PART IX
THE PRIMITIVE SOLAR NEBULA

1

HIGH-TEMPERATURE CONDENSATES IN CARBONACEOUS CHONDRITES

L. GROSSMAN

Equilibrium thermodynamic calculations of the sequence of condensation of minerals from a cooling gas of solar composition play an important role in explaining the mineralogy and trace element content of different types of inclusions in carbonaceous chondrites. Group IV B iron meteorites and enstatite chondrites may also be direct condensates from the solar nebula. Condensation theory provides a framework within which chemical fractionations between different classes of chondrites may be understood.

I. CONDENSATION OF A GAS OF SOLAR COMPOSITION

Figures 1-4 summarize the major conclusions of equilibrium thermodynamic calculations of the sequence of condensation of minerals from a cooling gas of solar composition. The computations were performed as in Grossman (1972) and Grossman and Larimer (1974) except that the abundance table of Cameron (1973) was employed. A total pressure of 10^{-3} atm is used here but detailed calculations show that the condensation sequence remains virtually the same at 10^{-4} and 10^{-5} atm (Grossman 1976).

The first condensate containing any of the major elements is corundum, Al_2O_3, which first appears at 1742°K and consumes essentially all of the Al above 1600°K (see Fig. 1). It begins to react with the gas at 1608°K to form the mineral melilite, a silicate of Ca, Al and Mg, which forms at the expense of the pre-existing corundum. Corundum left in excess of this reaction reacts with gaseous Mg at 1533°K to form spinel, $MgAl_2O_4$. In Fig. 2, it is seen that perovskite, $CaTiO_3$, is the first Ca-bearing phase to condense, appearing at 1632°K. Thermodynamic data for gaseous TiO have changed considerably since this figure was drawn and, as a result, the condensation temperature of perovskite should be raised to 1680°K. In either case, all the Ti is condensed in this phase above 1600°K. The major sink for Ca at high temperature is seen to be melilite into which the rest of the Ca condenses totally above 1500°K. Finally, melilite reacts completely at equilibrium to form Ca-rich pyroxene, $CaMgSi_2O_6$, at 1442°K.

Figure 3 shows that a significant fraction of the total Mg begins to condense only below 1430°K with the appearance of forsterite, Mg_2SiO_4, which later reacts with the vapor to form enstatite, $MgSiO_3$. The condensation curve for iron in a nickel-iron alloy is shown for reference in this figure from which it can be seen that a significant fraction of the total Fe begins to condense only below 1460°K. A similar situation is seen in Fig. 4 for Si which condenses in massive amounts

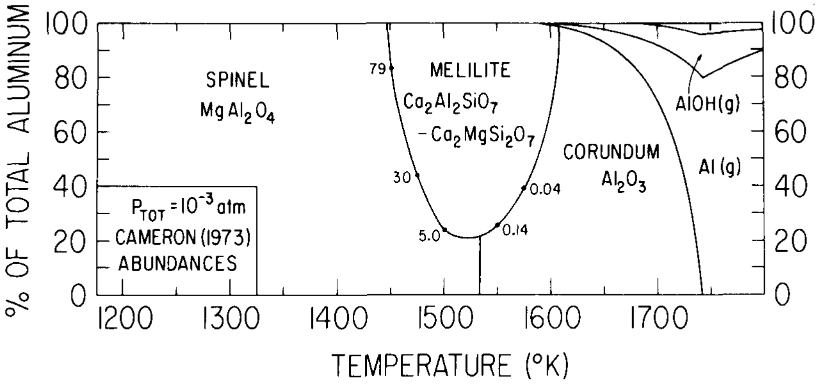

Figure 1. *The distribution of Al between crystalline phases and gas in a system of solar composition. At any temperature, the percent of the total Al present in each phase can be read from the figure.*

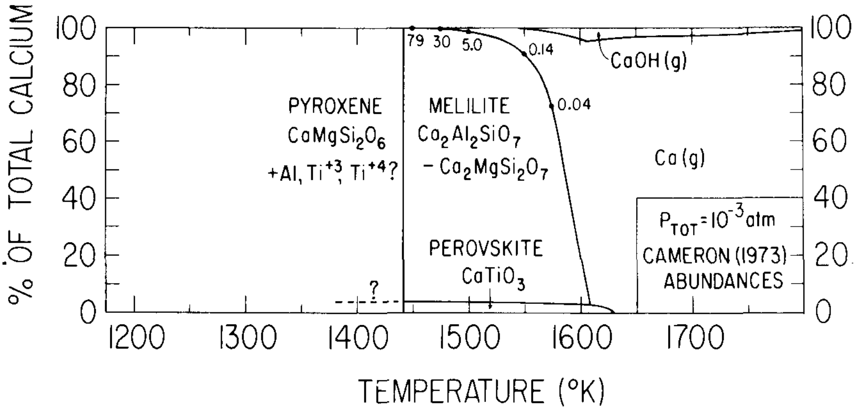

Figure 2. *The distribution of Ca between crystalline phases and gas in a system of solar composition.*

only below 1430°K with the appearance of magnesian silicates. The calculations thus show the rather unusual phenomenon that Ca, Al and Ti, relatively minor elements in terms of their solar abundances, are totally condensed at temperatures above the condensation points of the bulk of the Fe, Mg and Si, the most abundant, rock-forming metallic elements in the solar system.

It should be noted that forsterite and enstatite are the pure Mg end-members of the olivine and Ca-poor pyroxene solid solution series, respectively, in which Fe and Mg freely substitute for one another in the crystal structures of these minerals. In this temperature range, however, the nebula is so reducing that metallic Fe, rather than Fe^{+2}, is favored, leaving no divalent iron for solution in the magnesium silicates. These remain Fe^{+2}-free until the nebula becomes more oxidizing at much lower temperatures.

2. METEORITE CLASSIFICATION

Before examining evidence for primitive condensates in meteorites, a brief

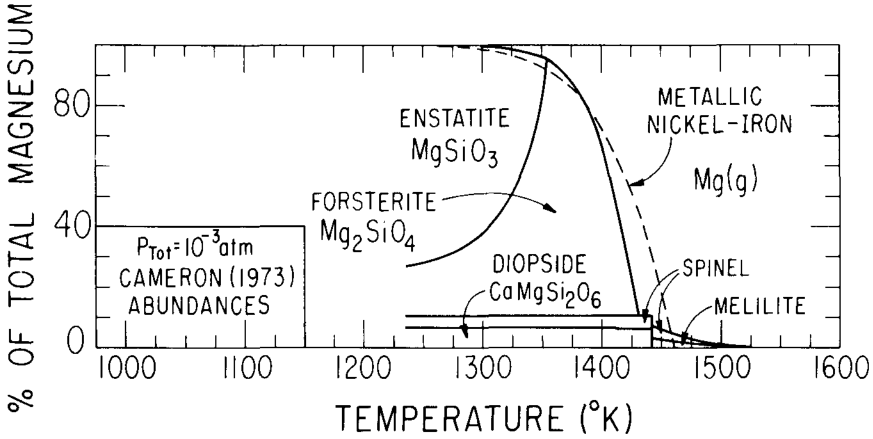

Figure 3. The distribution of Mg between crystalline phases and gas in a system of solar composition. The condensation curve for iron as a nickel-iron alloy is shown for reference.

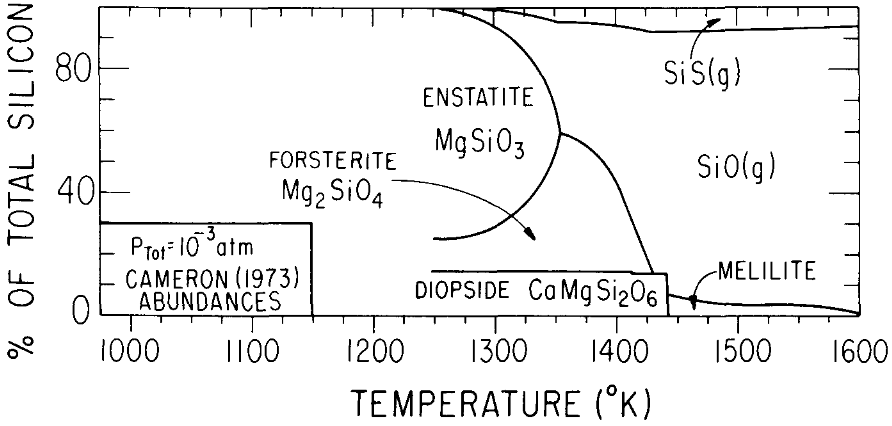

Figure 4. The distribution of Si between crystalline phases and gas in a system if solar composition.

review of the different types of meteorites will be useful. In Fig. 5, the meteorites are first subdivided according to the relative proportions of silicates, metallic nickel-iron and troilite (FeS), which they contain. Iron meteorites are composed almost entirely of metal and sulfide and achondrites almost entirely of silicates. Stony irons contain roughly equal proportions of silicates and sulfides + metal and chondrites are characterized by a greater proportion of silicates.

The iron meteorites are divided into sub-classes according to their nickel content and structure, the stony-irons according to their texture and chemistry and the achondrites primarily by their CaO and FeO contents. The chondrites are subdivided according to the relative proportions of iron in reduced (metallic or sulfide) and oxidized (oxide or silicate) form, with enstatite chondrites being the most reduced and carbonaceous chondrites the most oxidized. The ordinary

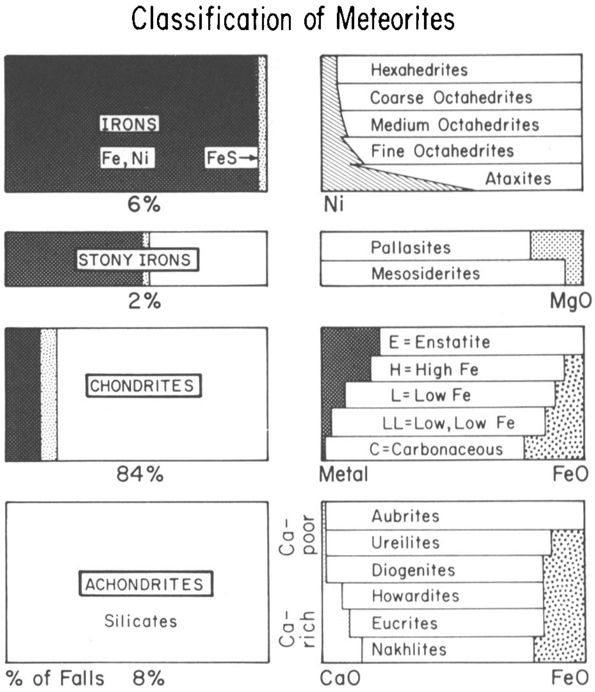

Figure 5. Meteorites can be broadly classified according to their relative proportions of silicate and metal phases. Further subdivision is based on composition and structure. After Anders (1968).

chondrites, consisting of bronzite or H-group chondrites, hypersthene or L-group and amphoterite or LL-group, occupy different positions between these two extremes. So far, the search for primitive condensates in meteorites has centered on carbonaceous chondrites, of which Allende is a prime example.

3. THE ALLENDE METEORITE

A. General

Over two tons of this type 3 carbonaceous chondrite fell in northern Mexico in February, 1969 (Clarke *et al.* 1970). Large samples were collected and distributed around the world shortly after its fall, accounting for the fact that it is the most thoroughly studied chondrite by far. Allende contains a wide variety of mineralogically-distinct, mm- to cm-sized inclusions, each of which can be individually sampled and analyzed. Some of these are discussed below.

B. Coarse-Grained, Ca-Rich Inclusions

These inclusions have been studied in great detail. See Grossman and Larimer (1974) and Grossman and Ganapathy (1976*a*) for references. Some of these inclusions are composed exclusively of melilite, spinel and perovskite, a phase assemblage identical to that predicted for the highest-temperature condensates from a gas of solar composition. Larimer and Anders (1970) and Marvin, Wood and Dickey (1970) were the first to ascribe a high-temperature condensation origin to them.

Thermodynamic calculations show that a number of trace elements are so refractory that they should condense from a solar gas at temperatures above or within the range of condensation temperatures of the major phases in these inclusions, 1442-1680°K. Condensation points are given in Fig. 6 for those which can condense as pure metals or oxides in this temperature range. The other elements listed in Fig. 6 probably also condense in this range but do so by dissolving in the major phases rather than by crystallizing as pure, separate phases. In fact, even many of those elements which can condense as pure phases will have higher condensation temperatures than those listed because of this effect.

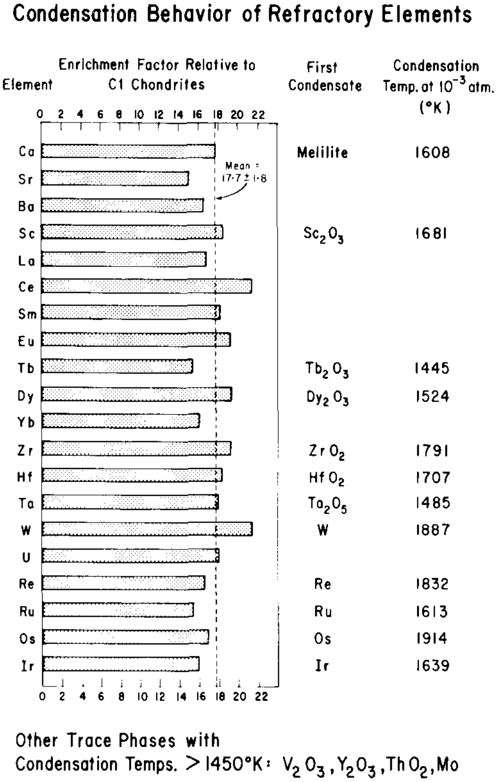

Figure 6. Condensation temperatures and enrichment factors of refractory elements in coarse-grained inclusions in Allende.

Figure 6 also shows the results of analyzing nine Allende coarse-grained inclusions by neutron activation. The mean concentration of each element is divided by its concentration in Type 1 carbonaceous (C1) chondrites whose compositions are taken to most closely represent the mean composition of the total condensable matter of the solar system (Ander 1971). In spite of great differences in their chemical properties and geochemical behavior, all these elements are seen to be enriched in the inclusions relative to their abundances in the solar system. The only thing common to all of them is that they should condense from a gas of solar composition in the same temperature range as the major mineral phases in the inclusions. Trace element data thus provide very strong evidence for the origin of the inclusions as high-temperature condensates. The trace elements and major phases probably became associated with one another because of their interdependence for condensation nuclei and the need for some trace elements to dissolve in the crystal structures of the major minerals during condensation. The enrichment factor is nearly the same for each element, 17.7 ± 1.8. This means that relatively little fractionation took place between the different refractories during their incorporation into the inclusions, implying that each of these elements was virtually totally condensed in the high - temperature condensate fraction.

Kurat (1970), Kurat, Hoinkes and Fredriksson (1975) and Chou, Baedecker and Wasson (1976) suggested that these inclusions are vaporization residues and Blander and Fuchs (1975) proposed that they formed by condensation as metastable, subcooled liquids. The internal oxygen isotopic heterogeneity of the inclusions (Clayton 1977), however, seems to argue against both of these ideas.

C. Amoeboid Olivine Aggregates

Grossman and Steele (1976) showed that these inclusions in Allende are composed predominantly of FeO-rich olivine and Na-rich silicates which are indicative of low nebular temperatures. They also observed tiny inclusions of spinel and perovskite in the amoeboids and suggested that when the more volatile constituents condensed, they incorporated residual grains of high-temperature condensate phases. This idea seems to be borne out by the trace element data presented in Fig. 7. The aggregates are enriched relative to C1's in refractory elements but not as much as the coarse-grained inclusions. When refractory element concentrations in the former are divided, element by element, by those in the latter, the relatively flat pattern of Fig. 7 results, suggesting that the amoeboid aggregates contain about 30% coarse-grained inclusions material, diluted by addition of 70% volatile-rich, refractory-free phases such as olivine. Large amounts of relatively volatile elements such as Na, Cl, Mn, Fe and Co are found in the amoeboid aggregates, unlike the coarse-grained inclusions. These inclusions suggest that high-temperature condensates did not always form their own separate, independent inclusions but sometimes accreted together with more volatile condensates before incorporation into the Allende parent body.

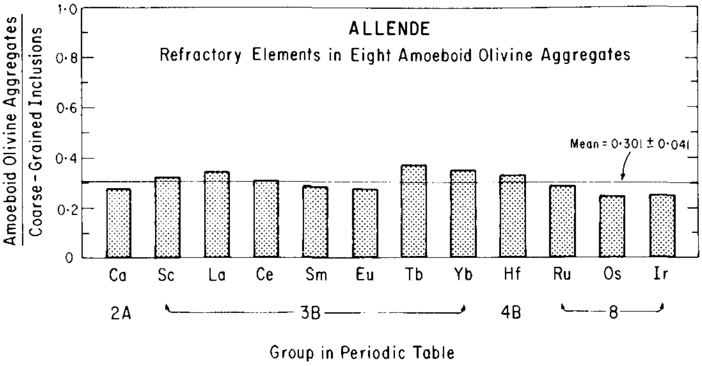

Figure 7. When the concentrations of refractory elements in amoeboid olivine aggregates are divided by their respective abundances in the coarse-grained inclusions, a relatively flat pattern results.

D. Fine-Grained, Ca-Rich Inclusions

These inclusions in Allende are irregular in shape and often pink or purple in color. Scanning electron microscope work (Grossman, Fruland and McKay 1975) reveals that they are delicate, cavernous aggregates of beautiful, euhedral, micron-sized crystals. These textural features are strongly suggestive of an origin by direct condensation. Fig. 8 shows that refractory elements are enriched in the fine-grained inclusions, but unlike the coarse-grained inclusions and amoeboids, the enrichment factors for different refractories are different from one another. Furthermore, these inclusions are very rich in more volatile elements like Zn, Na, Cl, Fe and Mn. Because of the fractionated refractory element enrichment pattern, the fine-grained inclusions cannot be simple mixtures of high-temperature condensates with lower temperature materials as is the case for the amoeboid olivine aggregates. They probably formed under non-equilibrium conditions when a small fraction of each of the refractories failed to condense into the coarse-grained inclusions at high temperature but, instead, condensed together with volatile elements in the vicinity of 1000°K (Grossman and Ganapathy 1976*b*). Boynton (1975) has proposed an alternative interpretation, also involving condensation from a gas phase which was fractionated during an earlier stage of partial condensation.

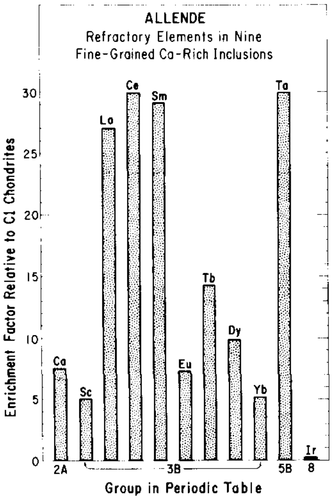

Figure 8. In the fine-grained inclusions, many refractory elements are enriched but highly fractionated from one another.

4. CHEMICAL FRACTIONATIONS IN CHONDRITES

A. Refractory Elements

It is seen in Fig. 9 that most of what has been discussed here involves only the most refractory 5% of the condensable matter of the solar system. The bulk of chondritic matter condenses in the form of magnesium silicates and metallic nickel-iron below the condensation temperatures of Ca, Al and Ti. At still lower temperatures, the alkali metals condense and then a number of volatile transition metals as alloys with nickel-iron. At about 700°K, gaseous H_2S reacts with metallic iron to form troilite and, at even lower temperature, Fe becomes oxidized.

Larimer and Anders (1970) showed that many refractory elements (Ca, Al, Ti, La, Sc, U, etc.) are depleted relative to magnesium silicates in the ordinary and enstatite chondrites compared to the carbonaceous and suggested that aggregates

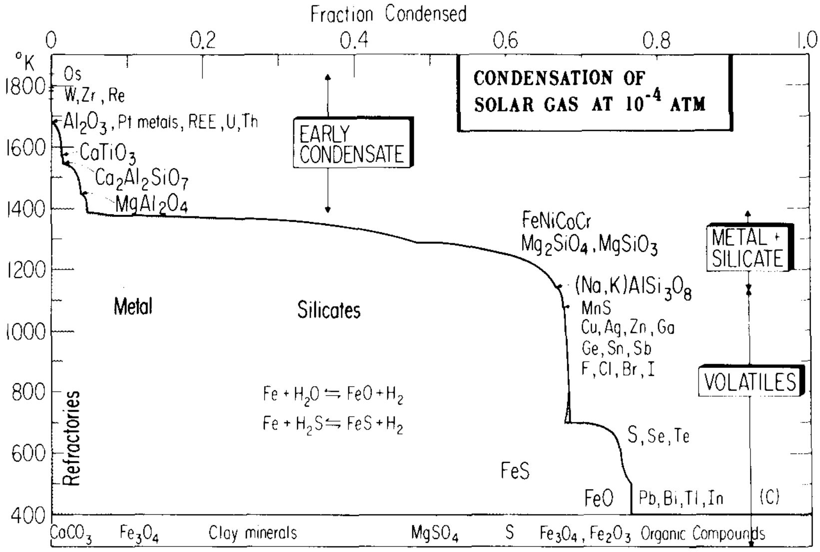

Figure 9. The fraction of chondritic matter condensed and its composition as a function of temperature. Note that the refractories are only 5 percent of the total condensable matter. From Ganapathy and Anders (1974).

of refractory condensates may have been lost from the nebular regions where the ordinary and enstatite chondrites formed before magnesium silicates condensed. It is tempting to speculate that these aggregates were identical to the coarse-grained inclusions in Allende but this does not appear to be the case. Ru, Os and Ir, the refractory platinum metals so prominently enriched in these inclusions (see Fig. 6), seem not to be depleted with the other refractories in ordinary and enstatite chondrites.

B. Metal-Silicate Fractionation

Grossman and Olsen (1974) and Kelly and Larimer (1976) have calculated the changing trace element content of metallic iron as it remains in condensation equilibrium with a cooling gas of solar composition. Kelly and Larimer pointed out that, of all the iron meteorite groups discussed by Scott and Wasson (1975), group IV B seems to have had the simplest history. These meteorites have trace element contents suggestive of direct condensation from the nebula, with cessation of equilibrium occurring at ~1400°K at 10^{-3} atm total pressure. Grossman and Olsen (1974) suggested that the aggregates and single crystals of euhedral forsterite in Murchison and other type 2 carbonaceous chondrites might be high-temperature condensates on the basis of their low divalent iron contents and the compositions of their occluded metal grains.

One of the long-standing problems in chondrite genesis is the mechanism of the metal-silicate fractionation (Urey and Craig 1953). The observation is that L- and LL-group ordinary chondrites are depleted in metallic iron relative to silicates compared to carbonaceous and H-group chondrites. Although many possible mechanisms have been suggested, the purpose here is to see what constraints, if any, are imposed on the fractionation process by condensation theory since the separation probably occurred in the nebula (Grossman and Larimer 1974). Many moderately volatile elements, such as Ni, Co, Au and Pd, are predicted to condense as alloys with metallic iron at temperatures above 1000°K. These elements are also depleted in the L-group compared to the H-group chondrites, implying that the nebular temperature was below 1000°K at the time metal grains were lost from the region where L-group chondrites formed (Larimer and Anders 1970). Sulfur, which condenses as troilite when metal grains react with gaseous H_2S at 700°K, is not depleted in the L-group chondrites which means that the temperature was above 700°K when the fractionation occurred. It may be no coincidence that the ferromagnetic Curie point of metal with these Ni contents, ~950°K, lies between these temperature limits. Weak magnetic fields may have played an important role in the metal-silicate fractionation.

C. The C/O Ratio

The enstatite chondrites are characterized by having vanishingly small amounts of divalent iron in their olivine and pyroxene. These meteorites formed under such reducing conditions that they contain metallic Si in solution in the nickel-iron and free carbon in the form of graphite. Ca, Mg and Mn, elements which occur in oxide or silicate compounds in other meteorite classes, are present as sulfides in enstatite chondrites. It has been recognized for some time that, if these meteorites are condensates, they must have formed from a gas phase quite different in composition from that which gave rise to carbonaceous chondrites (Larimer 1968). Although it is generally true that the condensation sequence is relatively insensitive to composition, minor changes in one crucial parameter, the C/O ratio, have profound effects on the mineral phases to be expected. Larimer and Bartholomay (1976) showed that graphite, CaS, nitrides and carbides replace the silicates and oxides as initial condensates, and the latter appear at lower temperature as the C/O ratio is varied from the solar value of ~0.6 to a value greater than 1. Trace element analyses of separated phases from enstatite chondrites could be used as a test of whether they condensed from such a vapor. If they did, the implication is that the nebula was heterogeneous with respect to its C/O ratio.

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DISCUSSION

WILLIAMS: *Can you not obtain a very similar sequence by changing pressure rather than temperature?*

GROSSMAN: *You could start at high temperature and gradually raise the total pressure to obtain the same condensation sequence at constant temperature.*

HERNDON: *The presence of graphite in enstatite chondrites has to be approached with some caution, as carbon in these meteorites is found in the metal phase.*