3 chondrites contain numerous chondrules that testify to melting episodes. No equilibrium melt phases occur in the various steps of the preferred model, which does not support the idea that the chondrules themselves represent nebular condensates or vaporization residues. Instead, chondrules may have formed by the melting of nebular precursors. On the other hand, chondrules in E3 chondrites often contain many of the phases that are predicted to be stable under the conditions assumed in the preferred model. This suggests that either (1) the remelting episodes that produced chondrules occurred under conditions somewhat similar to those that inferred for the precursors, or (2) chondrules were produced rapidly by disequilibrium processes, and they did not fully adjust to the new thermodynamic conditions in which they formed. Detailed studies
of mineral-textural assemblages in E3 chondrites, and further constraints on the kinetic processes involved in chondrule formation, are needed to evaluate these possibilities.

CONCLUSIONS

The mineralogy and chemical properties of type 3 enstatite chondrites could have been established by fractionation processes in the solar nebula, and by equilibration with nebular gas at low-to-intermediate temperatures (approximately 700–950 K). These chondrites are modelled as having formed by a three-step process involving: (1) an initial refractory element fractionation, caused by the removal of 56% of the condensed phases at 1270 K in a system of solar composition; (2) an average of 80–85% water-vapor depletion in the remaining gas, such as can occur sunward of the water-condensation front in the nebula; and (3) equilibration between most phases and nebular gas at temperatures of approximately 900–950 K, except for metal, which was sulfidized to temperatures as low as ~700 K. Such a difference in closure temperature is reasonable owing to differences in diffusion rates and reaction mechanisms involving silicates on the one hand, and Fe-metal and Fe-sulfide on the other. This multi-step model is relatively straightforward, consistent with our expectations for the nebula, and in remarkable agreement with the overall modal composition, bulk composition, and phase chemistry of enstatite chondrites.

Acknowledgments—The authors wish to thank Dante Lauretta, Katharina Lodders, and Ed Scott for helpful comments that improved the quality of this manuscript, John Wood for a copy of the PHEQ program, and John Lewis for providing support that made this work possible.

Editorial handling: E. R. D. Scott

REFERENCES


© Meteoritical Society • Provided by the NASA Astrophysics Data System


