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Condensation from supernova gas made of free atoms

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Abstract—Silicon carbide grains and graphite spherules containing TiC inclusions are found in the Murchison carbonaceous chondrite. The high ^{44}Ca (from ^{44}Ti) and ^{28}Si contents of these grains are strong evidence that all three minerals originated in the deep zones of Type II supernova ejecta. We present equilibrium calculations for SN shells, and show that TiC, but not graphite or SiC, is a stable condensate in the innermost shells where [Ti + Si] $>>$ [C + O], even though C/O < 1 in these shells. Because of the great stability of gaseous CO, however, neither carbides nor graphite can survive at chemical equilibrium in the massive O-rich shells which separate the heavy element-rich inner sources of ^{44}Ti and ^{28}Si from outer C-rich zones where these minerals would be stable. Clayton et al. (1999) found that, under circumstances where all gaseous molecules and particularly CO are completely dissociated by Compton electrons, specific choices of kinetic parameters enable the prediction of graphite formation, even in an O-rich supernova shell. Following up on this hypothesis, we calculated high-temperature equilibrium condensation sequences in the absence of polyatomic molecules for gases having canonical solar, and supernova shell compositions. Graphite is indeed predicted to be stable in O-dominated supernova zones in the absence of gaseous molecules. But the complementary phases found in meteorites, TiC and SiC, are not stable under these conditions, while SiO$_2$, which is not found, is produced in abundance. Without resolving these discrepancies between theory and observation, the problem of reconciling the zone where the mineralogical identities of supernova grains were established with the zone implied by their isotopic compositions remains unsolved. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Nearly a third of the low-density graphite spherules and 1% of the SiC grains (Zinner, 1998), known as "X-grains," isolated from the Murchison carbonaceous chondrite (Amari et al., 1992) exhibit large, correlated excesses of ^{28}Si and ^{44}Ca (from short-lived ^{44}Ti), indicative of their formation in a Type II supernova (Zinner, 1998). The supernova (SN) grains also show excesses of ^{15}N and ^{18}O, as well as large inferred initial ^{26}Al/^{27}Al and ^{41}Ca/^{40}Ca ratios (Amari et al., 1992; Amari et al., 1995a,b). The ^{44}Ca anomalies in graphite reside in euhedral to subhedral TiC subgrains, many of which clearly existed before the graphite, based on abundant textural and compositional data (Nittler et al., 1996; Bernatowicz et al., 1998; 1999). Unlike ^{44}Ti, the excess ^{28}Si and other isotopes are homogeneously distributed in graphite (Bernatowicz et al., 1998).

Because of the great stability of gaseous CO, thermodynamic equilibrium dictates that C is available to form graphite and carbides as high-temperature condensates only in cosmic gases in which C/O > ~0.98. Excess O forms oxides and silicates when C/O < 0.98. The innermost SN zones which produce ^{28}Si and ^{44}Ti have C/O $<<$ 1, and are separated from outer zones with C/O > 1 by massive intermediate zones with C/O $<<$ 1. The isotopic compositions of supernova TiC, graphite and SiC are, therefore, considered to be inconsistent with their mineralogical identities. How can ^{28}Si- and ^{44}Ti-rich solid or gaseous material from the innermost zones of the exploding star be mixed with the outer, C-rich zones, without substantial admixture of intervening oxygen, before or during condensation of graphite and SiC grains

in the outer zones? Travaglio et al. (1999) investigated numerous zone mixing scenarios, but were unable to quantitatively reproduce the isotopic ratios observed in grains and simultaneously maintain the condition C/O $\geq$ 1 for the mixtures.

As a way out of this predicament, Clayton (1998) has suggested that equilibrium thermodynamic calculations do not apply to supernova ejecta because ejecta are so intensely irradiated that CO and other gas phase molecules are nearly completely dissociated, liberating C atoms from CO and making them available to form graphite and carbides, even in O-rich ejecta. It is difficult to envision irradiation conditions that destroy nearly all molecules while simultaneously allowing thousands of atoms to bond to one another to form grains. Nevertheless, in an effort to extend the Clayton (1998) hypothesis to its ultimate conclusion, we perform condensation calculations for supernova zones in which C/O < 1 where, first, CO is prevented from forming and, second, where all polyatomic gaseous molecules are prevented from forming. The results are compared with results for condensation from zones of the same compositions where all molecules are allowed to form in complete chemical equilibrium with one another. The objective is to see, assuming that grains can even form under conditions where molecules are destroyed, what the most thermodynamically stable condensate phases would be and, in particular, whether graphite, SiC and TiC are among them. A preliminary version of this work was presented by Ebel and Grossman (1998).

2. SUPERNOVA STRUCTURE

We begin with the results of calculations by Woosley and Weaver (1995), for the mass fractions of 148 isotopes of elements H through Co produced by a combination of presupernova static burning and explosive nucleosynthesis, in 543

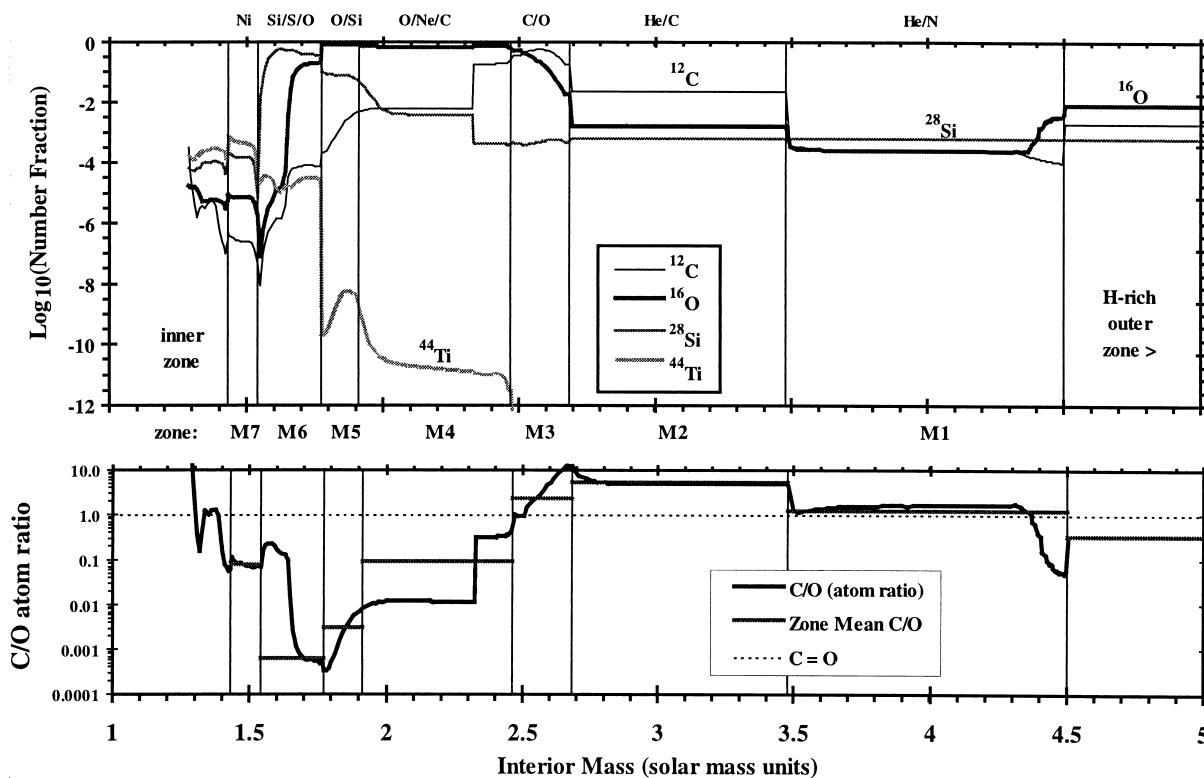*Author to whom correspondence should be addressed (debel@midway.uchicago.edu).

Fig. 1. Compositions and C/O ratios of inner regions of the 15 $M_\odot$ supernova model of Woosley and Weaver (1995), after Travaglio et al. (1999, their Fig. 10; S. Amari, private communication).

ejecta shells of a 15 solar mass supernova (Fig. 1). Meyer et al. (1995) grouped these shells into seven zones (M1-M7), each labeled for its most abundant elemental species. In Table 1, the average composition of each zone has been calculated from the compositions of its constituent shells, without accounting for isotope decay, for each of 22 elements. Inner zone M7 is rich in Si, Ca, Ti, Cr, Fe and Co, and also Ni (Ni was not modeled by Woosley and Weaver, 1995). Zone M6 is rich in S and Si. Zones M6 and M7 are highly enriched in ^{44}Ti and ^{28}Si and are thus thought to be the source of the ^{44}Ca and ^{28}Si anomalies in the SN grains. In these zones, C/O << 1, and the combined abundances of C, O and S are insufficient to combine with the available cationic elements, with consequences to be explored below. Zones M5 and M4 serve as an ^{16}O-rich barrier, ~1 solar mass wide, between the heavy-element rich inner zones and the outer, C-rich zones: M3, M2 and M1.

These zone compositions will be used below as initial bulk compositions for condensation calculations. The metal-rich zone interior to M7, which is not ejected, and the outer, H-rich zone will not be considered further. Travaglio et al. (1999) constructed a series of mixing models combining shells M1–M7, constrained to match as closely as possible the isotopic features of presolar, low-density graphite grains of presumed Type II supernova origin while maintaining the condition C/O ≥ 1. Below, we investigate whether this condition holds for equilibrium condensation in all supernova shells, and probe the proposal of Clayton (1998) that destruction of molecules in supernova shells allows graphite formation at C/O < 1.

3. EQUILIBRIUM CONDENSATION

To understand disequilibrium scenarios, it is useful first to consider equilibrium condensation. Even in a system where rates of molecular association and destruction are important factors, the bonding characteristics and relative thermal stabilities of condensed phases, as represented by their thermodynamic properties, are likely to influence strongly the mineralogical identities and composition of condensed matter. The calculations below explore the identities of condensates for various assumptions regarding molecular speciation in the vapor phase. All calculations described in this paper were performed using the methods and data described by Ebel and Grossman (2000) and Ebel et al. (2000), and were terminated when refractory elements (e.g., Ti, Si) became depleted in the gas phase to a mole fraction of $<10^{-24}$. A total pressure (P^{tot}) of 10^{-6} bar is adopted for all the calculations. At higher P^{tot}, sequences of condensates are similar, but vapor becomes saturated with liquid and/or solid phases at higher temperatures than at lower P^{tot}.

3.1. Equilibrium Condensation in Reference Cosmic Gas

The condensation of a gas of the canonical solar, or so-called 'cosmic', composition provides a well-understood reference point for discussion of condensation calculations for supernovae. The subject has been covered elsewhere in detail (e.g., Grossman, 1972; Yoneda and Grossman, 1995; Lodders and Fegley, 1995; Ebel, 2000; Ebel and Grossman, 2000). Figure 2

Table 1. Average elemental abundances in SN zones. Abundances are normalized to 10^6 atoms of Si in each zone, with solar abundance (Anders and Grevesse, 1989) for reference. Data sources as for Figure 1.

	SOLAR	Ni zone M7	si/S/O zone M6	O/Si zone M5	O/Ne/C zone M4	C/O zone M3	He/C zone M2	He/N zone M1	H zone
H	2.79E + 6	1.051E + 6	8.580E + 1	1.177E + 1	2.021E + 1	2.307E + 1	2.518E + 1	1.833E + 9	2.569E + 1
He	2.72E + 9	4.848E + 9	2.069E + 4	6.837E + 2	4.631E + 4	2.418E + 9	9.348E + 9	9.222E + 9	3.216E + 9
C	1.01E + 7	6.179E + 3	1.929E + 2	4.523E + 4	3.828E + 7	1.109E + 9	7.919E + 7	1.764E + 6	6.803E + 6
N	3.13E + 6	6.353E + 4	2.405E + 1	8.038E + 2	1.576E + 4	5.243E + 4	1.864E + 7	3.447E + 7	9.704E + 6
O	2.38E + 7	7.656E + 4	2.963E + 5	1.479E + 7	2.210E + 8	4.873E + 8	1.546E + 7	1.472E + 6	2.047E + 7
F	8.43E + 2	2.239E + 1	3.233E + 2	1.225E + 1	8.995E + 3	5.970E + 3	5.834E + 5	5.679E + 1	6.907E + 2
Ne	3.44E + 6	1.014E + 5	2.832E + 2	7.649E + 4	2.762E + 7	5.620E + 7	7.487E + 6	3.231E + 6	3.400E + 6
Na	5.74E + 4	3.361E + 3	2.560E + 0	1.235E + 3	6.529E + 5	3.974E + 5	3.095E + 5	3.029E + 5	9.908E + 4
Mg	1.074E + 6	1.674E + 5	1.881E + 3	4.828E + 5	6.601E + 6	1.095E + 7	1.052E + 6	1.019E + 6	1.072E + 6
Al	8.49E + 4	3.678E + 4	1.366E + 3	6.213E + 4	6.604E + 5	9.948E + 4	1.091E + 5	1.392E + 5	8.579E + 4
Si	1.00E + 6	1.000E + 6	1.000E + 6	1.000E + 6	1.000E + 6	1.000E + 6	1.000E + 6	1.000E + 6	1.000E + 6
P	1.04E + 4	1.848E + 4	1.912E + 3	1.929E + 4	4.192E + 4	7.571E + 4	1.107E + 4	1.045E + 4	1.040E + 4
S	5.15E + 5	3.756E + 5	5.570E + 5	1.700E + 5	5.501E + 4	2.604E + 5	5.045E + 5	5.143E + 5	5.148E + 5
Cl	5.24E + 3	9.971E + 3	1.260E + 3	2.679E + 3	7.216E + 3	3.057E + 4	6.220E + 3	3.951E + 3	3.774E + 3
Ar	1.01E + 5	5.473E + 5	1.107E + 5	4.793E + 3	9.342E + 3	6.659E + 4	9.822E + 4	1.009E + 5	1.011E + 5
K	3.77E + 3	2.736E + 5	1.611E + 3	1.164E + 2	9.072E + 2	2.469E + 3	4.274E + 3	3.802E + 3	3.778E + 3
Ca	6.11E + 4	2.064E + 6	8.068E + 4	1.105E + 2	2.630E + 3	2.403E + 4	5.958E + 4	6.105E + 4	6.111E + 4
Ti	2.40E + 3	1.868E + 6	2.716E + 2	4.431E + 1	5.130E + 2	2.149E + 3	2.396E + 3	2.402E + 3	2.401E + 3
Cr	1.35E + 4	3.181E + 6	1.523E + 3	3.653E + 1	1.015E + 3	8.172E + 3	1.336E + 4	1.351E + 4	1.353E + 4
Mn	9.55E + 3	1.555E + 5	1.054E + 3	1.400E + 1	2.173E + 2	5.247E + 3	1.247E + 4	9.813E + 3	9.566E + 3
Fe	0.00E + 5	4.309E + 6	6.070E + 4	1.266E + 3	4.379E + 4	6.010E + 5	8.911E + 5	9.006E + 5	9.011E + 5
Co	2.25E + 3	1.023E + 7	5.776E + 3	5.544E + 2	1.134E + 4	1.262E + 4	3.975E + 3	2.321E + 3	2.253E + 3
(Si + Ti)/(C + O):	0.0296	34.663	3.3737	0.0674	0.0039	0.0006	0.0106	0.3098	0.0368
C/O:	0.42437	0.0807	0.00065	0.00306	0.17322	2.27595	5.12229	1.19817	0.33238
^{16}O/^{18}O:	499	4900	2.39E + 10	2.37E + 10	3.83E + 6	1850	0.370	11	600
^{14}N/^{15}N:	272	0.211	0.005	0.003	0.046	0.891	61	27000	1870
^{26}Al/^{27}Al:		0.874	0.001	0.005	0.007	0.008	0.015	0.243	0.001

illustrates the distribution of atoms among condensed species with decreasing temperature, at $P^{tot} = 10^{-6}$ bar, in a gas of solar composition. The number density of gaseous molecules in this system is of order 10^{12} cm^{-3}. The important point is the order of condensation of oxides of Al, Ca, Ti, Mg, and Si, and metallic Fe. The dominant gaseous species of these metals in the P-T range where condensation of solids occurs are Al$_{(g)}$, Ca$_{(g)}$, Ti$_{(g)}$, Mg$_{(g)}$, SiO$_{(g)}$, and Fe$_{(g)}$. Refractory Al-, Ca- and Ti-oxides condense at high temperature, followed by Mg-silicates and metal. The stability of gaseous SiO prevents substantial condensation of Si into silicate minerals until a temperature several hundred degrees below the appearance temperature of the first condensed solid. In solar gas, SiO$_{(g)}$ accounts for a small fraction of the available oxygen.

3.2. Equilibrium Condensation in Supernova Shell Compositions

Travaglio et al. (1999) set C/O $\geq$ 1 as a condition for the condensation of graphite and carbides in supernova shell mixtures, based on the requirement that C/O $\geq$ 1 for equilibrium condensation of these phases from a gas of otherwise solar composition. Is this condition necessary for the radically non-solar bulk compositions of various supernova shells? The C/O $\geq$ 1 condition does, indeed, apply in gases with total C + O abundance greater than the total of oxide- and carbide-forming elements, particularly Si, but this condition does not hold in the inner zones M6 and M7. In these zones, [Si + Ti] $>>$ [O + C] (Table 1), and SiO$_{(g)}$ competes with CO$_{(g)}$ for the available O, complicating the simple condition assumed by Travaglio et al. (1999). Condensation in zone M6 is dominated by an ~50/50 Fe-Si alloy, condensing at

1670 K, with trace amounts of TiC appearing at 1560 K, and TiN at 1510 K. The stable alloy is likely to be iron silicide (FeSi), for which we do not have thermodynamic data. In zone M7, TiC appears at 1570 K, and TiN at 1540 K, containing all the C and N, respectively. Abundant metallic Ti appears at 1460 K, and Fe$_{0.65}$Si$_{0.35}$ alloy appears at 1430 K, incorporating 30% Co by 1330 K. In zones M6 and M7, neither graphite nor SiC form in the 200° temperature range over which condensation occurs and below which the computation was terminated.

Zone M5 is the innermost zone in which [Si + Ti] $<<$ [O + C]. Figure 3 illustrates the distribution of matter during equilibrium condensation of a fully speciated gas with the bulk composition of this O- and Si-rich zone. In the vapor, SiO$_{(g)}$, Mg$_{(g)}$ and Al$_{(g)}$ account for most of the Si, Mg and Al. From high to low temperature, condensation proceeds from Al-rich to Mg- and Si-rich phases, until the fraction of the atoms condensable at high temperature, ~0.25, is reached. Because condensation temperatures are so high in this hydrogen-poor gas, a silicate liquid co-condenses with olivine. Because the system is rich in Si, the liquid is also Si-rich, containing ~75 wt.% SiO$_2$, 15% MgO and 10% Al$_2$O$_3$ below 1760 K. Silica polymorphs crystallize from the liquid below 1550 K.

Upon cooling a gas having the composition of Mg-rich zone M4, corundum condenses at 2100 K, containing about 0.7% of the total atoms by 1880 K, where it reacts with gas to form MgAl$_2$O$_4$ (spinel), containing 0.9% of the atoms. Mg-olivine and periclase (MgO) form at 1790 K, and by ~1700 K, ~6% of the total atoms have condensed, 0.8% as spinel, 2.4% as olivine and 2.8% as MgO. This assemblage persists as the system cools to below 1380 K.
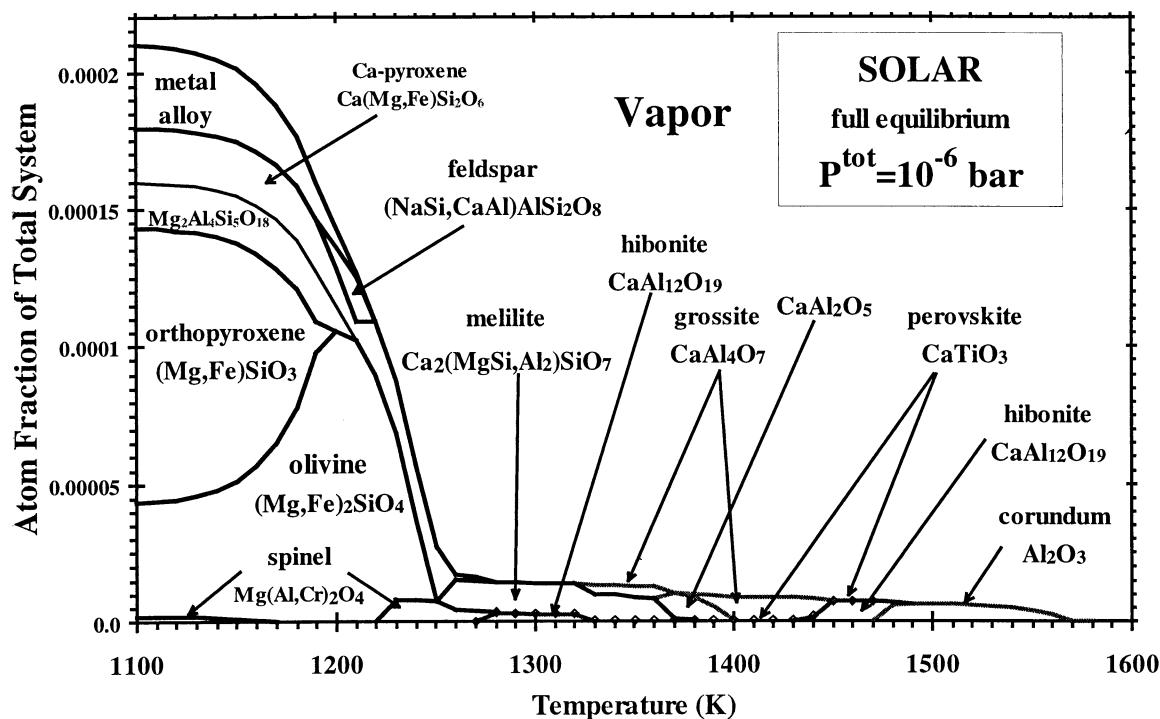
Fig. 2. Equilibrium condensation in a gas of solar (cosmic) composition. Gaseous molecules are not suppressed.

In C-rich zone M3, graphite condenses at ~2350 K and rapidly increases in amount until, at 2200 K, nearly all of the C in excess of O (C-O = 15.2% of the atoms in the system) has condensed. Upon further cooling, small quantities of TiC form at 1690 K, SiC at 1430 K, and metal alloy at 1250 K. In zone M2, graphite condenses at ~2170 K, incorporating nearly all the carbon not in $CO_{(g)}$ by 1980 K. Small amounts of SiC appear at 1460 K, metal alloy at 1270 K, and
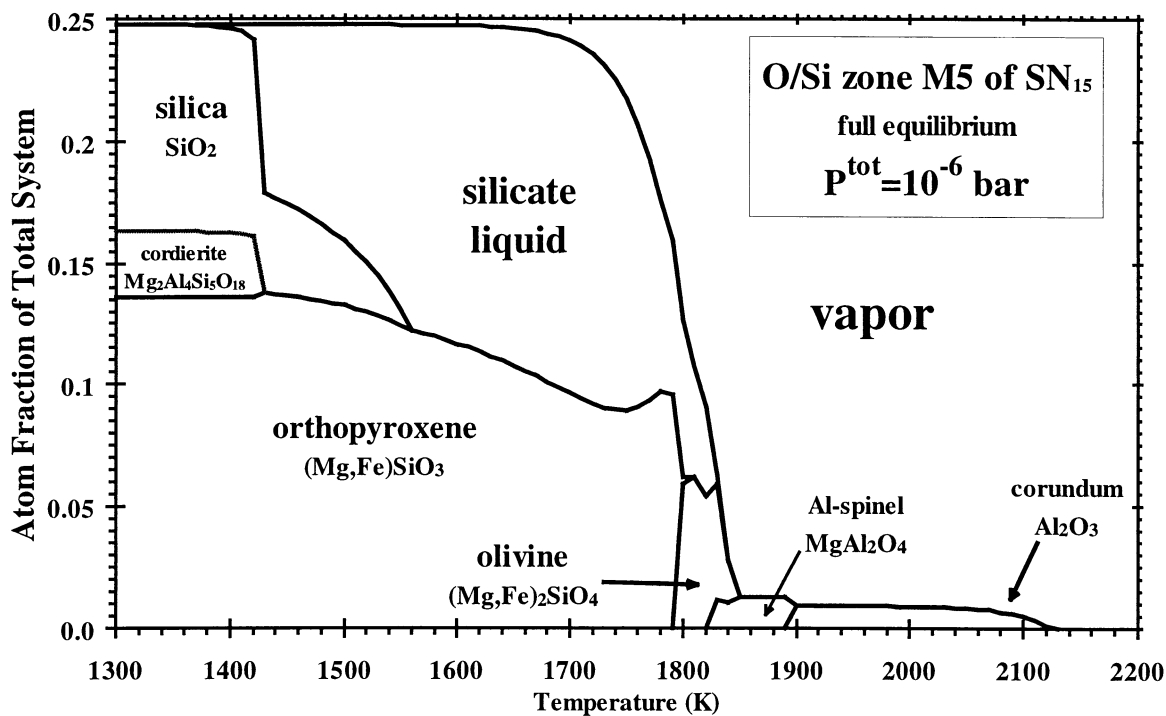
Fig. 3. Equilibrium condensation in O-, Si-rich zone M5.

chromium carbide (Cr_3C_2) at 1150 K. Above 1000 K, 98% of the condensed atoms are graphite, and no TiC has condensed.

These results suggest that Travaglio et al. (1999) were correct in imposing the condition C/O $\geq$ 1 for carbide formation at chemical equilibrium only in mixtures with [O + C] >> [Si + Ti]. Because the refractory metals are present in overwhelming abundances in zones M6 and M7, however, [44]Ti-rich TiC can form even though C/O < 1. The calculated condensation sequences of zones M3 and M2 are inconsistent with the textures observed in supernova grains (Bernatowicz et al., 1998; Nittler et al., 1996), as the calculations predict graphite to condense before TiC during cooling, while the textures suggest TiC formed first. If TiC grains from zone M6 or M7 somehow survived passage through the massive O-rich zones into the outer C-rich zones, they could have served as condensation nuclei for graphite or SiC in zones M3 and M2. If the [44]Ti in these grains was inherited from inner zone ejecta, what was the carrier for the correlated [28]Si, and why are there no subgrains of TiN or Si-rich metallic FeNi?

4. DISEQUILIBRIUM CONDENSATION

4.1. A Proposed Disequilibrium Model

Detection of gaseous CO in SN 1987A has given rise to physico-chemical models which compute the effects of the ultraviolet radiation field and of secondary electrons and He^{+} ions produced by gamma rays from decay of [56]Co on the abundance of CO in supernova ejecta. While Rawlings and Williams (1990) concluded that the CO abundance was most sensitive to the UV flux intensity and that secondary electrons have little effect on the chemistry, Liu and Dalgarno (1995) found that it was the secondary electrons and He^{+} ions that are most destructive of CO. Both models predict that the CO/C ratio in O-rich ejecta is 10^{-2} to 10^{-3} in the 2000 to 3000 K temperature range, a result very different from the case of chemical equilibrium, in which nearly all the C should be in CO.

Clayton (1998, 1999), Liu and Clayton (1999), and Clayton et al. (1999) suggested that CO dissociation by fast electrons, which are destructive "also for other molecules," makes C atoms available for "the growth of carbonaceous dust, either graphite or TiC and SiC." Because the destruction of gaseous CO frees both C and O, the chemistry of grain growth, assuming the existence of C_n 'clusters', would then be determined solely by the competing kinetics of C combination on grains, versus oxidation of grains by ionic O. Clayton (1998) speculated that very large differences in the sticking and/or bonding efficiencies of C and O might allow the formation of low-density graphite grains, even in an O-rich environment, because some fraction of clusters C_n survives to yield C_{n+1}, and so on to $n > 10^{12}$.

Numerous extraordinary phenomena will need to be accounted for to make an accurate and rigorous calculation of supernova ejecta chemistry possible, such as (1) high fluxes of energetic particles, (2) ionization states and lifetimes of gaseous species, (3) electronic activation of grain surfaces, and (4) sticking and bonding efficiencies of gaseous species interacting with grains, to name a few. The dynamics of heterogeneous grain nucleation and growth are poorly understood, even in laboratory contexts, and the sticking and bonding characteristics of C and O atoms or ions on grains, clusters, or molecules in the presence of a radiation field are unknown, free parameters in the Clayton (1998) model. In marked contrast, the standard thermodynamic properties of gaseous molecules, liquids, and mineral phases are well constrained. It may be dangerous to abandon this information, given that it allows parameterization of the thermal stabilities of a wide variety of mineral species relevant to the problem at hand. When mineral species are selected for kinetic investigation without regard for thermodynamic constraints, many of the phases chosen may be unstable relative to others whose formation kinetics, though uninvestigated, may make them even more probable reaction products than the chosen ones. An appropriate use of thermodynamic calculations is, then, to predict which mineral species would be most likely to persist under particular circumstances. To this end, we calculate here the equilibrium condensation of gases having the compositions of supernova shells, in which formation of either the CO molecule alone, or all of the gaseous molecules (e.g., CO, SiO, H_2O, etc.) has been completely suppressed. This scenario, admittedly artificial in the sense that grains are allowed to form while all molecules are absent, is pursued in an effort to see whether graphite, SiC and TiC are the most likely minerals to form in the environment envisioned by Clayton et al. (1999).

4.2. Condensation without the CO Molecule

Before considering the relatively complex case of how suppression of all molecules will affect the chemistry of a cosmic gas, it is instructive to consider first the simple case in which the only molecule prevented from forming is $CO_{(g)}$, the most crucial molecule in dictating the types of condensate phases which can form. When the CO molecule is prevented from forming in a gas of solar composition (C/O = 0.42), most of the oxygen forms CO_2 instead, reducing the partial pressure of molecular oxygen, relative to a gas containing CO, by slightly more than one log unit at 1570 K and $P^{tot} = 10^{-6}$ b. Consequently, the phases corundum, hibonite, perovskite, melilite, spinel, pyroxene and olivine all appear at temperatures 40 to 60° lower than in a solar gas with CO present. This can be seen by comparison of Figures 2 and 4. Simple removal of CO does not cause graphite or carbides to become stable in a gas of solar composition, nor does it substantially affect the identities of condensed species in the supernova shells. Several workers (Lattimer et al., 1978; Larimer and Bartholomay, 1979; Sharp and Wasserburg, 1995; Lodders and Fegley, 1997) have shown that in an otherwise solar gas, condensate chemistry becomes dominated by carbides and graphite when C is increased sufficiently that C/O > ~0.98. As illustrated in Figure 5, suppression of the CO molecule reduces this critical ratio to about 0.48, almost exactly one half its value when CO is present, because CO_2 consumes twice as much oxygen per carbon atom as CO. Inspection of Figure 5 reveals, however, that in the CO-absent case, the stability field of SiC does not expand to C/O ratios as low as that for graphite. In fact, it disappears entirely. When C/O > 0.48 in the CO-absent case, the excess C forms graphite at high temperature, just as it does in the equilibrium case at C/O ratios > 0.98. As the temperature falls, more graphite
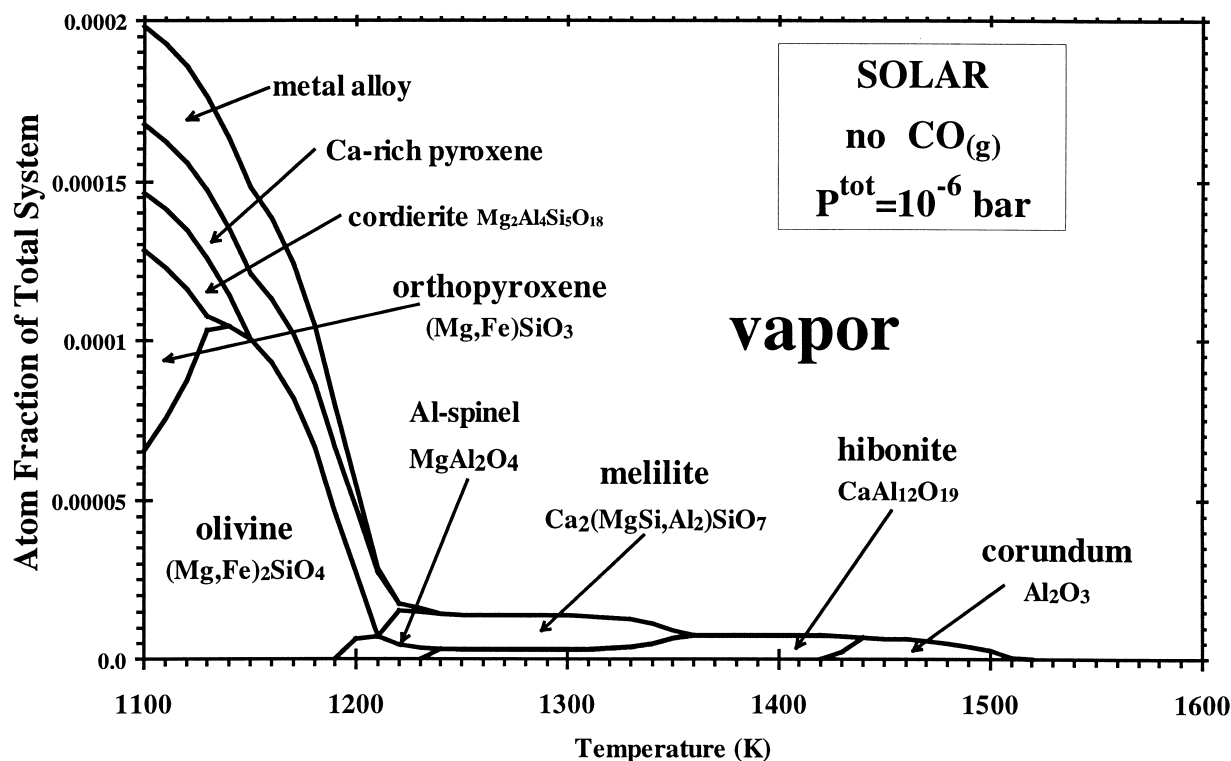
Fig. 4. Condensation from solar gas at $P^{tot} = 10^{-6}$ bar, with no $CO_{(g)}$ present.

condenses in both cases, liberating twice as much oxygen per atom of condensed C in the CO-absent case than in the equilibrium case. As a consequence, the oxygen fugacity is higher in the CO-absent case, causing stabilization of Si in the gas as $SiO_{(g)}$ and preventing condensation of SiC. The reason why an analogous suppression of TiC condensation does not occur in the CO-absent case is that the enhanced oxygen fugacity has a smaller effect on the relative proportions of $Ti_{(g)}$ and $TiO_{(g)}$.

4.3. Condensation from a Gas Made of Free Atoms

4.3.1. Reference solar gas

When all gaseous molecular species are prevented from forming, strange things happen. Graphite indeed condenses at ~2110 K in a cooling solar gas at $P^{tot} = 10^{-6}$ bar but, since $SiO_{(g)}$ cannot form, graphite is followed by silica (SiO_2) at ~1860 K, and various other oxygen-bearing phases as shown in Figure 6. Over 85% of the Si has condensed by 1825 K. Mg begins to condense as orthopyroxene solid solution (Mg,Fe) SiO_3 at 1570 K, and 85% of the Mg has condensed by 1530 K. Based on this example, one learns that the absence of $SiO_{(g)}$ stabilizes SiO_2-rich condensates, causing Si to condense before Al, Ca, Ti, Fe or Mg in free-atom gases, rather than after Al, Ca, and Ti, as in solar gas. Under such conditions, the condensation of SiC is even less likely than in a system where polyatomic gaseous molecules are present.

4.3.2. Supernova shell compositions

In the metal-rich innermost zones M6 and M7, [Si + Ti] >> [O + C] (Table 1). Generally, Si has a much greater affinity for

O than does Ti, and Ti has greater affinity for C than does Si. When C and O are free atoms, in zone M6, Ti condenses as TiN, TiC, and metal, while Si condenses as liquid and/or solid SiO_2, and also as metal alloyed with Fe. In zone M7, superabundant Ti combines with all the available C, O, N and S at temperatures above 1400 K. In the absence of gaseous molecules, neither SiC nor graphite are stable in zone M6 or M7.

Condensation in Si-, O-rich zone M5 illustrates the concepts which apply to all other zones where [Si + Ti] << [O + C]. When gaseous molecules are suppressed in the condensation of zone M5, the C liberated from CO does indeed condense as graphite, at 2240 K (Fig. 7). This is in accord with the suggestion of Clayton et al. (1999). The O liberated from CO, however, is available to form oxide and silicate condensates at higher temperatures than in a fully speciated gas, in which the SiO molecule stabilizes Si in the vapor phase. Because SN zone M5 is rich in Si, this free Si combines with the free O to condense as a liquid consisting of ~95 wt.% SiO_2 and ~5 wt.% Al_2O_3, at 2270 K. This liquid incorporates MgO as it condenses below 2000 K, with MgO reaching 20 wt.% by 1810 K, when orthopyroxene ($MgSiO_3$) begins to crystallize from the liquid. At 1800 K, Ti is concentrated in the liquid and must be removed from the calculation because its abundance in the vapor phase is below computational resolution. Titanium will crystallize from this liquid as an oxide or silicate, not a carbide. The computation was terminated at 1680 K, when Si became too depleted in the vapor phase.

A similar condensation sequence occurs in zone M4 in the absence of gaseous molecules. Graphite condenses at very high temperatures, followed by a SiO_2-rich liquid at 2200 K, and by
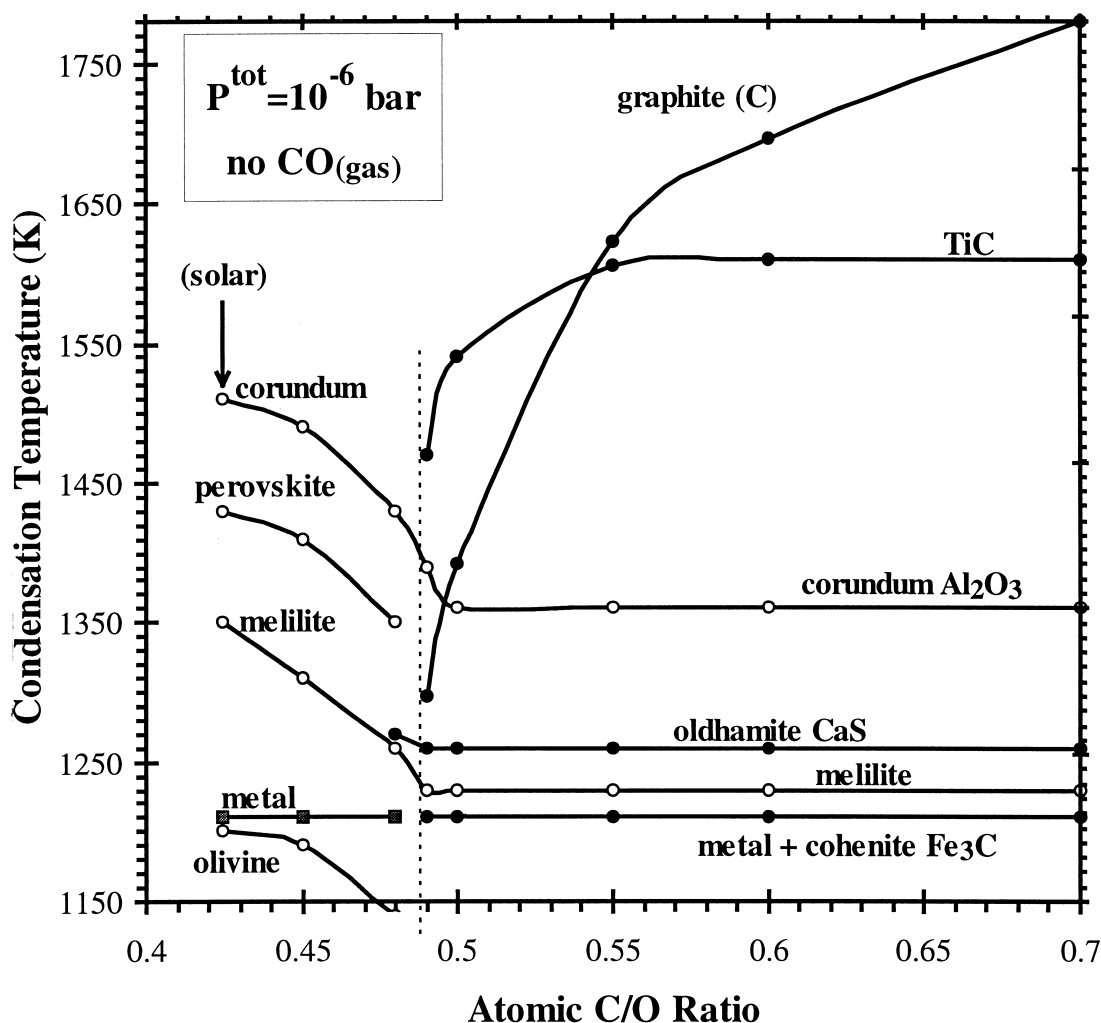
Fig. 5. Condensation of C-enriched solar gases at $P^{tot} = 10^{-6}$ bar, with no $CO_{(g)}$ present.

magnesite $MgCO_3$ below 1900 K. In the absence of gaseous molecules, Si condenses as SiO_2, not SiC, in all of the zones M1–M5.

These examples dramatically illustrate the central result of this exercise. If the partial pressures of molecules are virtually zero, the element Si, which is normally present as the gaseous oxide SiO, will condense (i.e., become thermodynamically stable) as a solid or liquid oxide at temperatures much higher than would occur in fully speciated gases. As a consequence, SiC is even less likely to form in O-rich gas devoid of molecular species than in a gas with equilibrium speciation. It is incumbent upon proponents of the idea that supernova condensates formed in the absence of molecules to discover realistic kinetic pathways that lead to condensation of the observed SiC, which is thermodynamically unstable, instead of SiO_2, which is thermodynamically stable, in O-rich gases. Alternatively, if graphite indeed formed in the absence of gaseous molecular species as Clayton et al. (1999) suggest, one might be justified in searching for presolar SiO_2, as this phase would be expected to accompany extrasolar graphite formed in this way. Inclusions of SiO_2 have not been discovered in searches of extrasolar graphite, but this may be due to the harsh HF treatments to which the meteorite residues have been subjected.

5. CONCLUSIONS

The assumption of Travaglio et al. (1999) that C/O ≥ 1 for carbide formation in chemical equilibrium, holds only in gases where [O + C] >> [Si + Ti]. Grains of TiC, and also of TiN and metallic Fe, Si and Ti, can form in cooling material from the innermost shells, but it is difficult to explain the survival of such grains on ejection through O-rich zones, into C-rich zones where they could be incorporated by stable graphite and SiC.

Equilibrium condensation calculations certainly do not address the complete reality of grain formation in supernova ejecta; however, an accurate treatment addressing kinetic phenomena is not possible given present knowledge. To ignore thermal stability relations is to discard valuable information bearing on the identities of potential condensate minerals. Even assuming that the gas chemistry is governed by kinetics, such as in the case of destruction of molecules by suprathermal electrons, relative mineral stabilities can be assessed and used
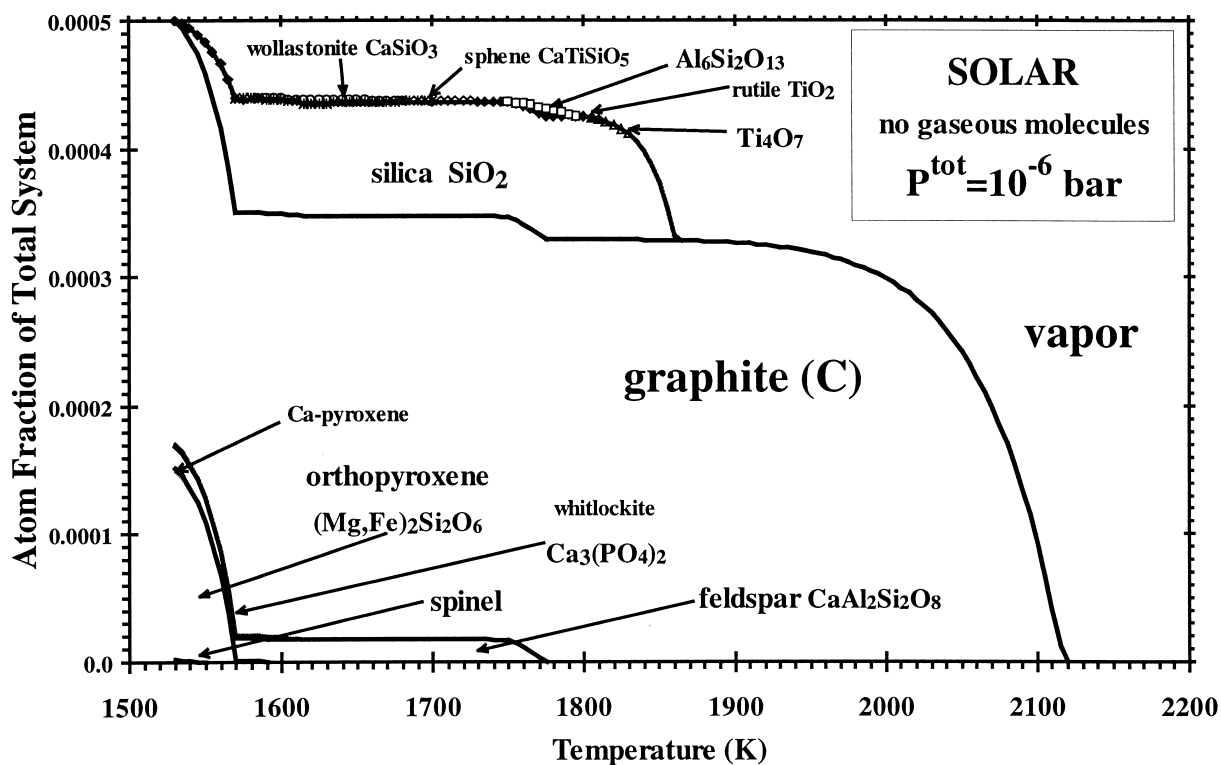
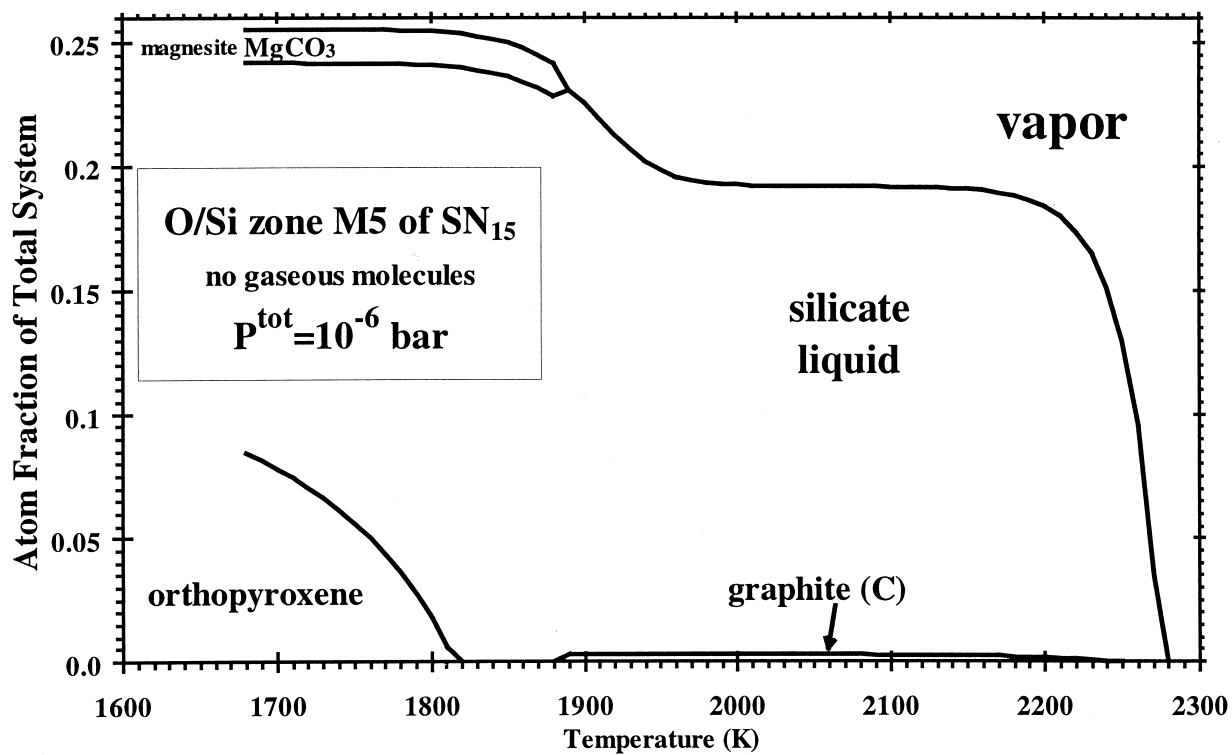Fig. 6. Condensation of solar gas, all gaseous molecules suppressed.

Fig. 7. Condensation of gas of SN zone M5, all gaseous molecules suppressed.

to predict the most likely condensates to form. It should be the aim of kinetic studies, preferably grounded in directly relevant experiments, to show specifically why critical equilibrium phases would not form and why specific, less stable phases would replace them. If the effective partial pressures of polyatomic molecules are extremely low, then supernova graphite grains are indeed thermodynamically stable, even in O-rich ejecta. But the requisite complementary phases found in meteorites, e.g., TiC and SiC, are not stable in the O-rich zones M5 and M4 under these conditions, while grains which are not observed (e.g., SiO_2) should be produced in abundance. Without an understanding of why TiC and SiC accompanied graphite formation, and SiO_2 did not, the problem of reconciling the zone where the mineralogical identities of supernova grains were established with the zone implied by their isotopic compositions remains unsolved. This may point to the need for serious revisions to initial compositions assumed in supernova shell models.

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