A POSSIBLE ORIGIN OF EL6 CHONDRITES FROM A HIGH TEMPERATURE-HIGH PRESSURE SOLAR GAS

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ABSTRACT

Calculations of condensates from a gas of "solar" composition were made to investigate the origins of EL6 chondrites using a unique free energy minimization computer program with a data base for the thermodynamic properties of multi-component molten silicates as well as for other liquids solids, solid solutions and gaseous species. Because of the relatively high volatility of silicon and silica, the high silicon content of metal (2.6 mole percent) can only be produced at pressures greater than 10^{-2} atm at temperatures greater than 1475 K. At very high pressures (100-500 atm), a liquid silicate phase crystallizes at a temperature where the silicon content of the metal, the ferrosilite content of the enstatite and the albite concentration in the plagioclase are close to measured values. It is well known in pyrometallurgy that liquid silicates are catalysts for reactions in which Si-O-Si bridging bonds are broken or formed. Thus, one attractive mode for freezing in the compositions of these three phases is the disappearance of the fluxing liquid. If the plagioclase can continue to react with the nebula without a liquid phase, then lower pressures of e.g. 10^{-1} to 1 atm might be possible. Even if the nebula is more reducing than a solar gas, the measured properties of EL6 chondrites might be reconciled with only slightly lower pressures (less than a factor of three lower). The temperatures would be about the same as indicated in our calculations since the product of the silicon content of the metal and the square of the ferrosilite content of the enstatite constitute a cosmo-thermometer for the mineral assemblage in EL6 chondrites.

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There has been a recent controversy concerning maximum temperatures in the solar nebula.¹ Astrophysical calculations of nebular formation¹ by gravitational collapse of interstellar (or prestellar) gas led to temperatures of <1000K which are considerably lower than those reflected by the properties of chondritic meteorites (>1500K).² Recent calculations of nebula formation by gravitational collapse have indicated the possibility of nebular temperatures which are high enough to have produced the precursors of chondrites³ as nebular condensates. In this report we present calculations for equilibria in enstatite type EL6 chondrites which appear to have frozen in at a high temperature and pressure in which the reactants and products are simultaneously in equilibrium with a solar gas⁴ at the same temperature. This result indicates that the last cooling event undergone by these chondrites was in a reducing nebular environment of "solar" composition and thus directly supports the idea of a hot, high pressure nebula as the source of chondrite precursors. Our calculations are more generally aimed at exploring non-equilibrium effects⁵⁻⁹ in the condensation of the precursors of enstatite chondrites from a "solar" nebula. The effect of the freezing in of equilibria in EL6 chondrites, in addition to providing information on the environment of the formation of chondrite precursors, may also pose an important constraint on the chemistry of all chondrites. The primary equilibrium is the reaction

Other equilibria involve the formation of plagioclase and the crystallization of molten silicates. In this paper we use a well known principle in pyrometallurgy that a liquid phase catalyzes reactions between solids. Thus, the disappearance of a liquid phase can halt reactions involving complex chain and cross linked silicates.

Enstatite (E) chondrites are highly reduced stones which have been thoroughly described by Keil.¹⁰ The major mineral is enstatite (MgSiO_3 containing small concentrations of FeSiO_3) with fairly large amounts of metal (mostly kamacite and rare taenite) and troilite. In addition to silica, albitic plagioclases and olivine (only in type EH 3, 4, 5) are present. There are a

number of minerals which reflect the reduced state of these chondrites, including the sulfides-oldhamite, alabandite, niningerite (in Type E3, 4 chondrites), sphalerite (ZnS), djerfisherite and daubreelite as well as the phosphide-schreibersite, sinoite ($\text{Si}_2\text{N}_2\text{O}$), cohenite (Fe_3C), and graphite. There are many other compositional features which have a significant bearing on their origins. The mineral assemblages in EL6 chondrites include a very small amount of silica, enstatite (containing, on the average, 0.25 mole% FeSiO_3),¹⁰ and metal (containing an average of 2.6 mole %Si).¹⁰ The origin of E chondrites is enigmatic. In this paper we discuss the origins of EL6 chondrites as condensates from a solar nebula at high pressure (0.01 - 1000 atm.) Because past calculations have been restricted to the much lower pressures suggested by astrophysical models, they were unable to account for the properties we discuss.

There are three separate equilibria involving the metal, silicon, silica and FeSiO_3 . The first equilibrium is Eq. (1) which involves only condensed phases. The other two equilibria are

and

which involve condensed phases and the nebular gas. Thus one can determine whether the compositions of the reactants and products were frozen in while the assemblage was still in effective contact and equilibrium with the nebula.

We used a computer program¹¹ which permits us to calculate equilibria in complex multicomponent-multiphase systems with over 1000 different species including solid, liquid and gaseous compounds and non-ideal solid and liquid solutions. We have extended our published work¹²⁻¹⁵ to perform reliable thermodynamic calculations for multicomponent liquid silicates including alumina.¹⁶ For pyroxene solid solutions we have utilized the analysis

of Blander,¹⁷ for plagioclase we utilized the data of Newton, Charlu and Kleppa¹⁸ and for solutions of silicon in metal, we have used the data of Sakao and Elliott¹⁹ combined with the Fe-Si phase diagram to deduce data for the BCC and FCC iron phases. The overall database contains over 5000 substances including the relevant data of Berman and Brown^{20,21} which we have optimized to be simultaneously consistent with the geologic equilibria used by Berman and Brown as well as with the binary or ternary phase diagrams which include these substances, and with the properties of the corresponding binary or ternary liquids. The composition of the "solar" gas was taken from Anders and Grevesse.⁴ Because the compositions and mineralogy of EL6 chondrites, especially the presence of silica, indicate that some of the most refractory constituents of basic high temperature condensates in the solar nebula have been segregated from the EL6 chondrites we subtracted an amount of aluminum as gehlenite equal to the difference in the relative aluminum content of these chondrites and the solar nebula. We have also removed 20% (at 0.1, 1.0, and 10 atm), 25% (at 100 and 500 atm) or 27% (at 1000 atm) of the total magnesium to account for the formation of spinel and forsterite at high temperatures and to take into account the high Si/Mg ratios in EL6 chondrites. The amount was chosen to also produce a small amount of silica in the final assemblage.

We discuss our equilibrium calculations for a nebular composition of the elements H, C, O, Si, S, Fe, Ca, Na, Al and Mg at pressures ranging from 0.01 - 1000 atm. These relatively high pressures have previously been found to be consistent with the chemistry of E chondrites⁷ and as discussed below, are consistent with the properties we examine in this paper.

The calculated mineral assemblages include enstatite, metal and silica at the pertinent temperatures of 1450-1600 K at 0.01, 0.1, 1.0, 10.0, 100, 500 and 1000 atmospheres total pressure. The H_2/H_2O ratios decreased somewhat with pressure, and are about 1280 at $p = 0.1$ and 1.0 atm, about 1000 at 10 atm and about 680 at pressures of 100 atm and

higher. The more reducing atmosphere for the solar gas at low pressures arises because the equilibrium

shifts to the right hand side with a decrease in pressure. Thus, one expects that, at a fixed temperature and at saturation with silica, the $FeSiO_3$ content of enstatite will usually be higher and the Si content of metal will usually be lower the higher the pressure. Our calculations are for the dissolution of Si in pure iron and not in the Fe-Ni alloy. Because of the similarity of the interactions of silicon with either Fe, Co, and Ni and because of the low concentrations of Ni, it is likely that our calculated values would be representative of the alloy. Table I gives our calculated values of these parameters as well as the mole percent of albite in the plagioclase at 1450, 1475, 1500, 1525, 1550, 1575, and 1600K at 0.01, 0.1, 1, 10, 100, 500, and 1000 atmospheres and indicates the presence (Y) or absence (N) of a liquid silicate.

At pressures of 10^{-2} atmospheres and below the concentration of Si in metal never reached 2.6 mole% because of the volatility of silica which forms SiO and SiS in the vapor. The value of 1.46 mole % Si at 10^{-2} atm is close to a maximum at this pressure with the concentration decreasing at temperatures below 1450 K. As can be seen, the closest matches to the measured average values of the compositions of Si and ferrosilite are at 1475 K at $p = 0.1$ atm. and 1.0 atm., 1500 K at $p = 10$ atm., 1550 K at 100 atm and 1575 K at 500 and 1000 atm. Since the concentration of Si in metal is more sensitive to temperature than the ferrosilite concentration in enstatite, we have used as a baseline the temperatures where the Si content of metal is 2.6 mole percent; the corresponding concentrations of ferrosilite (in mole percent) for the temperatures at the five pressures are: at 0.1 atm. $T = 1479$ K, $Fs = 0.182$; at 1.0 atm., $T = 1473$ K, $Fs = 0.201$; at 10 atm., $T = 1504$ K, $Fs = 0.246$; at 100 atm., $T = 1556$ K, $Fs = 0.339$; at 500 atm., $T = 1566$, $Fs = 0.318$ and at $P = 1000$, $T = 1569$ and $Fs = 0.365$. The ferrosilite concentrations at all these pressures differ from

the experimental average of 0.25% by an amount which is less than the uncertainties in the thermodynamic data for ferrosilite. The differences between the measured values for Si in metal and FeSiO_3 in enstatite (2.6 mole % and 0.25 mole %)¹⁰ and the five calculated pairs of values are within the uncertainties in the calculations. Thus all of these pressures and temperatures are possible based on these calculations.

In the reactions (1), (2) and (3), the different solids impose differing kinetic constraints on the reactions. For example, the reactions involving the formation or decomposition of SiO_2 or FeSiO_3 solid solution involve the making or breaking of Si-O-Si bridging oxygens in the siliceous minerals and are most likely to be kinetically constrained. This is most important for the formation or decomposition of the solid solutions of FeSiO_3 in enstatite which involves a complex process in which many Si-O-Si bonds are broken and reformed. Of all the solids considered so far, a reaction which removes Si from the metal is likely to equilibrate most easily and does indeed do so in the presence of a liquid silicate down to temperatures lower than 1473¹⁹. The fact that the temperatures for freezing reactions involving Si in metal in EL6 chondrites are not lower indicates that the metal phase does not react effectively with the nebular gas at temperatures below the temperatures given above (1473 - 1569 K) possibly because of the absence of a liquid phase to flux the production or reduction of silica. Thus, disappearance of a liquid phase could explain the freezing in of the three separate reactions at the same temperature, despite the fact that they are likely to have different rates.

Examination of our results (Table I) for the presence of a liquid phase provides clues concerning the apparent freezing in of the reactions (1), (2), and (3) at the same temperature. In Table II we give the lowest calculated temperature in which a liquid silicate is present, the composition of the liquid and the temperature ($T_{\text{Si}(eq)}$) where the equilibrium concentration of Si in metal is the same as the average value in EL6 chondrites. Since liquidus temperatures are quite sensitive to relatively small uncertainties in data, there is a significant uncertainty

in the temperature of disappearance of the liquid phase which is probably somewhat greater than 25° . In any case, the difference between the temperature of freezing in of the average composition of Si in metal and of FeSiO_3 in enstatite is within these limits at 1, 10, 100, 500 and 1000 atm. A liquid phase was present down to at least 1450 K at 0.1 atm. This anomaly arises because a significant fraction of the silicon is present as SiO in the gas and silica does not form in the assemblage so that the Si/Mg ratio in the condensate is lower than the value in EL6 chondrites. As will be seen below, there is independent evidence that EL6 chondrites did not form at this pressure.

If reactions involving enstatite freeze in upon the disappearance of silicate liquids then reactions involving plagioclase, which is a complex crosslinked silicate, are likely to freeze in too. Clearly, the plagioclase compositions in EL6 chondrites (average is 80.2% Ab, 15.2% An, and 4.6% Or¹⁰) are not close to the values calculated (when present) at 1 and 10 atm (Table I) near the temperature of disappearance of liquid because of the volatility of sodium; the calculated compositions of plagioclase at 100 and 500 atm (when normalized to account for the fact that our calculations did not include orthoclase) are in range of the measured values. The albitic content of the calculated plagioclase is too high at 1000 atm. Because of a lack of data for orthoclase solutions, we did not consider orthoclase which is in dilute enough solution in the plagioclase to act as a minor diluent. Consequently, to a good approximation, Henry's law is obeyed and one can consider that the composition of albite and anorthite can be normalized to 100% for comparison with our calculations. This leads to an effective composition of 84.4 Ab and 15.6 An. Thus, a plausible explanation for the composition of the assemblage is that they had condensed somewhere between 100 and 500 atmospheres from a solar gas which had been depleted of some of the most refractory condensates. Upon cooling to temperatures of about 1550-1570, the liquid crystallized and the compositions of the silicates and metal froze in. This scenario is based on the hypothesis that equilibria involving silica and silicates required contact with a liquid phase to equilibrate. If plagioclase but not the other silicate minerals can equilibrate down to lower temperatures, then the same

assemblage could be produced at lower pressures (i.e. 1.0 and 10 atm).

Discussion and Conclusions

The origins of E chondrites have posed an apparent mystery because prior calculations on enstatite chondrites have been made only at the low pressures suggested by astrophysical models of the solar nebula. The properties we have discussed suggest that EL6 chondrites are condensates from a hot, high pressure nebula of solar composition with a likely freezing in of reactions of silicates above 1550 K and at 100-500 atmospheres. The detailed chemistry imposes constraints on both the temperature and the pressure. For example, silica is volatile enough so that at 10^{-2} atmospheres and temperatures where equilibrium (3) leads to relatively high values of silicon in metal, much of the silicon is present as SiO(g) , the activity of solid silica is significantly below unity and the level of silicon in metal is always lower than the average found in EL6 chondrites. Thus, the pressure at which EL6 chondrite precursors could form from a solar nebula is higher than 10^{-2} atmospheres. The volatility of alkali oxides poses a further constraint on the pressure so that at the temperatures in which reaction (1) and presumably the reaction for formation of the albitic component of the plagioclase (when present) freeze in, the calculated plagioclase composition has considerably less albite than the measured values in EL6 chondrites at 0.1, 1.0 and 10 atm. The total chemistry at pressures between 100 and 500 atmospheres and temperatures above 1550 K are consistent with the properties of EL6 chondrites.

If true, our results have important implications for the origins of other chondrites. For example, it places a constraint on the mineralogical and chemical reactions in which silicates can participate below the temperature of disappearance of molten silicates. The high FeO content of silicates in many chondrules could thus be emplaced by a diffusive exchange process at low temperatures but not by a reaction which breaks Si-O-Si bonds. This requires cooling meteorite precursors to temperatures which are low enough to form iron oxides which could engage in an ion exchange process with solid silicates. Iron oxide can be readily emplaced in silicates in a solar nebula at the high temperatures where liquid silicates are present only

when the solar gas is supersaturated in Fe^5 or when enough of the constituents of the silicates (largely silicon) are not fully condensed. Thus, one might condense iron rich silicates directly. Our approach and results have the potential for deducing the temperatures and pressures at which properties of other chondrites might have been fixed and should help to further define the nebula (presumably the "solar" nebula) in which meteorites originated.

We have assumed a gas composition close to solar values and the ranges of temperature and pressure where we calculate the chemistry of EL6 chondrites would change with changes in gas composition. In order to alter the pressures significantly with changes in the abundances of the relatively volatile silicon or sodium would take large changes in relative abundances. An order of magnitude decrease in the pressure would take an unlikely order of magnitude increase in the relative abundances of these two elements. Changes in the $\text{H}_2/\text{H}_2\text{O}$ ratio could also alter the pressures at which one would calculate a chemistry similar to that of the EL6 chondrites. However, this is limited by the fact that some of the chemistry is related to a reduction process (i.e. emplacement of Si in metal as in Eq. (3)) and some to an oxidation process (i.e. emplacement of FeSiO_3 in enstatite as in Eq. (2)). Thus, to simultaneously get the equilibrium compositions of both metal and enstatite, one is limited to a relatively small change in this ratio of about a factor of 3.

In conclusion, we have shown that the compositional properties of EL6 chondrites¹⁰ indicate an origin in a solar nebula at temperatures above 1550 K and at pressures between 100 and 500 atmospheres. Lower pressures (but greater than 10^{-2} atmospheres) are possible if plagioclase can equilibrate with the nebula down to lower temperatures. These results, need to be considered in any astrophysical model of the "solar" nebula. Further detailed calculations are underway on EL6 and other chondrites.

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Table I.
Calculated Ferrosilite (Fs) Content (mole %) of Enstatite, Si Content (mole %) of Metal, and Albite Content of Plagioclase (mole %) From 1450 - 1600 K

		T(K)						
P(atm)		1450	1475	1500	1525	1550	1575	1600
0.01	Si	1.46	1.17	0.97	0.87	0.65	—	—
	Fs	—	—	—	—	—	—	—
	Ab	0.4	<0.1	<0.1	—	—	<0.1	—
	Liq.	Y	N	N	Y	N	N	N
0.1	Si	1.88	2.47	3.47	3.71	3.23	2.84	2.97
	Fs	0.191	0.183	0.177	—	—	—	—
	Ab	—	—	—	—	—	—	—
	Liq.	Y	Y	Y	Y	Y	Y	Y
1.0	Si	2.00	2.67	3.56	5.90	8.42	11.7	13.3
	Fs	0.209	0.200	0.173	0.165	0.156	0.147	—
	Ab	37.8	28.7	—	—	—	—	—
	Liq.	N	N	Y	Y	Y	Y	Y
10.0	Si	1.14	1.70	2.42	3.65	6.04	9.12	13.4
	Fs	0.292	0.271	0.249	0.230	0.189	0.172	0.155
	Ab	62.2	—	—	—	—	—	—
	Liq.	N	N	N	N	Y	Y	Y
100	Si	0.66	0.93	1.28	1.74	2.31	3.88	5.51
	Fs	0.407	0.391	0.375	0.360	0.345	0.318	0.295
	Ab	89.9	86.3	81.9	76.6	70.6	85.4	89.1
	Liq.	N	N	N	N	N	Y	Y
500	Si	0.577	0.807	1.10	1.51	2.08	2.79	4.54
	Fs	0.384	0.367	0.351	0.343	0.347	0.308	0.294
	Ab	95.9	94.1	91.8	89.2	86.8	89.9	80.2
	Liq.	N	N	N	N	N	Y	Y
1000	Si	0.60	0.84	1.16	1.56	2.07	2.96	4.31
	Fs	0.433	0.417	0.402	0.387	0.373	0.360	0.303
	Ab	97.8	96.9	95.6	93.9	91.7	89.2	92.6
	Liq.	N	N	N	N	N	N	Y

The symbol — means that the major phase (metal, enstatite or plagioclase) is not present.

Y(N) means a liquid is (is not) present.

Table II.

Compositions of Molten Silicates at Temperatures Somewhat Above
The Temperature of Complete Crystallization and
The Temperature at Which Reaction (1) Froze In
(Mole Percent)

P(atm)	T(K)	SiO ₂	MgO	CaO	Al ₂ O ₃	Na ₂ O	FeO	T _{Si(eq.)}
1	1500	57.5	24.1	7.9	10.3	0.01	0.2	1473
10	1550	57.6	25.5	7.2	9.4	0.1	0.3	1504
100	1575	60.2	23.0	8.2	7.5	0.7	0.3	1556
500	1575	58.6	22.7	11.3	5.4	1.7	0.3	1566

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