

Formation of *E* Chondrites and Aubrites—A Thermodynamic ModelD. W. SEARS¹*Department of Metallurgy, University of Manchester, Manchester M13, England*

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Condensation and accretion models for the formation of *E* chondrites have been examined. It is concluded that there is no simple equilibrium process which can explain all their fundamental properties. The nearest would seem to involve a complex accretion history, whereby metal and silicates which ceased to equilibrate at high temperatures and pressures (say about 1200–1600°K and about 1 atm) were mixed with material which ceased to equilibrate at the same pressures but over the temperature range 600–700°K. In this way the level of reduction displayed by this class, and the fractionation of several major, minor, and trace elements, may be explained. It is difficult to escape the conclusion that two assemblages are required, even if it is assumed that these meteorites formed from a gas of nonsolar composition. However, when the lithophile element fractionation and uncertainties in the thermodynamic and cosmic abundance data are taken into account, it is possible that the gas from which this meteorite class formed had a cosmic composition prior to the beginning of condensation.

1. INTRODUCTION

The small class of *E* chondrites provides a challenge to the simple condensation and accretion models for meteorite formation. On the one hand, their volatile trace element abundances resemble the most primitive class of chondrites—the C1 chondrites (Larimer and Anders, 1967; Herndon and Suess, 1976)—but, on the other hand, their high state of reduction has led several authors to propose that they did not form in a gas of solar composition (Baedecker and Wasson, 1975; Larimer 1968). In this paper, I attempt to describe a model which accounts for the major properties of this class and bears strong similarities to existing models for the other chondrite classes. It may even be that the nebula gas from which these meteorites formed also had a cosmic composition. Wasson and Wai (1970) showed that the aubrites (enstatite achondrites) form a single genetic sequence with the *E* chondrites, and I have found that the aubrites fit neatly into this model.

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The mineralogy and petrology of *E* chondrites has been thoroughly studied by Keil (1968) and Mason (1966), and their chemistry described by Binz *et al.* (1974) and Baedecker and Wasson (1975). Data on the aubrites have recently been reviewed by Watters and Prinz (1979). I have attempted to briefly review the properties of these meteorites in the next section of this paper. Section 2 describes the thermodynamics used and Section 3 describes the present model, dealing with the main properties of this class systematically. Existing models for their formation are considered in Section 4 and some general comments on the present model and its implications are made.

1.1. Main Properties of the *E* Chondrites

1.1.1. *Lithophile element fractionation.* The *E* chondrites may be conveniently defined as meteorites having an Mg/Si ratio of 0.83, and Ca/Si and Al/Si ratios of 0.036 and 0.051, respectively (e.g., Sears, 1978a). Table I lists these and other data for all known members of this class. For comparison, Cameron's (1973) values are also given for mean solar system abundances. The event which caused these geochemically

similar elements to be lower in abundance in *E* chondrites than in *C1* chondrites is generally termed the lithophile element fractionation. Larimer and Anders (1971) and Baedecker and Wasson (1975) identified this event as the removal of an early-formed, high-temperature condensate; the most striking feature these and similarly fractionated elements have in common is that they form refractory compounds. Even so, we do not know the details. Larimer and Anders (1971) suggested that the assemblage removed consisted of forsterite with minor additional minerals, but they did not calculate the conditions required to produce such an assemblage. Baedecker and Wasson suggested that it was the assemblage which "Grossman (1972) shows to be stable at *ca.* 1500–1550°K, but generously spiked with Mg." Kerridge (1979) has argued that if the assemblage contained forsterite then, at any assumed nebula pressure greater than 7×10^{-5} atm, metal would also have been removed during the lithophile element fractionation. One possible explanation is that an important, high-temperature Mg-rich phase is missing from the condensation sequence. Alternatively, the event which fractionated the lithophile elements affected silicates more than metal; perhaps their density difference was a relevant factor.

The aubrites also seem to have suffered an important lithophile element fractionation, since their Ca/Si and Al/Si ratios are generally even lower than those for *E* chondrites. However, the details must have been different since the Mg/Si ratio in aubrites is generally nearer to cosmic. In fact, Grossman's (1972) 1500–1550°K assemblage is a very good candidate for the material removed.

1.1.2. Siderophile and chalcophile element fractionations. A particularly important feature of this class is that iron, and other siderophile elements, show marked variations in their abundance. This led Anders (1964) to divide the class into *E1* (high

iron, Fe/Si greater than 0.85) and *EII* (low iron, Fe/Si less than 0.85) members, with two intermediate representatives. The S/Si ratio is also much larger in *E1* chondrites, being about 0.30, compared with 0.15 in *EII* chondrites (Fig. 1). The Fe/Si values straddle the cosmic values, and have a much greater range than in any other chondrite class. Baedecker and Wasson (1975) noted that the fact that the S/Fe ratio was the same in *E1* and *EII* chondrites implied that FeS and Fe–Ni were in the same component during the metal–silicate fractionation. The aubrites present an even greater extreme, having S/Si and Fe/Si ratios more than a factor of 10 lower than cosmic. Mason (1966) observed that the fractionations in *E* chondrites correlated with the extent of metamorphism, so that when Van Schmus and Wood (1967) defined their classification scheme for chondrites, *E1* and *EII* chondrites were termed *E4* and *E6*, respectively, and the two intermediate meteorites became *E5* chondrites. Subsequently, Happy Canyon has been identified as an *E7* chondrite by Olsen *et al.* (1977).

The Fe/Si fractionation has analogs in other chondrite classes and is almost certainly associated with the separation of

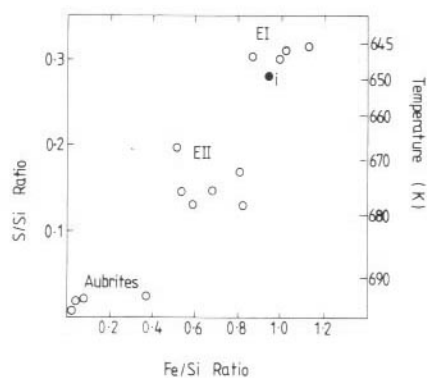


FIG. 1. The siderophile and chalcophile element fractionation in *E* chondrites as demonstrated by variation in the Fe/Si and S/Si ratios. There is a correlation between these ratios, where *E1* chondrites have the highest values. The right-hand scale indicates the temperatures at which the S/Si ratio passes through the value on the left-hand scale during sulfur condensation.

TABLE I
KNOWN E CHONDRITES AND AUBRITES AND THEIR PROPERTIES

Meteorite ^a	Class ^b	Composition (at./at)						Si in Metal			Accessory minerals		
		Mg/Si	Ca/Si	Al/Si	S/Si	Fe/Si	Ref.	Mole fraction	Ref.	CaS	TiN	Si ₂ N ₂ O	
Abee	E4	0.79	0.037	0.050		1.00	c	0.064	e	√ ^e			
		0.75	0.029	0.021	0.30	0.86	d						
Adhi-Kot	E4	0.69	0.036	0.033	0.29	1.00	d	0.067	e	√ ^e			
Atlanta	E6	0.83	0.015	0.058		0.71	c	0.024	e		? ^e		
		0.84	0.011	0.042	0.13	0.82	d						
Bethune	E4,5												
Bllthfeld	E6	0.83	0.019	0.052		0.45	c	0.031	c				
		0.86	0.022	0.029	0.20	0.52	d	0.020	f				
Daniel's Kuil	E6	0.84	0.047	0.027	0.17	0.81	d	0.024	e	√ ^e			
								0.035	f				
Hvittis	E6	0.85	0.036	0.052		0.68	c	0.022	e	√ ^e		√ ^e	
		0.83	0.036	0.022	0.15	0.65	d	0.035	f				
Indarch	E4	0.76	0.034	0.049		0.92	c	0.067	e	√ ^e			
		0.74	0.051	0.024	0.31	1.01	d	0.054	f				
Jajh deh Kot Lalu	E6	0.79	0.033	0.027	0.14	0.54	d	0.026	e	√ ^e		√ ^e	
								0.025	s				
Khairpur	E6	0.81	0.043	0.024	0.12	0.59	d	0.024	e	√ ^e			
								0.035	f				
Kota Kota	E4							0.051	e				
Parsa	E4,5												
Pillistfer	E6	0.82	0.036	0.056		0.71	c	0.028	e	√ ^e		√ ^e	
		0.78	0.035	0.032	0.16	0.74	r	0.075	g				
South Oman	E4,5												
Saint Sauveur	E5	0.76	0.065	0.058	0.33	1.13	d	0.056	e				
								0.039	f				
St. Marks	E5	0.75	0.035	0.050		0.93	c	0.069	e	√ ^e			
		0.78	0.036	0.027	0.28	0.95	d	0.052	f				
Ufana	E6							0.033	e	√ ^e		√ ^e	
Yamato 69-01	E4,5	0.76	0.013	0.024	0.23	0.84	h			√ ^h			
Yilmia	E6							0.028	g	√ ^u			

Aubres	Aub.									0.013	<i>b</i>
Bishopville	Aub.	0.88	0.038	0.018	0.010	0.019	<i>i</i>			0.0046	<i>w</i>
Bustee	Aub.	1.05	0.024			0.068	<i>k</i>			<10 ⁻⁴	<i>b</i>
Cumberland Falls	Aub.	1.05	0.031	0.004	0.027	0.044	<i>l</i>			0.047	<i>w</i>
Khor Temiki	Aub.	0.96	0.027	0.013	0.002	0.004	<i>m</i>			0.028	<i>w</i>
Mayo Belwa	Aub.	0.86	0.017	0.046	0.012	0.010	<i>v</i>			<10 ⁻⁴	<i>b</i>
Norton County	Aub.	1.15	0.026	0.006		0.026	<i>c</i>			0.0024	<i>w</i>
Pena Blanca Spring	Aub.	0.98	0.019	0.013	0.024	0.032	<i>n</i>			<2 × 10 ⁻⁴	<i>b</i>
Pesyano	Aub.	0.99	0.020	0.002	0.039	0.029	<i>p</i>			0.0030	<i>w</i>
Shallowater	Aub.	1.05	0.018	0.008	0.049	0.560	<i>q</i>			0.017	<i>v</i>
Cosmic		1.06	0.072	0.085	0.50	0.83	<i>t</i>			0.047	<i>w</i>
										0.013	<i>b</i>
										0.018	<i>w</i>
										10 ⁻³	<i>b</i>
										0.011	<i>b</i>
										0.0057	<i>w</i>
										0.019	<i>b</i>

^a Finds in italics.

^b Wasson and Wai (1970).

^c Von Michaelis *et al.* (1969); X-ray fluorescence method.

^d Mason (1966).

^e Keil (1968).

^f Ringwood (1961).

^g Reed (1968).

^h Shima and Shima (1975).

ⁱ Smith (1864).

^j Derham *et al.* (1964).

^k Maskelyne (1870), p. 208.

^l Merrill (1921).

^m Hey and Easton (1967).

ⁿ Wiik (1969).

^o Beck and LaPaz (1951).

^p Lonsdale (1947). Metal-free portion.

^q Foshag (1940). Calculated by assuming 16.69% "soluble portion" and 83.31% "enstatite."

^r Jarosewich and Mason (1969).

^s Keil and Anderson (1965).

^t Cameron (1973).

^u Buseck and Holdsworth (1972).

^v Graham *et al.* (1977).

^w Watters and Prinz (1979).

metal and silicates. Larimer and Anders (1971) attempted to estimate the temperature at which this separation occurred in ordinary chondrites by identifying those trace elements which were involved. Their thesis was that those elements displaying the same distribution as Fe condensed before the metal-silicate separation, while those that do not must have condensed afterward. In fact, the most volatile elements thought to be involved were Ga and Ge. According to Larimer's (1967) calculations these elements condensed at about 1000°K, which is also the Curie Point of iron. Larimer and Anders (1971) therefore proposed that the mechanism removing the iron involved magnetism. The condensation calculations for Ga and Ge have been considerably revised since 1967 (Wasson and Wai, 1976; Kelly and Larimer, 1977; Sears, 1978b). It now seems that these elements are present in the metal in chondritic proportions between 500 and 700°K, depending on the pressure assumed. Following Larimer and Anders' argument, this temperature range would be a better estimate for the temperature at which the iron was removed from the ordinary chondrite location. Müller *et al.* (1971) also argued that the siderophile elements in ordinary chondrites were fractionated in this temperature region, since they correlate with oxidation state; oxidation of iron takes place in a cooling solar nebula between 500 and 600°K.

No model for the formation of the *E* chondrites takes the S/Si fractionation into account, although Baedeker and Wasson (1975) suggested that, since it correlates with the Fe/Si fractionation, some sulfur was removed along with the metal.

1.1.3. Oxidation state. The *E* chondrites and aubrites contain several minerals which require a uniquely reducing environment for their formation; in this respect they could hardly differ more from the highly oxidized *C1* chondrites. Details of their mineralogy are given in Table I. The most important points are that they contain Si in

the metal and Ca, Ti, and Mn as sulfides, while in every other chondrite class these elements are present as silicates. Furthermore, the Bishopville and Bustee aubrites, the Yilmia, and probably the Atlanta *E6* chondrites contain osbornite (TiN) and many *E* chondrites contain sinoite (Si₂N₂O). Osbornite and sinoite are terrestrially unknown and also require highly reducing conditions. Cohenite ((Fe, Ni)₃C) has been reported in several *E* chondrites, and Keil (1968) observed that graphite was more abundant in *E6* than *E4* chondrites. Larimer (1968) and Baedeker and Wasson (1975) argued that it was impossible to achieve the observed level of reduction in a gas of solar composition, and proposed that the gas composition in the formation location of this class was unusual. Herndon and Suess (1976) claimed that the levels of reduction can be achieved at high pressures and temperatures in a gas of solar composition. These possibilities are discussed below.

1.1.4. Trace elements. Because of their great diversity in geochemical properties, and their great number, trace elements provide a powerful test for any model. Remarkably, most trace elements in *E* chondrites are present in *C1* proportions, with *E1* chondrites having a small (approximately a factor of 2) enrichment in most elements (Fig. 2). This has been interpreted by Larimer and Anders (1967) as reflecting their difference in chondrule/matrix ratio. Chondrules, they propose, are depleted in these elements, while matrix is not. Baedeker and Wasson (1975) have proposed an alternative mechanism involving the loss of nebula gases after the formation of the *E1* chondrites. At the moment it is impossible to choose between these explanations, but the effects are very small and do not seem to be unique to the *E* chondrites. They are not, therefore, discussed further. The only elements in *E* chondrites to differ markedly in their abundance from those in *C1* chondrites are the highly volatile In, Bi, Tl, Pb, and Cd. These show a

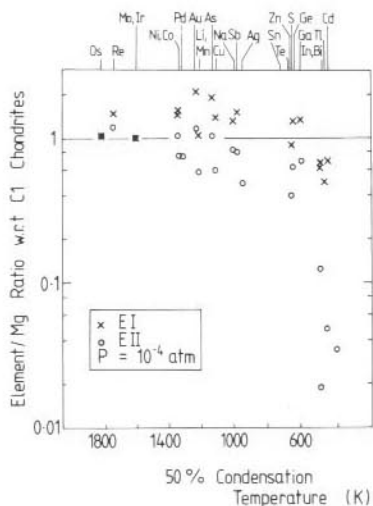


FIG. 2. Normalized trace element abundances in *E* chondrites as a function of condensation temperature. Crosses represent *E1* chondrites and circles represent *E2* chondrites. The abundance data are from Baedecker and Wasson (1975) and the condensation temperatures, except those for Ga and Ge, are from Wai and Wasson (1977). The Ga and Ge condensation temperatures are from Sears (1978b).

100-fold depletion in *E2* chondrites, while in *E1* chondrites they are present in almost *C1* proportions. The same elements show a 1000-fold depletion in type 6 ordinary chondrites and the arguments as to their cause are the same for the two classes. Essentially there seem to be two possibilities: (i) Their abundance correlates with the extent of metamorphism, so they may have been "boiled off" during the metamorphic episode (Wood, 1962; Dodd, 1969; Wasson, 1972). (ii) They are the last elements to condense, so it is possible that they were not fully condensed when the accretion of the *E2* chondrites took place (Urey, 1952; Larimer and Anders, 1967). Whichever possibility most closely approximates the truth, it is obvious that the highly volatile elements must have at least started to condense when accretion occurred. This point is central to the present model. It will be seen that there are certain advantages to the second possibility.

The trace element data for aubrites are

sparse and show considerable scatter (e.g., Fig. 4.6 in Sears, 1978a). They seem to reflect the extensive nature of the siderophile, chalcophile, and lithophile element fractionations referred to previously. The highly volatile elements probably display depletions similar to *E2* chondrites.

2. METHODS

The condensation and accretion models have in common the assumption that there was a primordial solar nebula, and that in the region in which the meteorites formed the temperature was once above about 2000°K. As the nebula cooled, solids condensed as a fine submicrometer smoke capable of maintaining chemical equilibrium with the gas. At some temperature it became impossible for equilibrium to be maintained; in some instances it seems that the solids formed into millimeter-sized grains almost simultaneously with condensation and became too large to maintain equilibrium with the nebula gases as they cooled (e.g., the calcium–aluminum-rich inclusions in Allende and similar meteorites) (Grossman, 1973), while in others equilibrium with the nebula gases seems to have been maintained to very low temperatures (e.g., the *C1* chondrites are frequently assumed to have formed below 400°K).

It is possible to present the results of condensation calculations in a variety of ways. Some of the present results are presented in the manner of Grossman and Larimer (1974) which may require a little explanation. Condensation occurs when the partial pressure of a species in the nebula, PP , exceeds its vapor pressure, VP . The partial pressure is determined by reactions such as



for which the equilibrium constant, K_1 , is given by

$$K_1 = PP(\text{CaTiO}_3)/P(\text{Ca})P(\text{Ti})P(\text{O})^3,$$

and hence,

$$\log \frac{PP(\text{CaTiO}_3)}{K_1} = \log P(\text{Ca}) + \log P(\text{Ti}) + 3 \log P(\text{O}),$$

where P refers to the partial pressure of the monatomic gaseous species in question. The condensation reaction is



for which, taking the activity of the solid as unity, the equilibrium constant, K_2 , can be written

$$-\log K_2 = \log P(\text{Ca}) + \log P(\text{Ti}) + 3 \log P(\text{O}).$$

Since, in the presence of the pure solid, the partial pressure of a species equals its vapor pressure

$$\log K_2 = \log [VP(\text{CaTiO}_3)/K_1].$$

The partial pressure of the monatomic species must be calculated from mass balance equations, which reflect the cosmic abundance of each element and allow for reactions which produce gaseous molecules. Equations must also be added which allow for reactions between solids and the nebula gases. These procedures have been well documented by Urey (1952), Lord (1965), Larimer (1973), and Grossman (1972) and need not be described further here. Sources of thermodynamic data are listed in Table II, and the cosmic abundances of Cameron (1973) have been used throughout.

3. RESULTS—THE PRESENT MODEL

The present model is based on two properties which make the E chondrites unique: their state of reduction and the S/Si fractionation. The aubrites and the remaining important E -chondrite properties are also readily incorporated into the model, the Fe/Si fractionation in a particularly significant way.

3.1 The Reduction Level

3.1.1 Silicon content of the metal. Figures 3 and 4 show how the Si content of the

TABLE II
SOURCES OF THERMODYNAMIC DATA

	Source
Gaseous species	
O, CO, CO ₂ , H ₂ O, H ₂ , C, CH ₄ , H ₂ S, HS, S ₂ , S, SiO, Si, Ca, Al, AlO, AlH, Ti, TiO, TiO ₂ , N ₂ , N	JANAF ^a
Fe, Ni	Hultgren <i>et al.</i> (1973)
Solid species	
CaS, Si, MgSiO ₃ , Mg ₂ SiO ₄ , TiN, C, Al ₂ O ₃	JANAF ^a
Ca ₂ Al ₂ SiO ₇ , CaTiO ₃ , FeS, Fe ₂ SiO ₄ , MgAl ₂ O ₄ , CaMgSi ₂ O ₆	Robie and Waldbaum (1968)
Si ₂ N ₂ O	Ryall and Muan (1969)
In, Bi, Tl, Cd and associated data	Larimer (1973)
FeSiO ₃	Larimer (1968)

^a The most recent compilation for a given species from Stull and Prophet (1971) or Chase *et al.* (1974, 1975, 1978).

metal varies with temperature in a gas of solar composition. Only a marginal difference results from assuming removal of up to 20% of the nebula oxygen by the lithophile element fractionation. The calculations differ from those already published (Larimer, 1968; Baedeker and Wasson, 1975; Herndon and Suess, 1976) in two ways: (i) I have used new data for the activity coefficient of Si in iron (Sakao and Elliott, 1975), namely,

$$\log \gamma(\text{Si}) = 1.19 - \frac{7070}{T} + \left(-6.30 + \frac{18,300}{T} \right) X(\text{Si}),$$

where $X(\text{Si})$ is the mole fraction of Si in solid solution and T is temperature. (ii) I have carried the calculations below the temperature at which condensation of the silicates occurs. At pressures greater than

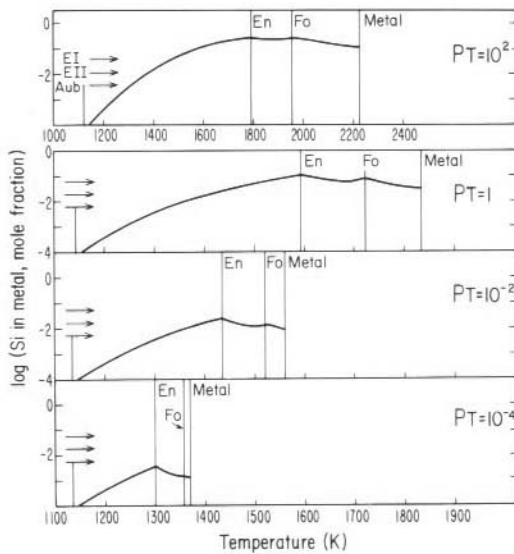
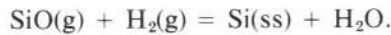
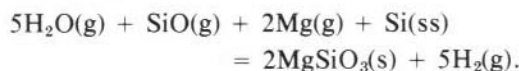


FIG. 3. Silicon content of the metal at equilibrium with the solar nebula as the temperature falls. The values of PT refer to the assumed nebula pressure in atmospheres.

about 10^{-2} atm, the amount of Si dissolved in the metal increases as the temperature drops until silicates start to condense. The relevant reaction is



At pressures greater than about 10^{-4} atm, silicates condense after the metal. With current uncertainties in the thermodynamic data, we cannot say with certainty whether the stable silicate is olivine or pyroxene. [See, for example, Grossman's (1972) Fig. 5. The errors he quotes for the condensation temperature are 15–20°K.] Whichever condenses first suppresses condensation of the other by 50°K or so. From the point of view of the Si content of the metal, however, it makes little difference. After the formation of the silicates, the silicon content of the metal slowly falls according to the reaction



For a given pressure, there are therefore two temperatures at which the Si content of

the metal equals that observed in *E* chondrites. The pressures required, greater than about 10^{-2} atm, are quite high compared with values preferred by Larimer and Anders (1967, 1971) and Baedeker and Wasson (1975). As with the earlier models described in Section 4.1, the metal must be isolated from the gases soon after condensation of the silicates, and therefore accretion must occur at high temperatures; probably it was simultaneous with condensation.

3.1.2. Oldhamite (*CaS*). The condensation calculations for CaS are shown in Fig. 5a. The partial pressure of CaS never exceeds its vapor pressure because of the previous condensation of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$). Depending on the assumed pressure, gehlenite condensation occurs between 30 and 130°K, ahead of the condensation temperature of CaS otherwise calculated. An extrapolation of the CaS curves, assuming gehlenite did not form, predicts condensation temperatures very similar to those calculated by Herndon and

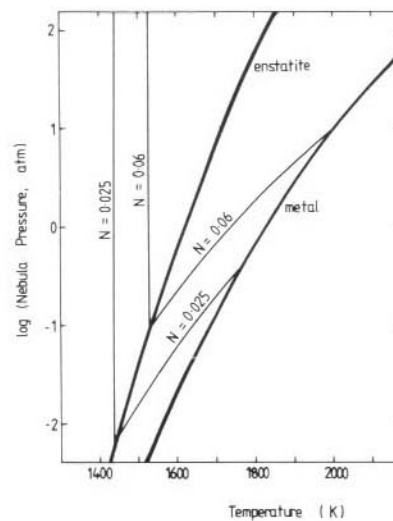


FIG. 4. Plot of the nebula pressure and temperature at which the metal contains *E*I and *E*II abundances of Si, 0.06 and 0.025 mole fraction, respectively. For aubrites, this figure varies from 0.01 to less than 10^{-4} . The amount increases as the temperature falls until enstatite forms, when silicon transfers from the metal to the silicates in a pressure-independent fashion.

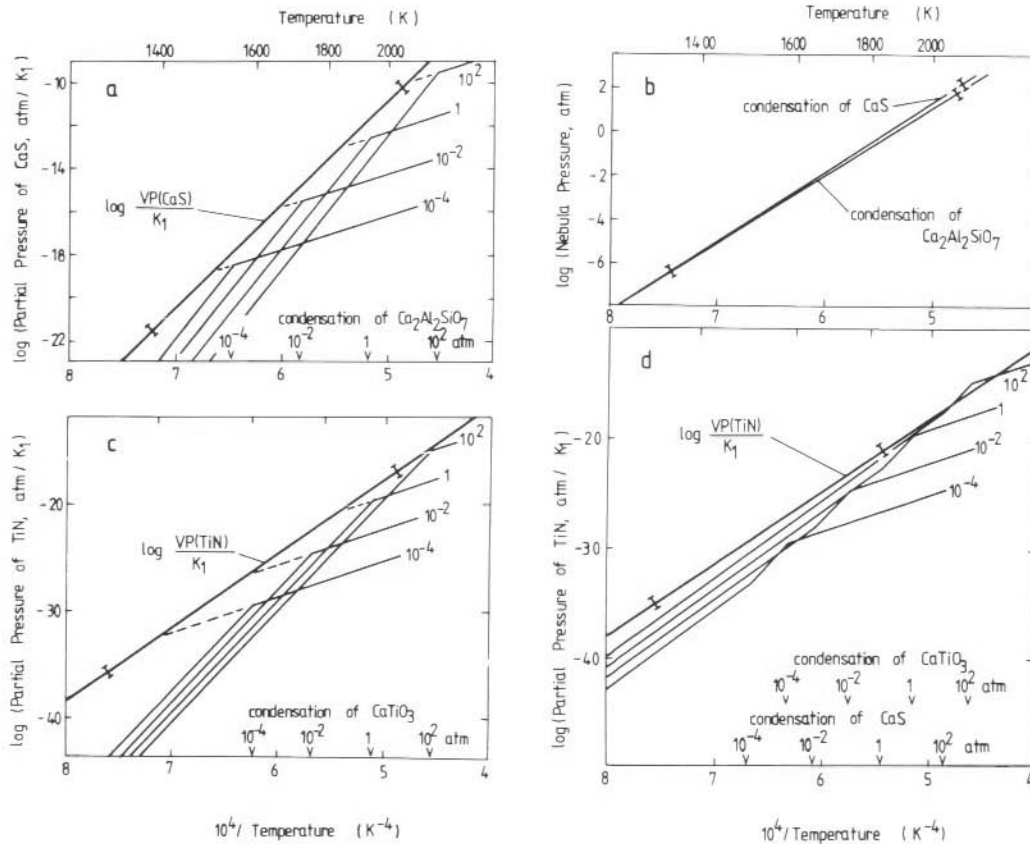


FIG. 5. Condensation of CaS and TiN. Condensation occurs when the partial pressure of a species equals its vapor pressure. The constant K_1 is defined in the text. Partial pressure curves are given for four assumed nebula pressures (in atm). The ticks on the temperature scales refer to the condensation temperatures, at the pressures indicated, of species affecting the partial pressure curves. The error bars are semiquantitative estimates of the uncertainty of the thermodynamic data; similar uncertainty probably applies to the partial pressure curves. (a) In a gas of cosmic composition the condensation of CaS is prevented by the formation of $\text{Ca}_2\text{Al}_2\text{SiO}_7$. (b) CaS and $\text{Ca}_2\text{Al}_2\text{SiO}_7$ form simultaneously in a gas in which 20% of the oxygen has been removed, and the formation of CaS is feasible. (c) Similarly, TiN does not condense in a gas of cosmic composition, except at pressures exceeding $10^{2.5}$ atm. (d) However, it forms at much lower pressures in a nebula in which 20% of the oxygen has been removed.

Suess (1976). However, CaS is unstable in a gas of cosmic composition, at any pressure considered, when minerals which form at high temperature are taken into account.

The situation is different if one allows for a prior lithophile element fractionation. The removal of refractory silicates, containing oxygen, increases the H/O ratio of the remaining system. Since the oxidation state of the system is governed by the reaction $\text{H}_2\text{O}(\text{g}) = \frac{1}{2}\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2(\text{g})$, it is highly sensitive to H/O. After the lithophile ele-

ment fractionation, the new solids condensing will have a lower oxidation state than they would have had if this fractionation had not occurred. In Fig. 5b the condensation temperature of CaS and gehlenite are given for a gas in which Ca/Si, Al/Si, Ti/Si, and Mg/Si have been adjusted to *E*-chondrite values, and 20% of the nebula oxygen has been removed. Under these conditions, the condensation temperature of the two species is the same within experimental error. It is possible that CaS would

form and depress the condensation of gehlenite by 20 or 30°K depending on the estimated error of the two sets of data. These calculations assume the presence of CaTiO_3 , but if this species were reduced to $\text{TiS}(s)$, the stability field of CaS would be enlarged.

3.1.3. Osbornite (TiN). The situation for TiN is similar to that for CaS . At most pressures, its condensation is prevented by the formation of CaTiO_3 , but at pressures in excess of about $10^{2.5}$ atm it becomes stable in the nebula gas for a very small temperature interval. The estimated condensation temperatures of TiN in the absence of CaTiO_3 formation agree very closely with those estimated by Herndon and Suess (1976) (Fig. 5c). When the lithophile element fractionation is allowed for as before, the condensation of CaTiO_3 is depressed slightly and the lower limit for TiN formation is about 1 atm (Fig. 5d). The smallness of the stability field for TiN is consistent with its scarcity, being observed in only two aubrites and, possibly, two *E* chondrites.

3.1.4. Sinoite ($\text{Si}_2\text{N}_2\text{O}$). The presence of CaTiO_3 and gehlenite do not affect the condensation of sinoite, and Herndon and Suess' calculations are essentially correct. Although the thermodynamic data are poor, it is possible to produce this solid in a gas of solar composition, but again isolation must be simultaneous with condensation. Pressures on the order of 1 atm and temperatures around 1900°K are required.

3.2. Sulfur and the Highly Volatile Trace Elements

If the *E* chondrites formed by accretion at temperatures high enough for the reduced phases to be stable, then sulfur and the highly volatile trace elements would not be present. Figure 6 shows the condensation curve for sulfur, which condenses as FeS . This curve is pressure independent. Condensation of sulfur starts at 695°K and is 50% complete by 655°K, and 90% condensation occurs at 580°K. Early calcula-

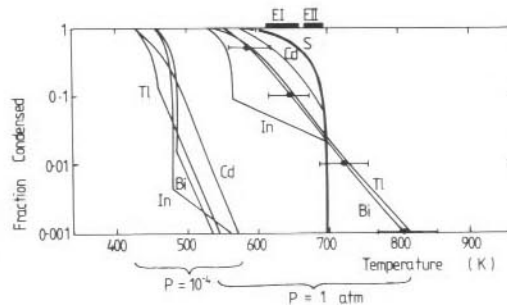


FIG. 6. Condensation of sulfur and the highly volatile trace elements Tl, In, Bi, and Cd. At low pressures these trace elements form at much lower temperatures than sulfur—whose condensation curve is independent of pressure. However, for a nebula pressure of 1 atm, they condense simultaneously with sulphur and have a range in abundance similar to that observed in *E* chondrites.

tions gave 680°K as the condensation temperature for FeS , but I suspect these were based on thermodynamic data taken over a very wide temperature range (something like 500–2000°K).

The condensation curves for the highly volatile trace elements (Cd, In, Bi, Tl) are pressure dependent and are given for two assumed nebula pressures. At 10^{-4} atm they condense around 500°K, while at 1 atm the range is roughly 600–700°K. It is clear that, whether we make *E* chondrites by accretion of material condensing from a fractionated, or unfractionated, solar nebula, we must mix together condensates which were isolated at different temperatures, the high-temperature assemblage containing the reduced species, and the low-temperature assemblage containing sulfur and the volatile trace elements.

The precise nature of the condensation curves for the highly volatile elements have been the subject of much debate (Larimer and Anders, 1975; Blander, 1975). To calculate the condensation curves, I have used Larimer's (1973) equations and thermodynamic data without modification. In response to Blander's comments, I have inserted error bars on the curve for Bi; similar error bars apply to other elements, but are omitted for clarity. Whatever the

exact nature of the curves, it is clear that these elements condense over a temperature range which is pressure dependent. When the pressure is increased to about 1 atm, the temperature range is not so narrow and has moved to 600–700°K, the same range as that calculated for sulfur condensation.

3.3. A Scenario for the Present Model

The previous two sections of this paper underline an apparent contradiction in the composition of *E* chondrites. The presence of phases like Si-bearing metal, osbornite, oldhamite, and sinoite seems to suggest that these meteorites accreted at temperatures not too far removed from the condensation temperature of metal. On the other hand, the presence of sulfur and highly volatile trace elements like In, Tl, Bi, and Pb clearly demonstrates that some component was still equilibrating with the nebula at very low temperatures; even at 1 atm, these elements are not stable solids above 700°K.

As described in Section 4.1, this apparent contradiction is not removed by adjusting the H/O or C/O ratio; this device produces suitable redox conditions at low pressures ($\sim 10^{-5}$ atm) but still requires isolation of the reduced phases soon after the condensation of metal. As far as the reduced phases are concerned, the main reason for believing that these meteorites formed at reasonably high pressures is that the formation of TiN and Si-bearing metal are favored by high pressures. Even so, currently accepted values for the thermodynamic and abundance data for TiN and CaS suggest that these phases are not stable at 1 atm at any temperature. Minor adjustments in the thermodynamic or cosmic abundance data suffice to make these minerals stable nebula condensates. Since the *E* chondrites are not only the most reduced meteorites, but have also suffered the most severe loss of high-temperature condensates, the loss of oxygen trapped in the refractory minerals may have tipped the balance and made it possi-

ble for reduced species like CaS and TiN to become temporarily stable. If the refractory minerals which were lost are those identified by Larimer and Anders (1971), this mechanism runs into a problem. These authors suggested that the major mineral which was lost was forsterite, but this condenses about 200°C lower than the formation of CaS and TiN requires (see Fig. 5). There are two ways around this problem: (1) The nebula cooled enough for forsterite to condense and then suffered a reheating—maybe the “pre-*E* chondrite dust” underwent an orbit change, or the Sun’s luminosity fluctuated; (2) there is a major, high-temperature Mg-rich phase missing from the condensation sequence. [See also Section 1 and Baedeker and Wasson (1975).]

So much for calculations. What would be the physical setting of the process by which the reduced phases were formed and prevented from reacting further? One might imagine that the nebula cooled and the first solids condensed, perhaps using preexisting, stellar solids as condensation nuclei. As part of a nebula-wide process, there was a continual removal of these early-formed solids so that the Mg/Si ratio of the residual material was reduced from its cosmic value of 1.05 to 0.8, the value more appropriate to *E* chondrites. Throughout this phase of nebula history, the residual gases and solids maintained equilibrium with the gases, so that some of the $\text{Ca}_2\text{Al}_2\text{SiO}_7$ reacted with the gases to give CaS(s) and Ti condensed as TiN(s). Gradually, as more silicates condensed, these reduced phases became trapped inside silicate aggregates and were unable to react further with the gas. At this stage, the solid aggregates may typically have been only a few millimeters in size. A few may have consisted entirely of metal. Some became melted by impacts, or lightning effects, to produce the metal and silicate chondrules observed in *E* chondrites.

These aggregates remained free in the nebula, growing very little, since after mafic silicate condensation the major phase of condensation is over. At 700°K the sur-

faces of the larger metal grains—some globular and some irregular in shape—reacted with the gases to form FeS. Smaller grains were at equilibrium with the gases throughout their bulk. At the same time, the highly volatile elements were condensing as pure solids or as solid solutions in the FeS and metal. The nebula then contained mixtures of aggregates which formed at high temperatures and contained the reduced phases and metal/sulfide aggregates containing some Tl, Bi, Pb, and Cd. At this time (when the temperature was $\leq 700^\circ\text{K}$) the grains seem to have started the process of accretion onto a large body. The first mixture of aggregates to accrete had less than cosmic proportions of S and highly volatile elements and we would identify these with *EII* chondrites. When the temperature had fallen to $\sim 600^\circ\text{K}$, the aggregates would contain cosmic proportions of S and highly volatile elements, and would be the parental material for *EI* chondrites. The aubrites seem to fit the model, if they are assumed to have accreted at $\sim 700^\circ\text{K}$.

4. DISCUSSION

4.1. Previous Models for the Formation of *E* Chondrites

The most important genetic feature of the *E* chondrites is usually assumed to be their state of reduction. The elements which govern the oxygen fugacity of the nebula are carbon, oxygen, and hydrogen, or, more precisely, the relative abundances of the gaseous species CO, CH₄, and H₂O. The pressures and temperatures at which each form is dominant are given in Fig. 7. Figure 7a gives the predictions of a gas of solar composition from which it can be seen that CO and H₂O are dominant at high temperatures, and CH₄ and H₂O are the most important gas species at low temperatures. Over a very restricted pressure-temperature region graphite forms. The basic features of this plot were first described by Urey (1953), who also pointed out that significant solid solution of carbon in metal

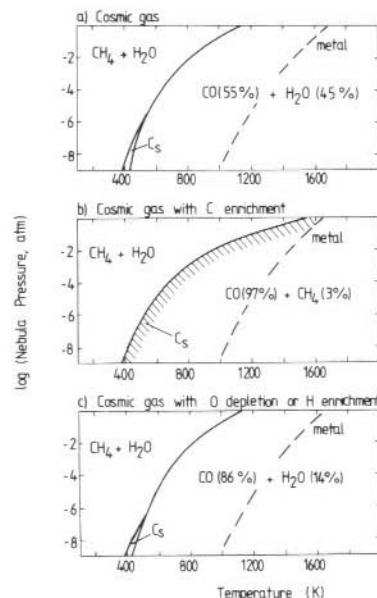


FIG. 7. Distribution of carbon, hydrogen, and oxygen in nebula gases with three different compositions. (a) Cosmic. (b) Cosmic with an enrichment of carbon, such that $C/O = 0.9$. The size of the carbon stability field is critically dependent on the amount of oxygen assumed to be present in silicates, the cosmic abundance figures, and thermodynamic data used. It may extend to the condensation curve for metal, or be negligibly small. (c) Cosmic with 62% of the oxygen removed such that $P(\text{H}_2\text{O})/P(\text{H}_2)$ is one-fifth its cosmic value. The percentage figures refer to the amount of gaseous oxygen [cases (a) and (c)] or carbon [case (b)] in each form. In all cases 13% of the oxygen is assumed to be present as silicates.

occurs at high pressures and where CO gives way to CH₄ as the dominant C species. The calculations have been repeated here, with new thermodynamic and cosmic abundance data, and were used by Sears (1978b) to explain the high-carbon abundance in IAB iron meteorites.

Larimer (1968) argued that the reduced species in *E* chondrites could not have formed in a gas of solar composition. He therefore proposed that this class formed in a region of the solar nebula where carbon enrichment caused the C/O ratio to be 0.9 instead of the cosmic value which is nearer 0.6. In this case, CO is the dominant O species at high temperature, instead of H₂O (Fig. 7b). The gas is then sufficiently reduc-

ing to produce CaS and Si in the metal. Even so, scrutiny of Larimer's Tables 4 and 5 reveals that the reduced species must be isolated from the nebula gases soon after they form, and that CaS is not stable below 1600°K (when the nebula pressure is 10^{-2} atm). Larimer did not propose a mechanism for the inclusion of sulfur and the highly volatile elements, but the mechanism discussed here is an obvious possibility.

If 13% of the oxygen is bound up as silicates, there is insufficient oxygen remaining in the gas to tie up all the carbon as CO(g). In Larimer's calculations, the excess carbon was usually present as CH₄, but below 1000°K, and at 10^{-2} atm, graphite formed. The size of the graphite stability field is critically dependent on the amount of oxygen assumed to be trapped in silicates and the cosmic abundance tables and thermodynamic data used. It is not unreasonable that it extends to the temperature regions in which the reduced species formed. Larimer (1968) proposed that *E* chondrites formed in a region of the nebula where a C-enrichment occurred because *E* chondrites contain graphite. However, Blander and Lewis have argued (in separate private communications to Baedecker and Wasson, 1975) that a C/CO buffered nebula would be too reducing. Species like SiC and TiN are predicted. SiC has never been observed in *E* chondrites but TiN is present in Yilmia and may be present in Atlanta. Clearly, however, it is not ubiquitous. Also, the relatively highly oxidized ordinary chondrites contain graphite (Ramdohr, 1963). Graphite in ordinary chondrites may well be a result of metamorphism of carbon compounds which formed in a manner similar to those in *C* chondrites (Lewis *et al.*, 1979). In *E* chondrites it seems very likely that it was formed by exsolution of carbon in solid solution in metal (Keil, 1968, p. 6968), as in IAB iron meteorites (Sears, 1978b). It is doubtful that graphite in any class of meteorite formed by direct equilibrium condensation from the nebula gases.

Because C/O fractionation is likely to produce a nebula which is too reducing, Baedecker and Wasson (1975) considered a nebula with an H/O fractionation (Fig. 7c). A decrease in the $P(\text{H}_2\text{O})/P(\text{H}_2)$ ratio by a factor of a 5 was proposed. This produces *E*-chondrite proportions of Si in the metal at a temperature of 1350°K, for a nebula pressure of 10^{-4} atm. As with Larimer's calculations, immediate isolation of the metal from the nebula gases is required. Baedecker and Wasson proposed that the fractionation could occur by the removal of 62% of the oxygen, by the condensation of H₂O in the outer solar system. This requires considerable transport of H₂O from the inner to the outer solar system; *E* chondrites, being the most reduced meteorites, are generally assumed to have formed nearest the Sun. The H/O ratio required by Baedecker and Wasson may also be achieved by an 80% hydrogen enrichment. The gaseous species are the same as for a gas of cosmic composition. The question then is the feasibility of such an H enrichment. In even a poorly mixed gaseous nebula it seems unlikely that gaseous regions of such different composition can exist within a few astronomical units of a region in which, say, the *C* chondrites formed, unless it was in a protoplanet. Probably the only guides we have as to what is feasible in a protoplanet are the major planets. These have mean densities greater than predicted from cosmic abundances, suggesting, if anything, a hydrogen depletion (Podolak and Cameron, 1974).

All the nebula models, including the present one, require that material become isolated from the nebula over two discrete temperature ranges. This is a problem in that one would intuitively expect one range in accretion temperature. The question would then be whether the range is small (say 50–100°K) or large (from condensation downward, until all the material was used up). There are apparently two ways around this problem: (1) Accretion may have occurred in two discretely different locations

where widely differing accretion temperatures would be expected. Clayton (1977) has proposed that the CAI formed in the expanding shell of a supernova, that these were transferred to the cool primordial solar nebula where they were accreted together with the matrix at ambient (low) temperatures. This explanation might be applicable to the Larimer (1968) and Baedecker and Wasson (1975) models, but here I have argued that the high-temperature assemblage and the low-temperature assemblage formed at the same pressure and this explanation is less attractive. (2) We can invoke kinetics (Blander, personal communication). Each condensation reaction has a temperature at which it becomes favorable and 50°K, perhaps 100°K, below this temperature it becomes kinetically unfavorable. The upper of our two accretion temperature ranges really refers to the temperature interval during which the reactions which produce the reduced phases are kinetically favorable. There may well be reactions at intermediate temperatures, but we have failed to identify them because they produce inconspicuous results.

Larimer suggested that the C/O ratio increased as a result of the transport of graphite from outside the inner solar system, while Baedecker and Wasson (1975) proposed that the H/O increase was caused by the transport of large amounts of H₂O ice from the inner to the outer solar system prior to the nebula's transient heating to over 2000°K. I have shown that when 20% of the original cosmic abundance of O is assumed to have been removed during the lithophile element fractionation it is possible in light of present thermodynamic data to produce the level of reduction without these transport mechanisms. Unlike graphite or H₂O transport, we have evidence that the lithophile element fractionation actually occurred. It is thought very significant that the most highly reduced meteorites have also suffered the most severe lithophile element fractionation. However, 20% is a lot of oxygen to have been removed during

the lithophile element fractionation (Section 1.1.1.); in fact, only 10–15% could have been removed this way if we take Cameron's (1973) cosmic abundance tables. Unlike most elements, the cosmic abundances of O and H still appear to be subject to some revision; the best estimates for the H/O ratio went from 1860 in 1956 to 1102 in 1968 and to 1479 in 1973 (see Cameron, 1973). A value of about 1600 would give a sufficiently reducing nebula.

The aubrites can be fitted quite easily into the nebula condensation models, even though they were not specifically designed for them. In fact, most authors favor an igneous origin for this group, the only published exceptions being Wasson and Wai (1970) and Richter *et al.* (1979). The former authors observed that the *E* chondrites and aubrites form a continuous sequence in numerous chemical and physical trends, while Richter *et al.* (1979) based their preference for a nebula origin on a comparison of trace elements in aubrites with those of *E* chondrites and diogenites using a factor analysis. In their recent review, Watters and Prinz (1979) favor an igneous origin mainly because rare-earth element data show a negative Eu anomaly suggestive of fractional crystallization. Present evidence seems to favor equally a nebula and an igneous origin for the aubrites.

4.2. Metamorphism

In the present model, I have assumed metamorphism affected only the petrology of these meteorites, and has not changed their composition. Some authors have argued that it has played a major role, especially with regard to the highly volatile elements (Section 1.1.4). Takahashi *et al.* (1979) have claimed that the trace element data do not fit the predictions of the thermal release experiments of Ikramuddin *et al.* (1976) any better than they fit the condensation curves (assuming a pressure of 10⁻⁴ to 10⁻⁶ atm). In fact, there is a better fit to the condensation curves when a pressure of 1 atm is assumed, because solid solution

plays a more important part in the condensation process (Fig. 6). It is also possible to argue that the S/Si fractionation is due to metamorphic heating; Herzog *et al.* (1979) have shown that a 30% loss of sulfur from Allende occurs when it is heated to 1270°K for 1 hr. How applicable the results are to *E* chondrites is debatable. More compelling is the argument that if metamorphism caused loss of S from *E* chondrites, why did it not do so in the case of ordinary chondrites which have suffered similar metamorphic histories? Metamorphic temperatures for ordinary chondrites are 960–1320°K (Wasson, 1972) and 950–1100°K for *E* chondrites (Larimer and Buseck, 1974; Skinner and Luce, 1971).

The present model predicts that the aubrites accreted first, the *EII* chondrites accreted next, and the *EI* chondrites last. In view of their similarity to each other and dissimilarity to other classes, it seems most likely that the *E* chondrites came from a single parent body. *EII* chondrites, which have suffered greater metamorphism than *EI* chondrites, would have been buried at the greater depth. Similarly, the aubrites have suffered even greater recrystallization, consistent with an even greater burial depth. It would seem that the heat source which caused the metamorphism was internal, due either to primordial heat of accretion or to trapped radioactivities. Wasson and Wai (1970) argued that the relative burial depths were the reverse of this, and that the heat source was external—most probably meteoritic bombardment. This was mainly because *EII* chondrites tend to have lower exposure ages than *EI* chondrites. However, exposure age is a very poor guide to burial depth.

4.3. S/Si Fractionation in Relation to the Fe/Si Fractionation

An Fe/Si fractionation also occurs in the ordinary chondrites (Urey and Craig, 1953; Mason and Wiik, 1964) and it correlates with oxidation state (Prior, 1916; Müller *et al.*, 1971), or, more precisely, the FeO

content of the silicates. The formation of FeO and FeS are very similar processes; both, for example, are pressure independent, the major difference being that while oxidation occurs between 500 and 600°K, sulfuration takes place between 600 and 700°K. The reactions involved are shown in Fig. 8. It is thought particularly significant that while Fe/Si fractionation in *E* chondrites correlates with the S/Si ratio, in ordinary chondrites it correlates, although inversely, with oxidation state. In the present model this is interpreted as a consequence of *E* chondrites accreting during sulfuration (600–700°K), while for ordinary chondrites, accretion occurred during oxidation (500–600°K). The aubrites formed at the very beginning of sulfuration and when metal accretion efficiency was apparently very low. In fact, if one can assume that the total Fe and S contents of aubrites are due to preterrestrial contamination—i.e., small admixtures of other classes which have impacted the aubrite parent bodies at some time and caused their brecciated textures—

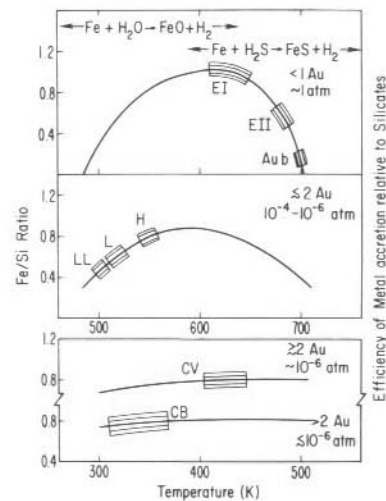


FIG. 8. Schematic illustration of an explanation for the Fe/Si variations in *E* chondrites and ordinary chondrites, and the associated sulfuration and oxidation trends. It should be emphasized that the classes are assumed to have formed at different pressures; *E* chondrites and aubrites at 1 atm, and ordinary chondrites between 10^{-4} and 10^{-6} atm with a pressure decrease along the sequence H, L, LL.

we might imagine the aubrites accreted simultaneously with condensation of the enstatite, at a temperature of about 1200°K.

The reason for the O/Si or S/Si versus Fe/Si correlation being positive in *E* chondrites, and yet negative in ordinary chondrites, remains to be explained. I propose that throughout the accretion of the *E* chondrites iron accretion became progressively more efficient, relative to silicate accretion, while throughout the accretion of ordinary chondrites iron accretion became relatively less efficient. In other words, the *H* chondrites accreted at higher temperatures than *L*, etc. Presumably, *H* chondrites formed at higher pressure than *L* and *LL*, since the highly volatile elements are present in *C1* proportions in type *H3*, *L3*, and *LL3* chondrites. Figure 8 illustrates this idea schematically, bearing in mind also that the extent of metal-silicate fractionation seems to have varied with distance from the Sun. I have argued elsewhere that most iron meteorite classes accreted between 600 and 700°K (Sears, 1978b), the temperature interval in which I now argue that iron accretion became progressively more efficient. It is interesting to note that silicates in IAB iron meteorites have extremely low FeO contents, also suggestive of accretion well before ordinary chondrites, say above 600°K. IAB irons also contain abundant sulfides and must have formed after the beginning of sulfuration. Iron meteorite class IVB accreted simultaneously with condensation, but at pressures below 10^{-3} atm (Sears, 1978b; Kelly and Larimer, 1977). This is analogous to the metal in *E* chondrites in the present model, although at much lower pressures.

4.4. Analogy with CV Chondrites

The model proposes that *E* chondrites are the result of mixing two equilibrium assemblages, one which formed by simultaneous condensation and isolation from the nebula gases, and one in which most of the silicates had already condensed and were isolated at much lower temperatures. In

many respects this is analogous to the popular model for the *CV* chondrites. In the case of the *CV* chondrites, the assembly which became isolated as soon as it condensed were the calcium-aluminum-rich inclusions (CAI), and the low-temperature assemblage is the matrix. In *CV3* chondrites the matrix is an Fe-rich olivine which forms in the solar nebula between 400 and 500°K, while in *CV2* chondrites it is Fe_3O_4 , and hydrated clay-like minerals, which form below 400°K. The major distinction is that while in *CV* chondrites the high-temperature assemblage exists as distinct inclusions, usually several millimeters in size, in *E* chondrites it now consists simply of the reduced minerals which are not obviously isolated from the matrix. The explanation offered for this is that the *E* chondrites have suffered a much higher degree of metamorphism than the *CV* chondrites, and this has homogenized their overall texture. According to Larimer and Buseck (1974) all *E* chondrites have been metamorphosed to at least 950°K. Even so, particularly large inclusions may have survived metamorphism and would be available for study should they be specifically sought.

4.5. Formation Location

Since the early 1950s, it has usually been assumed that the most highly reduced species will be formed nearest the Sun. On this basis, assuming they formed from a gas of solar composition, *E* chondrites formed nearer the Sun than any other chondrite class—Larimer and Anders (1967) suggest the inner fringes of the Asteroid Belt, while Baedeker and Wasson (1975) proposed a formation location within 1 AU. According to the present model, the *E* chondrites formed in a region of the solar nebula where the ambient pressure was about 1 atm. The models of Cameron and Pine (1973) and Lewis (1974) suggest that the ambient nebula pressure at Mercury's distance from the Sun was between 10^2 and 10^{-2} , depending on the value assumed for the opacity of the nebula. Cameron's (1978) more recent

model, incorporating protoplanets, predicts a value of around 10^{-2} atm (see Sears, 1979, Fig. 8). It seems that an orbit near or within the orbit of Mercury is a likely location for the formation of the *E* chondrites. The *E* chondrites are an extremely small class (2.5% of all falls are of this class), which seems consistent with the difficulty in constructing dynamic models to carry out the necessary orbital change to bring the meteorites to Earth.

There is another postulated region of the primitive solar nebula where pressures well in excess of 1 atm may have existed—inside protoplanets. The concept of protoplanets, as large high-density regions of the primordial nebula in which the planets formed, is attributed to Kuiper (1951) and has recently been resurrected by Cameron and co-workers (e.g., Cameron, 1978). As far as formation locations for any meteorite class is concerned, they present the major problem that any shock event capable of ejecting meteorite precursors would have destroyed the objects. The products of such a forceful ejection would resemble the nickel-iron spherules found around meteorite impact craters or, at best, tektites.

5. CONCLUSIONS

My main conclusions are that the reduced species in *E* chondrites and aubrites were isolated from the nebula soon after their formation, and if the nebula pressure was on the order of 1 atm, the nebula composition may have been near to cosmic. The requirement of immediate isolation is common to models invoking a fractionated nebula, as well as those assuming the nebula was cosmic in composition. The presence of highly volatile elements in *E* chondrites and aubrites requires a low-temperature component to also be present, and if the pressure was about 1 atm the fractionations in S/Si can also be explained by a condensation and accretion process—the S/Si fractionation cannot have been the result of metamorphic heating because the ordinary chondrites, which

have been metamorphosed to the same extent, do not show this property. The siderophile element fractionations are understood in terms of the efficiency of iron accretion, relative to silicate accretion, reaching a maximum around 600°K. It is thought unlikely that these meteorites formed in protoplanets, but rather as much smaller objects near or within the orbit of Mercury.

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