METEORITICAL AND ASTROPHYSICAL CONSTRAINTS ON THE OXIDATION STATE OF THE SOLAR NEBULA

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We review efforts to constrain the oxidation state of the solar nebula by using the chemistry and mineralogy of primitive chondritic meteorites (i.e., type 3 carbonaceous, ordinary, and enstatite chondrites). Our review shows that the nebular redox state varied from several orders of magnitude more oxidizing than a solar gas to several orders of magnitude more reducing than a solar gas. Mechanisms to explain such large variations are reviewed, and their implications for planetary chemistry are also discussed. An important part of our effort is the attempt to disentangle the signatures of parent body and nebular processes. Parent body processes, such as thermal metamorphism and fluid/rock interactions, have altered, sometimes significantly, the original nebular signatures preserved in primitive (e.g., type 3 carbonaceous) chondrites and make interpretation of the nebular record difficult.

I. INTRODUCTION

In 1971 Ed Anders wrote, "Chondrites contain a unique archeological record of physical and chemical conditions in the solar nebula. It is the job of meteoriticists to decipher this record—to translate structure, composition, and mineralogy into temperature, pressure, time, and chemical environment" (Anders 1971). Anders goes on to emphasize the "fortunate coincidence" that theoretical models have, at the same time, evolved to a point where they allow detailed predictions of pressure, temperature and composition at various times in the evolution of the solar nebula. In the period since 1971, meteoriticists have learned that both tasks are more

difficult than initially thought. Meteorites are far more complex, and the theoretical treatment of the protosolar nebula and young stellar objects with circumstellar disks (e.g., Hartmann 1996) is much more complicated, than was anticipated in the early 1970s.

The problems, however, remain. Under what conditions did the components of meteorites form? What do these conditions tell us about the solar nebula on a local or on a global scale? What are the effects of asteroidal processing (fluid-rock interaction and thermal metamorphism) on nebular records in meteorite components? How do we distinguish between nebular and asteroidal records in meteorites?

The most primitive (i.e., the least altered and thermally metamorphosed) meteorites are carbonaceous (CO, CV, CK, CH), ordinary (H, L, LL), and enstatite (EH, EL) chondrites of petrologic type 3, which largely consist of various amounts of chondrules, Ca-Al-rich inclusions (CAIs), and fine-grained matrices. Detailed mineralogical, experimental, and isotopic studies have shown that these chondritic components have experienced a complex formation history in the solar nebular and asteroidal environments (e.g., Kerridge and Matthews 1988; Hewins et al. 1996; Zolensky et al. 1997).

CAIs are products of high-temperature processes in the early solar nebula. By "high-temperature" we mean temperatures so high that materials with approximately solar compositions for nonvolatile elements would not survive very long (minutes to hours) if exposed to them. Some CAIs are condensates and residues from these events; others crystallized from refractory melts, which may themselves represent condensates (e.g., MacPherson et al. 1988; Palme and Boynton 1993). Both types may have experienced subsequent alteration at lower temperatures by gas-solid reactions in the solar nebula, by fluid-rock interaction in an asteroidal environment, or both (MacPherson et al. 1988; Russell et al. 1998). Chondrules probably formed by multiple, localized, brief episodes of melting of preexisting solids; some suffered subsequent low-temperature nebular or asteroidal alteration similar to that observed in CAIs (Kimura and Ikeda 1995). The origins of matrix material remain obscure; a minor component of matrix is presolar (Huss and Lewis 1995), and the remainder is a complex mixture of material resulting from both nebular and asteroidal processes (Brearley 1996).

The solar nebula did not produce chemically and isotopically uniform objects. The most primitive type 3 carbonaceous, ordinary, and enstatite chondrites contain components that formed under different temperatures and redox conditions. Preservation of this apparent disequilibrium in these meteorites for billions of years indicates that their parent asteroids were not heated to above 600–700 K at any length of time and that the extent of reaction with liquid water was moderate, although there is some diversity in opinion about the exact degree of water/rock interaction (see section III.G). Meteorites of higher petrologic types, from 4 to 6 (CK, H, L, LL, R, EH, EL), reflect increasingly more intense parent body heating, whereas mete-

orites of lower petrologic types, 2 and 1 (CM, CR, CI), indicate increasing degrees of reaction with water, erasing the high-temperature record of various minerals.

An important parameter for the mineralogy of meteorites is the oxygen fugacity (fO_2, which is identical to the oxygen partial pressure for an ideal gas) under which the minerals formed or equilibrated. The solar nebula gas is very reducing (see section II), producing on condensation only metallic iron and almost no FeO in silicate or oxide condensates. Parent body processes, if water is present, may imprint a high fO_2 on the minerals that were produced or that have equilibrated with the nebular gas. Some of the oxidized meteorite components may have been produced in the solar nebula environment.

In this chapter we will review the evidence constraining the fO_2 under which the components of meteorites were formed. We will also attempt to disentangle nebular and parent body effects to constrain the variations in fO_2 of the solar nebula in the formation location of the type 3 carbonaceous, ordinary, and enstatite chondrites. We also discuss mechanisms responsible for possible variations in redox conditions in the solar nebula.

II. OXYGEN FUGACITY OF THE SOLAR NEBULA

The elemental abundances of the ten most abundant elements in a solar gas (gas of a solar composition) are listed in Table I, which shows that H, O, and C are the three elements we expect (by virtue of their large abundances and their chemistry) to control the fO_2 of solar gas. To a very good first approximation, the fO_2 of solar gas is regulated by the reaction

$$H_2 + 0.5O_2 = H_2O \tag{1}$$

TABLE I
Elemental Abundances and Major Species
in a Solar-Composition Gas[a]

| Element	Atomic abundances	Major gas(es)
H	2.82×10^{10}	H_2, H
He	2.82×10^9	He
O	2.09×10^7	CO, H_2O
C	1.00×10^7	CO, CH_4
Ne	3.31×10^6	Ne
N	2.63×10^6	N_2, NH_3
Mg	1.023×10^6	Mg
Si	1.00×10^6	SiO, SiS
Fe	8.91×10^5	Fe
S	4.47×10^5	H_2S, HS
All other elements combined	4.16×10^5	Various

[a] from Lodders and Fegley (1998).

The temperature-dependent equilibrium constant (K_1) for reaction (1) is given by the equation

$$\log_{10} K_1 = -2.836 + 12{,}832/T \tag{2}$$

with temperature (T) in kelvins. The fO_2 (bar) for reaction (1)

$$\log_{10} fO_2 = 2 \log_{10}(H_2O/H_2) + 5.67 - 25{,}664/T \tag{3}$$

is valid from 298 to 2500 K, where the (H_2O/H_2) number ratio (i.e., the molar ratio) is used in equation (3). The amount of water vapor in solar gas depends on the partitioning of carbon between CO and CH_4 via the net thermochemical reaction

$$CO + 3\,H_2 = CH_4 + H_2O \tag{4}$$
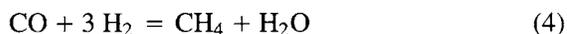
and on the amount of oxygen consumed by rock-forming elements. As we shall discuss below, essentially all carbon is bound in CO in the solar nebula, and mass balance dictates that $\sim 15\%$ of total oxygen is bound in rock (i.e., the amount of O bound in $MgO + SiO_2 + CaO + Al_2O_3 + Na_2O$). Thus, under conditions where negligible dissociation of water vapor and hydrogen occurs, the H_2O/H_2 ratio in solar nebula gas is $\sim 5 \times 10^{-4}$, and equation (3) can be rewritten as

$$\log_{10} fO_2 = -0.85 - 25{,}664/T \tag{5}$$

Equation (5) gives $fO_2 \sim 10^{-17.9}$ bar at 1500 K, vs. $10^{-17.8}$ bar at the same temperature from a chemical equilibrium calculation using the CONDOR code (Fegley and Lodders 1994; Lodders and Fegley 1995) considering several thousand species in a solar gas. Comparisons of CONDOR code results and equation (5) indicate that $\log_{10} fO_2$ from equation (5) reproduces the code results within ± 0.2 log bar units below 2000 K and within ± 0.3 log bar units from 2000 to 2500 K.

Equation (5) shows that the fO_2 of a solar gas is extremely reducing; as a consequence, iron alloy is more stable than iron oxides and FeO in minerals in the solar nebula. For example, at 1600 K, solar gas is 6 log bar units more reducing than the iron-wüstite (IW) buffer (i.e., firmly inside the iron metal stability field). However, the difference between the fO_2 of solar gas and the fO_2 needed to stabilize Fe oxides decreases with decreasing temperature until FeO-bearing minerals become stable at 500 K and below. At these low temperatures, however, solid-state diffusion is so slow that Fe cannot be incorporated into the Mg silicates within the nebular lifetime. Thus, the dominance of FeO-bearing minerals in chondritic meteorites indicates either that they were not formed by equilibrium condensation from a solar gas or that they were later modified on a parent body.

A. Carbon Chemistry in a Solar Gas

As can be seen from Table I, the C/O atomic ratio in solar gas is ~ 0.5; as a consequence, the oxygen not bound in minerals is almost evenly di-

vided between CO and H_2O. Carbon monoxide is the dominant carbon gas at high temperatures and low pressures in solar-composition material (cf. Lewis et al. 1979). However, at complete chemical equilibrium the CO/CH_4 ratio decreases dramatically with decreasing temperature, because reaction (4) proceeds toward the right. Eventually, $CO/CH_4 \ll 1$ and CH_4 becomes the dominant carbon gas. The oxygen released from CO increases the H_2O abundance almost twofold. However, as first demonstrated by Lewis and Prinn (1980), the kinetics of the CO $\rightarrow$ CH_4 conversion are so slow that reaction (4) is quenched at very high temperatures. As a consequence, CO remains the dominant carbon gas throughout the solar nebula, and the H_2O/H_2 ratio remains constant at $\sim 5 \times 10^{-4}$ until water ice condenses. The water ice condensation point is pressure dependent and varies from ~ 150 K at 10^{-7} bar total pressure to ~ 190 K at 10^{-3} bar total pressure. As discussed later in this chapter, the nebular snowline was at ~ 5.2 AU throughout most of the time that nebular gas was around, because water ice condensation led to runaway accretion of Jupiter (Lissauer 1987; Stevenson and Lunine 1988). As the nebula cooled, the snowline moved inward (e.g., Ruden and Lin 1986), and some ice condensed in the asteroid belt, providing a source of water for subsequent hydration reactions on asteroids.

III. OXYGEN BAROMETERS IN CHONDRITES

Chondritic meteorites (chondrites) largely consist of chondrules, CAIs, and fine-grained matrices. There is general agreement that these chondritic components originated in the solar nebula; hence, they potentially give us insights into the processes that were operative in the early solar system. In this section we review indicators of fO_2 of the solar nebula gas that have been proposed for CAIs, chondrules, and matrices in carbonaceous chondrites (Table II). Because all chondrites were altered to some degree after accretion into planetesimals and asteroids by fluid-rock interaction and thermal metamorphism, these processes may have modified the nebular features. As a result, some of the mineral and chemical indicators of fO_2 discussed in this section may reflect conditions during asteroidal alteration. There are two fundamentally different types of oxygen fugacity indicators: (a) mineral indicators and (b) chemical indicators. In mineral indicators the valence state of an element reflects the fO_2 of the ambient gas or fluid from which the mineral formed; the valence states either are determined directly or are reflected in physical properties of minerals, such as color. Chemical indicators are based on elemental abundances (in most cases normalized to solar abundances) in minerals; for example, the mineral sequence condensing from a gas and the trace element patterns in the condensed minerals are strongly dependent on the oxygen fugacity of the gas. Also, element patterns produced during evaporation or in igneous processes (e.g., crystallization) will be influenced by fO_2. In general, mineral indicators are much more susceptible to later alterations, either in the solar nebula or on a parent body, than trace element patterns.

TABLE II

Proposed Oxygen Fugacity Indicators in Chondrites

Proposed indicator	Reversible	References
Oxidized solar nebula gas:		
Color of hibonite	Yes	1–3
(Ti^{3+}/Ti^{4+}) ratios in hibonite	Yes	4
(Ti^{3+}/Ti^{4+}) ratios in fassaite	Yes	5,6
Rhönite	No	6
Sr, Ba, U, V depletions in CAIs	No	7
Ce depletions in CAIs	No	7–10
Mo and W depletions in CAIs	No	11
Fe, Ni, Co abundances in fine-grained CAIs	No	12
Secondary Ca-rich minerals in CAIs		
(e.g., andradite, wollastonite, grossular, kirschsteinite)	No	13–17
Fremdlinge minerals (e.g., powellite, molybdenite)	No	18,19
Fayalite	No	20–22
Fayalitic olivine	No	23–25
Reduced solar nebula gas:		
Mineralogy of enstatite chondrites		
e.g., oldhamite, niningerite, alabandite, Ti-rich troilite	No	26, 27

References 1: Stolper and Ihinger (1983); 2: Ihinger and Stolper (1986); 3: Live et al. (1986); 4: Beckett et al. (1988); 5: Stolper et al. (1982); 6: Beckett and Grossman (1986); 7: Boynton and Cunningham (1981); 8: Davis et al. (1982); 9: Boynton (1978); 10: Fegley (1986); 11: Fegley and Palme (1985); 12: Kornacki and Wood (1985); 13: Allen et al. (1978); 14: MacPherson et al. (1981); 15: Hashimoto and Grossman (1987); 16: McGuire and Hashimoto (1989); 17: Kimura and Ikeda (1995); 18: Armstrong et al. (1987); 19: Bischoff and Palme (1987); 20: Brigham et al. (1986); 21: Wood and Holmberg (1994); 22: Hua and Buseck (1995); 23: Palme and Fegley (1990); 24: Nagahara et al. (1988); 25: Dohmen et al. (1998); 26: Keil (1968); 27: Larimer (1968).

A. Color and Ti^{3+}/Ti^{4+} Ratios in Hibonite, Fassaite, and Rhönite

1. Hibonite [$Ca_2(Al,Ti)_{24}O_{38}$]. Hibonite is a Ca-Al-Ti oxide occurring in several types of CAIs. Some hibonites condensed from solar gas, whereas others are evaporative residues and crystallization products from a melt at high temperatures (Kornacki and Fegley 1984; Ireland et al. 1992). In meteorites hibonite occurs in three colors: blue, orange, and colorless. Ihinger and Stolper (1986) showed that the color of hibonite heated at 1430°C (close to its condensation temperature) depends on fO_2. An fO_2 increase changes the color of hibonite from blue to orange and to colorless; these changes are reversible and extremely rapid even under quenching. These authors proposed that the color of hibonite can be used as an fO_2 indicator of the environment where hibonite equilibrated last. Beckett et al. (1988) found that the color of hibonite is a function of the Ti^{3+}/Ti^{4+} ratio, which also can be used as an fO_2 indicator. Titanium is present in terrestrial and

extraterrestrial samples as Ti^{4+}. Under the extremely reducing conditions of the solar nebula, Ti^{4+} is partly converted to Ti^{3+}. The Ti^{3+}/Ti^{4+} ratio is thus an indicator of the fO_2 that prevailed during condensation and/or crystallization of Ti-bearing minerals.

Beckett et al. (1988) measured Ti^{3+} contents of a blue hibonite in a CAI from the CM2 chondrite Murchison and concluded that this hibonite equilibrated with a solar gas. Ihinger and Stolper (1986) estimated the fO_2 recorded by blue hibonites in the Blue Angel CAI from Murchison and concluded that the hibonite equilibrated in a gas that was four or five orders of magnitude more oxidizing than a gas of solar composition. However, this CAI experienced asteroidal alteration under oxidizing conditions (Armstrong et al. 1982), so it seems possible that the color and Ti^{3+}/Ti^{4+} ratio in its hibonite reflect reequilibration during alteration (Beckett et al. 1988).

The coexistence of colorless or orange hibonite, reflecting oxidizing conditions, with fassaite with high Ti^{3+}/Ti^{4+} ratios, indicative of reducing nebular fO_2 (see subsection 2 below), was also found in other CAIs and is interpreted to indicate later oxidizing conditions that affected the color of hibonite but not the Ti^{3+}/Ti^{4+} ratios in fassaite (Ihinger and Stolper 1986).

2. *Fassaite [Ca(Mg,Ti,Al)(Al,Si)$_2$O$_6$] and Rhönite [Ca$_2$(Mg,Al,Ti)$_6$ (Si,Al)$_6$O$_{20}$].* Fassaite is a Ti-rich Al-diopside occurring in several types of CAIs. Fassaites in Type B CAIs crystallized from a melt at $\sim 1200°C$ and contain variable amounts of Ti^{3+} and Ti^{4+}. Beckett and Grossman (1986) obtained a relationship between the Ti^{3+}/Ti^{4+} ratio in fassaite and fO_2 in the coexisting gas and concluded that crystallization of fassaite in Type B CAIs from Allende took place in solar gas.

The mineral rhönite, although less commonly observed in CAIs, can be used in a similar fashion. Beckett and Grossman (1986) calculated fO_2 for compact Type A CAIs from Allende and concluded that crystallization of rhönite took place in solar gas.

To summarize, the observed Ti^{3+}/Ti^{4+} ratios in fassaite and rhönite crystallizing from CAI melts are consistent with their origin in a canonical solar gas. The observed colors and Ti^{3+}/Ti^{4+} ratios of hibonites in Allende may not reflect the redox conditions during their crystallization but instead may reflect a later equilibration with oxidized gases, either in nebular or asteroidal environments.

B. Chemical Indicators: Trace Element Concentrations in CAIs

A variety of factors, including fO_2, host phase, equilibration temperature, gas-solid fractionation, and low-temperature alteration may affect the abundances of trace elements in CAIs (Boynton 1975; Palme and Wlotzka 1976; Davis and Grossman 1979; Boynton and Cunningham 1981; Ekambaram et al. 1984; Fegley and Palme 1985). If the effects of fO_2 can be decoupled from those due to other factors, then trace elements can be used as oxygen barometers. Below we review several trace element oxygen barometers proposed for CAIs.

1. Ce Depletion. At fO_2 three to five orders of magnitude higher than a solar gas, Ce becomes highly volatile (the major gas species of Ce is CeO_2) relative to other rare earth elements (REEs), which occur as monoxides in the gas (e.g., LaO). If REEs condensed in a mineral from such a gas, large negative Ce anomalies are expected (Boynton 1975; Boynton and Cunningham 1981; Davis et al. 1982; Fegley 1986). It was found that five hibonite-rich CAIs and C1 (a type B CAI), all of which are FUN (Fractionation and Unidentified Nuclear isotopic anomalies) inclusions, exhibit strong negative anomalies in Ce (Fig. 9 in Floss et al. 1996). Thermodynamic calculations for the CAI C1 (Fegley 1986) show that its Ce depletion could have been produced under oxidizing conditions, similar to those proposed to explain Mo and W depletions (see subsection III.B.3 below). Because one of the best-studied CAIs exhibiting Ce depletion, the HAL inclusion, was originally interpreted as an aggregate of nebular condensates (Allen et al. 1980), this depletion was proposed as an indicator of oxidizing conditions in the solar nebula (Davis et al 1982; Rubin et al. 1988; Palme and Boynton 1993). However, several isotopic studies and vacuum evaporation experiments (Ireland et al. 1992; Davis et al. 1995; Floss et al. 1996) showed that the FUN inclusions formed by kinetically controlled evaporation (Fig. 1 from Davis et al. 1995). Because the evaporating CAI material was not in equilibrium with a solar gas, the Ce depletions in the FUN inclusions cannot be used as indicators of the redox conditions in the solar nebula. Apparently, conditions during evaporation are generally much more oxidizing than reflected in the ambient gas phase into which evaporation occurs.

With a few rare exceptions (e.g., a small Ce anomaly in a fine-grained CAI from Efremovka; Boynton et al. 1986), there is no evidence for Ce anomalies in most CAIs (e.g., Wänke et al. 1974; Grossman and Ganapathy 1976*a,b*; Davis et al. 1978; Mason and Taylor 1982; Ekambaram et al. 1984). This suggests either that condensation of the REEs in most CAIs took place in solar gas or that CAIs equilibrated with the nebular gas at such a low temperature that complete condensation of Ce occurred.

2. Yb Depletion in the HAL-type CAIs. At solar gas fO_2, most REEs are stable as monoxide gas species except for Yb, whose predominant gas species is metallic Yb. This leads to a depletion of Yb relative to the other REEs in condensed oxide or silicate phases. Under more oxidizing conditions, however, Yb approaches the behavior of the other REEs, and the anomaly disappears. Ytterbium depletions were found in five HAL-type hibonites that also showed strong Ce depletions (Fig. 9 from Floss et al. 1996). The presence of both Ce and Yb anomalies in the same mineral grain is incompatible with equilibrium between gas and solid at any fO_2. Ireland et al. (1992) suggested that to produce anomalies in both, there must be two evaporation episodes, one under oxidizing conditions, the other reducing. Floss et al. (1996) inferred instead that Yb anomalies were inherited from the precursor materials.

3. Mo and W Depletions. Alloys of metals with low vapor pressures (W, Os, Re, Ir, Mo, Ru, Pt, Rh) are expected as the first metal condensates from a cooling gas of solar composition. CAIs commonly have high concentrations of these elements, which now reside in mineralogically complex inclusions that probably formed from initially homogeneous alloys by exsolution and reaction with ambient gases. However, in one Allende CAI, submicrometer homogeneous alloys of all refractory metals, including W and Mo, with solar relative abundances, were found. These are presently the best candidates for primary unaltered condensates (Eisenhour and Buseck 1992). Tungsten and molybdenum form volatile oxides under moderately oxidizing conditions. Their presence in the refractory metal alloys reflects the reducing conditions of formation that are created by the solar gas. Larger CAIs often show depletions of W and Mo (Fegley and Palme 1985). The observed depletions have a very characteristic pattern, with Mo always being more depleted than W, and have been interpreted as indicating condensation of refractory metals under more oxidizing conditions than those of a solar gas. Fegley and Palme (1985) found that the same Mo and W depletion pattern occurs in refractory metal alloy condensation calculations done under increasingly oxidizing conditions (Fig. 7.7.3 from Rubin et al. 1988). They also showed that observed patterns could be matched by refractory metal alloy condensation calculations done at oxygen fugacities 10^3 to 10^4 times greater than in a solar gas at the same temperature and pressure (Fig. 1).

Subsequent work showed that Mo and W depletions were found in ~80% of the 30 samples from the CV3 Allende, Grosnaja, Leoville, and CO_3 Ornans carbonaceous chondrites analyzed (Fegley and Kong 1989;
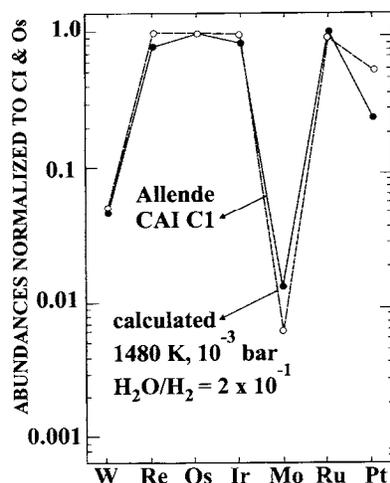

Figure 1. Observed and calculated refractory metal abundances in Allende FUN inclusion C1 (after Rubin et al. 1988).

Fegley and Prinn 1989). Although this database is still limited in size, several important conclusions can be drawn: (1) Mo is always more depleted than W. (2) The depletions are found in both normal and isotopically anomalous (i.e., FUN) CAIs. (3) The depletions are not simply a volatility effect, because W is the most refractory of these seven metals, and Mo has a vapor pressure very similar to that of Ir. (4) The Mo and W depletions do not simply reflect redistribution of these two metals inside CAIs; they are bulk depletions of Mo and W from CAIs.

Fegley and Palme (1985) considered several potential mechanisms, including fractional condensation, reactions with sulfur compounds, and metamorphic alteration, to form the Mo and W depletions. However, none of these processes reproduced the observed depletions. They concluded that the Mo and W depletions were produced by high-temperature oxidation during condensation or vaporization in the solar nebula. However, Fegley and Palme (1985) also noted that the rarity of Ce anomalies in CAIs seemed to be inconsistent with oxidizing conditions in the solar nebula, because Ce depletions should also form under the oxidizing conditions that produce Mo and W depletions. Fegley and Palme (1985) suggested that the REEs and refractory metals last equilibrated under different conditions at a different time or place. According to this scenario, CAIs accumulated as mixtures of Mo- and W-depleted refractory metals that condensed under oxidized conditions and silicate-lithophile components that formed under reduced conditions. This explanation is consistent with the fact that refractory metals and REE were carried into CAIs in different phases with different chemical and physical properties.

Beckett et al. (1988) also noticed the differences between the higher fO_2 indicated by Mo and W depletions in CAIs and the lower fO_2 indicated by Ti^{3+}/Ti^{4+} ratios in oxide and silicate minerals in CAIs. They speculated that the Mo and W depletions formed at low temperatures during oxidation in the solar nebula or during asteroidal metamorphism. The latter alternative appears to be contradicted by the characteristic pattern of the Mo and W depletions, because Fegley and Palme (1985) calculated that metamorphic alteration gave W depletions equal to or larger than Mo depletions.

In this regard we note that Palme et al. (1994) studied one CAI (Egg-6 from Allende) that has variable W and Mo depletions unlike the characteristic patterns produced by high-temperature oxidation (Fig. 7.7.3 from Rubin et al. 1988 and Fig. 2a, this chapter). However, the W in this inclusion has also been redistributed from refractory metal alloys into the surrounding silicate, and Mo is more depleted than W. Palme et al. (1994) concluded that Egg-6 was affected by later oxidation at moderately high temperatures. This conclusion is supported by vaporization experiments by Köhler et al. (1988) and Wulf (1990), which showed that W is redistributed into the surrounding silicates, while Mo is lost to the ambient gas, when chondritic material is heated under oxidizing conditions (Fig. 2b).
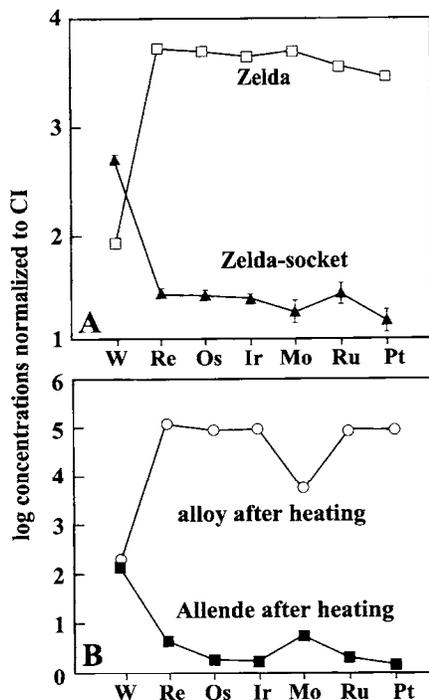
Figure 2. (a) CI chondrite-normalized refractory siderophile element abundances in Fremdling (see section III.E) Zelda in the Egg-G CAI from Allende and silicate portion of the host CAI (socket). The complementary patterns of the Fremdling and its socket indicate *in situ* mobilization of W from the Fremdling into silicates. (b) CI chondrite-normalized refractory siderophile element abundances of the heating experiments (at 1150°C for one week at Ni-NiO) on a refractory metal alloy embedded in Allende reproduces the pattern in Fig. 2a (from Palme et al. 1994).

The overall picture that seems to emerge is that Mo and W depletions in CAIs resulted from high-temperature oxidation in the solar nebula, which is the only process shown to produce the characteristic patterns in refractory metal alloys, with Mo always more depleted than W.

C. Fe, Ni, and Co Abundances in Fine-grained CAIs in Allende

Kornacki and Wood (1985) showed that spinel grains in the fine-grained CAIs in Allende are enriched in FeO, whereas bulk compositions of these CAIs have Fe/Ni and Fe/Co ratios significantly higher than chondritic. These results suggest that the major enrichment of spinels in FeO did not result from oxidation of Fe, Ni-metal grains inside the CAIs; an external source of Fe is required. In a gas of solar composition, the oxidation of Fe metal takes place at low temperatures, where Fe transport in a gas form is insignificant. Kornacki and Wood (1985) inferred that if FeO

concentrations in the CAIs were largely established in the hot nebula, the nebular fO_2 locally may have approached the iron-wüstite buffer, which is ~5–6 orders of magnitude more oxidizing than the equilibrium fO_2 of a gas of solar composition at high temperatures (>1000 K).

High-temperature experiments (1300–1400°C for 10–20 hr) in a Knudsen cell with metal and spinel by Dohmen et al. (1998b) show that Fe, Ni, and Co could have been transported into spinel by the gas phase. The reaction forming Fe-rich spinel is

$$MgAl_2O_4(s) + Fe(g) = FeAl_2O_4(s) + Mg(g) \qquad (6)$$
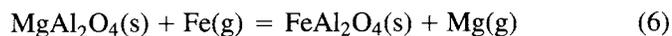
Dohmen et al. (1998b) concluded that the enrichment of the Allende spinels in FeO took place by reaction (6) at high temperatures under oxidizing conditions.

Hashimoto and Grossman (1987) found that the FeO content of spinel in the Allende CAIs increases with the degree of low-temperature alteration of associated phases (e.g., melilite or anorthite) to nepheline, sodalite, and phyllosilicates. Because it is commonly accepted that phyllosilicates formed during aqueous activity in an asteroidal environment, it seems plausible that oxidation of Fe and its diffusion into spinel occurred during planetary metamorphism (McSween 1977). It is, therefore, unclear to what extent spinels in Allende inclusions have acquired FeO during high-temperature oxidation and to what extent during low-temperature alteration.

D. Loss of Ca from CAIs and Chondrules and Formation of Secondary Ca-Fe-bearing Silicates

It has been shown that CAIs and chondrules in Allende experienced alteration resulting in formation of secondary Ca-, Na- and Fe-bearing minerals, such as wollastonite ($CaSiO_3$), andradite ($Ca_3Fe_2Si_3O_{12}$), diopside-hedenbergite pyroxenes ($CaMgSi_2O_6$-$CaFeSi_2O_6$), grossular (Ca_3Al_2 Si_3O_{12}), anorthite ($CaAl_2Si_2O_8$), nepheline ($NaAlSiO_4$), sodalite ($Na_4(AlSiO_4)_3Cl$), and phyllosilicates (MacPherson et al. 1988; Kimura and Ikeda 1995; Krot et al. 1998d). Largely based on textural observations, Allen et al. (1978) and MacPherson et al. (1985) inferred that these minerals formed by rapid growth from a gaseous phase. Because several of these minerals cannot condense from a canonical solar nebula gas (Grossman 1972), it has been postulated that they condensed from a gas of nonsolar composition (H_2O/H_2 ~ 5×10^{-1}–5×10^{-2}). However, subsequent thermodynamic calculations of condensation from nonsolar gas under various oxidizing conditions failed to reproduce these secondary Ca-rich minerals (Wood and Hashimoto 1993; Petaev and Wood 1998).

During the alteration, Ca and Al were lost, whereas Si, Mg, Fe, Na, Cl, and H_2O were introduced into CAIs (e.g., MacPherson et al. 1981; Hashimoto and Grossman 1987; McGuire and Hashimoto 1989). Hashimoto (1992) showed that in oxidizing gases Ca, Al, Si, Mg, and

Fe can be volatilized as hydroxides [$Ca(OH)_2$, $Al(OH)_3$, etc.]. Assuming vapor-phase transport, Hashimoto (1992) estimated a lower limit for the Allende CAI alteration time. His calculations, done for a highly oxidized gas ($H_2O/H_2 \sim 500 \times$ solar) at 10^{-3} bar total pressure, gave alteration times of 2 yr (1500 K) to 500 yr (1200 K). Lower temperature (< 950 K; Hutcheon and Newton 1981), lower total pressure ($\sim 10^{-5}-10^{-6}$ atm; Wood and Morfill 1988) and lower fO_2 translate into much longer reaction times (10^5-10^6 yr). Hashimoto (1992) concluded that this timescale is implausibly long, because a zone of locally oxidized gas could be expected to dissipate within hours or days by convection in the nebula.

An alternative model of Ca mobilization from CAIs and chondrules involves low-temperature reactions in an asteroidal environment in the presence of aqueous solution (Armstrong et al. 1982; Meeker et al. 1983; Greenwood et al. 1994; Krot et al. 1998d). The minor phyllosilicates in Allende CAIs and chondrules (Hashimoto and Grossman 1987; Brearley 1997) and the high mobility of Ca, Si, Mg, Fe, and Al in aqueous solutions (Brearley and Duke 1998) are consistent with this model. Krot et al. (1998d) described wollastonite, diopside-hedenbergite pyroxenes, and andradite in veins in and rims around chondritic clasts (dark inclusions) in Allende (Fig. 3). Because veins in and rims around chondritic clasts can be formed only after aggregation and lithification of these rocks, Krot et al. (1998d) concluded that wollastonite, diopside-hedenbergite pyroxenes, and andradite formed in the presence of aqueous solution below 300°C in an asteroidal environment.

To summarize, the observed loss of Ca from CAIs and chondrules, and formation of the secondary Ca- and Fe-rich minerals in Allende, require the presence of an oxidizing fluid. Arguments favoring nebular and asteroidal environments have been presented, but no agreement has been reached yet.

E. Metal-Oxide-Sulfide Assemblages in CAIs (Fremdlinge)

Metal-oxide-sulfide assemblages in CAIs, largely studied in Allende, were originally inferred to have an exotic origin unrelated to the host CAIs and were called *Fremdlinge* (German for "strangers"; El Goresy et al. 1978). Fremdlinge commonly contain minerals requiring oxidizing conditions much higher than in a solar gas during formation, such as magnetite (Fe_3O_4), awaruite (Ni_3Fe), wairuite (CoFe), powellite ($CaWO_4$), scheelite ($CaMoO_4$), and phosphates. Fremdlinge were once believed to have formed as pristine nebular condensates of Pt-group element-rich metallic phases, Ni-Fe alloys, sulfides, and oxides that were later mixed and incorporated into CAIs (Armstrong et al. 1985, 1987; Bischoff and Palme 1987). As a result, Fremdling mineralogy has been considered as indicator of oxidizing conditions in the solar nebula prior to CAI formation (Rubin et al. 1988). Although it was subsequently shown (Blum et al. 1989; Palme et al. 1994) that Fremdlinge formed from homogeneous metallic
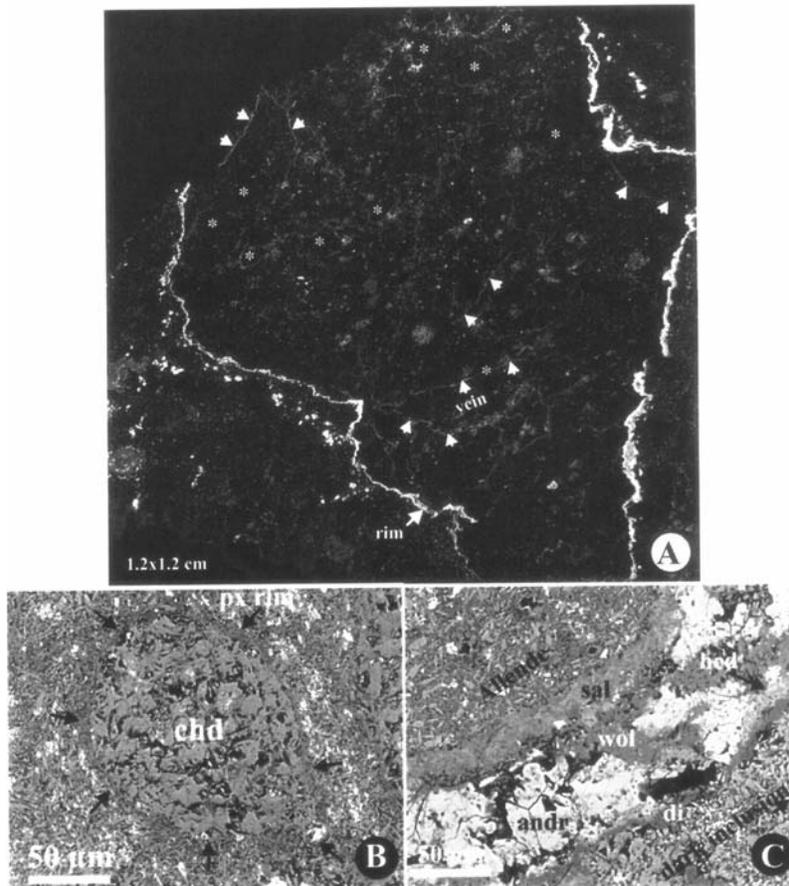
Figure 3. X-ray elemental map in Ca Kα (a) and backscattered electron images (b, c) of the lithified chondritic clast in Allende. (a) The clast consists of chondrules (indicated by stars) surrounded by Ca-rich rims; it is crosscut by Ca-rich pyroxene veins (indicated by arrows) and surrounded by a continuous Ca-rich rim. (b) Chondrule (chd) replaced entirely by fayalitic olivine and surrounded by a Ca-rich pyroxene rim (indicated by black arrows). (c) Ca-rich rim around the clast consists of andradite (andr), wollastonite (wol), hedenbergitic (hed), salitic (sal) and diopsidic (di) pyroxenes. Krot et al. (1998b) inferred that the clast experienced two stages of low-temperature alteration after lithification. An early alteration resulted in replacement of chondrules by fayalitic olivine. Calcium lost from the chondrules was redeposited as rims around chondrules and veins. Then clast was excavated from its original location (probably CV3 parent body) and introduced into Allende. In situ alteration resulted in dissolution of Ca-bearing phases inside the clast and their precipitation along the boundary with the host meteorite.

Figure 4. Equilibrium conditions (fO_2 vs. temperature) for opaque assemblages in CAIs, chondrules, and matrix in Allende. Opaque assemblages in all three components reflect low-temperature conditions, which are consistent with an asteroidal environment. The $Ni_{67}Fe_{33}$ alloy and coexisting magnetite observed in most Allende CAIs define an fO_2 1.5 log units above the $FeO-Fe_3O_4$ buffer and 6 log units above the fO_2 defined by the solar gas at temperatures below 800 K (from Blum et al. 1989).

nodules as a result of exsolution, oxidation, and sulfidization reactions *in situ*, there is no agreement on the place and temperature of this oxidation. Based on the similar ranges of equilibration temperatures and fO_2 of the opaque assemblages in CAIs, chondrules, and matrix in Allende, which are significantly higher than those in solar gas (Fig. 4), Blum et al. (1989) concluded that oxidation of Fremdlinge occurred in the CV3 asteroid. On the other hand, Palme et al. (1994) argued that conditions of oxidation of the Allende CAIs were quite variable and inferred that oxidation occurred before final accretion of the meteorite.

To summarize, Fremdling mineralogy reflects late-stage oxidation of metal assemblages either in the solar nebula or in an asteroidal environment; no consensus has been reached yet.

F. Fayalite

In a gas of solar composition, FeO-poor olivine (forsterite, Mg_2SiO_4) is the first major mineral to condense. At about the same temperature, Fe will condense as metal (FeNi alloy). With decreasing temperatures, most of the forsterite is converted to enstatite [$Mg_2(SiO_3)_2$]. At temperatures of 500 K, enstatite is calculated to react with FeNi and H_2O to produce FeO-rich olivine. At this temperature, however, reaction of enstatite with metal, which is diffusion controlled, is so slow that formation of FeO-rich olivine grains larger than 1 μm appears impossible (Palme and Fegley 1990).

There are two possible ways to circumvent this problem. Formation of FeO-rich olivine at higher temperatures by condensation from a gas more oxidized than the solar gas or by reaction of fluids on the parent body at elevated temperatures. These two endmember models will be used below in discussing the various occurrences of FeO-rich olivine.

1. Fayalite in Carbonaceous Chondrites. Hua and Buseck (1995) described large grains (up to 100 μm) of nearly pure fayalite (Fe_2SiO_4) containing up to 1 wt% MnO and associated with magnetite in the Kaba and Mokoia CV3 chondrites. They inferred that these fayalite grains formed by replacement of magnetite in an oxidized nebular gas ($H_2O/H_2 \sim 2 \times 10^3$–$10^4$ times solar) at 800–1200 K:

$$2\,Fe_3O_4(s) + 3\,SiO(g) + H_2O(g) = 3\,Fe_2SiO_4(s) + H_2(g) \qquad (7)$$
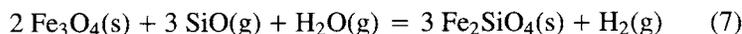
Based on the textural observations, thermodynamic calculations, and O-isotopic compositions of the coexisting fayalite and magnetite, which plot close to the terrestrial fractionation line with $\Delta^{18}O_{fayalite-magnetite}$ fractionation $\sim 20\%$, Krot et al. (1997, 1998c) concluded that fayalite formed at relatively low temperatures ($< 300°C$) during fluid-rock interaction in an asteroidal environment:

$$2\,Fe_3O_4(s) + 3\,SiO_2(aq) + 2\,H_2(g) = 3\,Fe_2SiO_4(s) + 2\,H_2O(g) \quad (8)$$
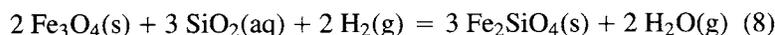
Recently, Hutcheon et al. (1998) studied the $^{53}Mn/^{53}Cr$ isotopic systematics of the Mokoia fayalites. They discovered large excesses of ^{53}Cr, which provide evidence for *in situ* decay of ^{53}Mn and show that these fayalites formed ~ 7–10 Myr after crystallization of Allende CAIs. Hutcheon et al. (1998) concluded that the Mokoia fayalites must have formed in an asteroidal environment and, hence, cannot be used as an oxygen barometer for nebular gas.
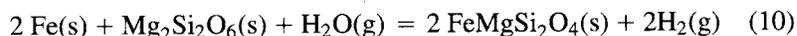
2. Fayalite in Silica-bearing Chondrules in Ordinary Chondrites. Brigham et al. (1986) and Wood and Holmberg (1994) described fayalite (Fa_{70-100}) replacing silica (SiO_2) in ordinary chondrite chondrules and suggested that fayalite formed by reaction between silica and a hot ($>1300°C$), oxidized nebular gas by the reaction

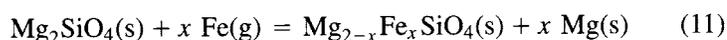$$SiO_2(s) + Fe(s) + H_2O(g) = Fe_2SiO_4(s) + H_2(g) \qquad (9)$$

Based on the presence of troilite in the fayalite-bearing chondrules, Wasson and Krot (1994) and Krot and Wasson (1994) argued against the high-temperature formation of fayalite, because troilite must have evaporated under such conditions. These authors inferred instead that fayalite formed by reaction (9) at low temperatures in an asteroidal environment. We conclude that fayalite in ordinary chondrite chondrules cannot be used as a strong indicator of oxidizing conditions in the solar nebula.

G. Fayalitic Olivine

1. Mineralogical Observations Nebular and Asteroidal Models. Fayalitic olivine [$(Fe,Mg)_2SiO_4$] is a ubiquitous constituent of carbonaceous and ordinary chondrites. The reactions controlling the fayalite content of olivine in the presence or absence of enstatite are

$$2\,Fe(s) + Mg_2Si_2O_6(s) + H_2O(g) = 2\,FeMgSi_2O_4(s) + 2H_2(g) \quad (10)$$

and

$$Mg_2SiO_4(s) + x\,Fe(g) = Mg_{2-x}Fe_xSiO_4(s) + x\,Mg(s) \quad (11)$$

respectively. Reaction (11) has been used by Larimer (1967, 1968), who tabulated fayalitic contents (X_{Fa}) in olivine, assuming ideal solid solution of fayalite and forsterite in olivine, as a function of temperature and of the H_2O/H_2 ratio in a gas of solar composition:

$$\log_{10} X_{Fa} = \log_{10}(H_2O/H_2) - 0.74 + 1690/T \quad (12)$$

This equation shows that fayalitic content in olivine increases with decreasing temperature and with increasing oxygen fugacity of a gas in equilibrium with the olivine. In a gas of solar composition, the calculated fayalite content in olivine is ~0.4 mol% at 1000 K and ~22 mol% at 500 K. Palme and Fegley (1990) concluded that the low-temperature formation of fayalitic olivine in a solar gas is kinetically inhibited and suggested that fayalitic olivine formed at high temperature under highly oxidized conditions (see section III.G.2). High-temperature formation of fayalitic olivine has been reproduced in laboratory experiments by Nagahara et al. (1988, 1994) and Dohmen et al. (1998a). These experiments are discussed below (see sections III.G.2 and 4 below).

High-temperature mechanisms of fayalitic olivine formation are largely used to explain the postulated (and controversial) nebular origin of fayalitic olivine in Allende (e.g., Peck and Wood 1987; Hua et al. 1988; Weinbruch et al. 1990; Krot et al. 1995, 1997, 1998c, d; Brearley and Prinz 1996; Brearley 1997). Fayalitic olivine in Allende occurs as lath-shaped grains in the matrix; it also rims and veins forsterite, enstatite, and magnetite and forms halos around Ni-rich metal inclusions in forsterite (Fig. 5). Both nebular and asteroidal models have been proposed to explain these textural types of fayalitic olivine. According to the nebular models, fayalitic olivine rims, veins, and halos formed by high-temperature gas-solid reactions in the oxidized solar nebula; matrix olivine condensed from the gas (Peck and Wood 1987; Hua et al. 1988; Weinbruch et al. 1990). According to the asteroidal models, fayalitic olivine in Allende resulted from low-temperature alteration in the presence of aqueous solutions and hence does not reflect redox conditions in the solar nebula (Krot et al. 1995, 1997, 1998a,c,d; Brearley and Prinz 1996; Brearley 1997).
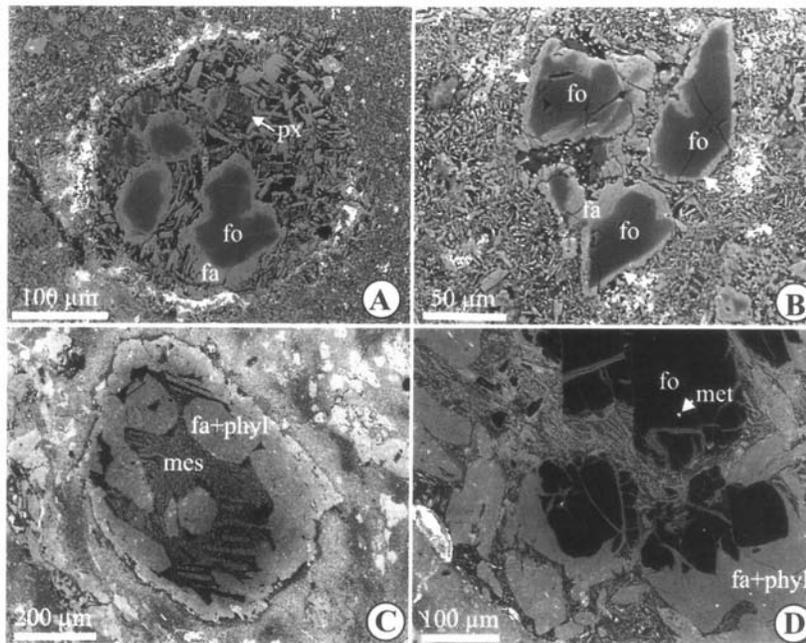
Figure 5.   Backscattered electron images of fayalitic olivine in the CV3 chondrite
ALHA81258 (a) and lithified chondritic clasts in the CV3 chondrites Allende
(b) and Efremovka (c, d). (a) Magnesian chondrule with low-Ca pyroxene (px)
and forsteritic olivine phenocrysts (fo) replaced by fayalitic olivine (fa). Fay-
alitic olivines around the chondrule's periphery contain inclusions of Fe,Ni sul-
fides. Since sulfides are not stable above $\sim$700 K, high-temperature formation
of fayalitic olivine is unlikely. (b) Fayalitic olivine rims surround three parts of
a single forsterite grain, indicating that these rims formed by *in situ* replacement
of the forsterite. (c, d) Chondrules replaced to various degrees by a fine-grained
mixture of fayalitic olivine and phyllosilicates (phyl), suggesting that fayalitic
olivine formed by low-temperature alteration in the presence of aqueous solu-
tion (modified from Krot et al. 1998c).

2.   Condensation   Calculations   from   an   Oxidized   Gas. Thermody-
namic calculations by Palme and Fegley (1990) show that the first con-
densing olivine is always forsteritic ($Fa_{<1}$), independent of the H_2O/H_2
ratio (Fig. 6). At lower temperatures, when the major fraction of Mg
and Si is condensed and at appropriately high fO_2, the Fa content of the
condensed olivine will gradually increase until a temperature is reached
where iron metal, wüstite (FeO), or magnetite would be stable as a sep-
arate phase. According to these calculations, the condensation of fay-
alitic olivine must have occurred before condensation of other Fe-bearing
phases. Palme and Fegley (1990) applied these calculations to the origin
of all textural types of fayalitic olivine in Allende.

Brearley and Prinz (1996) and Krot et al. (1997) found that fay-
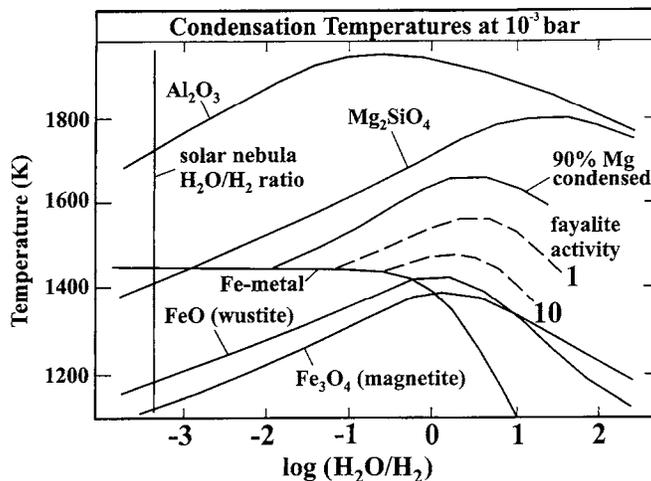alitic olivine in the matrix of Allende commonly contains inclusions of

Figure 6. Calculated condensation temperatures of corundum, forsterite, fayalite, Fe-metal, wüstite, magnetite as a function of $\log(H_2O/H_2)$ ratios. Temperatures for fayalite activities of 1 mol% and 10 mol% are indicated (from Weinbruch et al. 1990).

pentlandite $[(Fe,Ni)_9S_8]$ and poorly graphitized carbon, suggesting that both phases predated formation of fayalitic olivine. However, neither pentlandite nor poorly graphitized carbon are predicted to be high-temperature condensates, even at more oxidizing conditions than those in Palme and Fegley's (1990) calculations (Wood and Hashimoto 1993; Petaev and Wood 1998). Brearley (1997) described talc and biopyriboles in the Allende chondrules and inferred that these hydrous minerals predated formation of fayalitic olivine replacing forsterite and enstatite in these chondrules. Since hydrous minerals are most likely to be asteroidal in origin (Prinn and Fegley 1989) and cannot survive high-temperature processing, Brearley (1997) concluded that high-temperature condensation origin of fayalitic olivine in Allende is unlikely.

3. Vaporization-Recondensation of Forsteritic Olivine. Nagahara et al. (1988) heated forsteritic olivine (Fo_{89-94}) 1450–1600°C in a Knudsen cell kept in a vacuum chamber at $P_T = 3 \times 10^{-9}$ bar for 6–72 hr. The pressure and fO_2 in the Knudsen cell were not controlled. The gas flowed from the cell to lower pressure and temperature, where the gas recondensed at 1200–500°C. The residue after the experiments was stoichiometric olivine (Fo_{92-98}). The condensing phases were forsterite at ~1200–1150°C, enstatite at ~1100°C, silica at ~1000°C, mixture of Fe-bearing pyroxene and silica at ~800°C, and fayalitic olivine with lesser amounts of silica and metallic Fe at ~500°C. Nagahara et al. (1988) concluded that the low-temperature condensates are quench products from the gas vaporized from olivine of the starting composition, not equilibrium condensates; the latter should consist exclusively of fayalitic olivine (Nagahara et al. 1994).

Mineralogical observations (e.g., Nagahara 1984; Keller 1997) indicate that matrices in type 3 ordinary and carbonaceous chondrites consist of disequilibrium mineral assemblages similar to those produced by Nagahara et al. (1988). If fayalitic olivine in these matrices formed as a quench product (not as equilibrium condensate) of vaporization-recondensation of forsteritic olivine, it cannot be used as indicator of oxidizing conditions in the solar nebula.

In contrast to the matrices of most type 3 chondrites, the Allende matrix consists largely of fayalitic olivine; enstatite, forsterite, and metal are absent (Krot et al. 1995). Although matrix olivine in Allende may have formed as equilibrium condensate during vaporization-recondensation of forsteritic olivine (Nagahara et al. 1994), mineralogical observations indicate that forsteritic olivine in Allende was enriched in Fe, not depleted (e.g., Krot et al. 1997). Additional arguments against high-temperature formation of fayalitic olivine in Allende are discussed in subsection 2 above.

4. Gas-Solid Exchange Reactions. Dohmen et al. (1998a) heated forsterite and Fe metal at 1400°C in a vacuum for 2 hr and showed that forsterite incorporates gaseous Fe produced by evaporation of Fe metal, while Mg is released to the gas phase. The formation of the Fe-rich olivine is explained by the following two steps. First, forsterite evaporates and dissociates into gaseous Mg, SiO, and O_2:

$$MgSi_{0.5}O_2(s) = Mg(g) + 0.5\ SiO(g) + \tfrac{3}{4}\ O_2(g) \qquad (13)$$
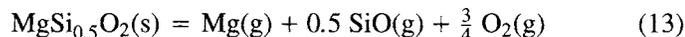
Second, mixing of evaporation products with Fe vapor produced by evaporation of Fe metal results in condensation of fayalitic olivine:

$$Mg(g) + Fe(g) + 0.5\ SiO(g) + \tfrac{3}{4}\ O_2(g) = (Mg, Fe)Si_{0.5}O_2(s) \quad (14)$$
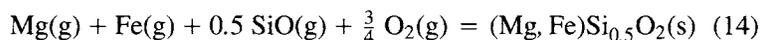
Summing the two reactions, the net reaction may be written as

$$MgSi_{0.5}O_2(s) + Fe(g) = FeSi_{0.5}O_2(s) + Mg(g) \qquad (15)$$

The composition of the olivine produced is proportional to the ratio of partial pressures of Fe and Mg: $X_{Fa}/X_{Fo} = K \times (P_{Fe}/P_{Mg})$. Providing that P_{Fe} is buffered by Fe metal, it follows that the fayalitic content of the olivine is inversely proportional to P_{Mg} in the gas phase. Although P_{Mg} is controlled by variations in fO_2 (the higher the fO_2 the lower P_{Mg} and the higher X_{Fa}), it was found (Dohmen et al. 1998a) that X_{Fa} in olivine is largely controlled by variable Fe/Mg ratios in the gas phase, which result from the difference in kinetics of evaporation of Fe metal (fast) and forsterite (slow). Since the kinetics of the forsterite evaporation plays a key role in these experiments, it is difficult to derive from the fayalite content of the olivine the fO_2 at which these olivines formed.

Dohmen et al. (1988a) inferred that their experiments simulated growth of fayalitic olivine rims around forsterite grains in Allende, which are illustrated in Fig. 5. Arguments against high-temperature formation of fayalitic olivine rims in Allende are discussed in section III.G.2 above.

H. Variations in fO_2 during Chondrule Formation

There are two major groups of chondrules: FeO-poor and FeO-rich. It has been suggested that FeO-poor chondrules formed in solar gas, whereas FeO-rich chondrules formed under oxidizing conditions ($H_2O/H_2 \sim 10^4$– $10^6 \times$ solar) (e.g., Huang et al. 1996; Hewins et al. 1997). Mineralogical observations indicate that chondrules formed by multiple episodes of incomplete melting of mineralogically and chemically heterogeneous precursor materials (e.g., Grossman 1988, 1996). Although brief, localized variations in fO_2 may have accompanied chondrule formation (e.g., Connolly and Love 1998), there is no evidence for an equilibrium between nebular gas and chondrule melts (e.g., Jones 1990, 1996; Zanda et al. 1994). Some FeO-poor chondrules show evidence for internal reduction of FeO-bearing silicates by carbon-rich solid precursors (e.g., Connolly et al. 1994; Hanon et al. 1996). As a result, the inferred fO_2 recorded by chondrules could be an artifact of their precursor composition; that is, chondrules may have behaved as internally buffered systems. We infer that chondrules cannot be used as reliable indicators of redox conditions in the solar nebula.

I. Mineral Indicators of the Reduced Solar Nebula

The chalcophile behavior of typically lithophile elements such as Mg, Ca, Ti, Mn, Cr, K, and Na, which form various sulfides in enstatite chondrites [e.g., oldhamite, CaS; niningerite, MgS; alabandite, MnS; Ti-bearing troilite, FeS; heideite, $Fe_{1+x}(Ti,Fe)_2S_4$; caswellsilverite, $NaCrS_2$; djerfisherite [$K_3(Cu,Na)(Fe,Ni)_{12}S_{14}$]; daubreelite, $(FeCr_2S_4)$]; osbornite (TiN); and high contents of Si in Fe, Ni metal provide clear evidence for reducing conditions in the region of enstatite chondrite formation (e.g., Keil 1968). However, model-independent estimates of fO_2 of a gas equilibrated with the enstatite chondrite minerals in the solar nebula are absent.

IV. MECHANISMS PROPOSED TO ACCOUNT FOR LARGE fO_2 VARIATIONS IN THE SOLAR NEBULA

The foregoing discussion shows that a wide spectrum of oxidation states, ranging from several orders of magnitude more oxidizing than a solar gas to several orders of magnitude more reducing than a solar gas is recorded in chondritic meteorites. We now consider two key questions: (1) How were variations in nebular fO_2 produced? and (2) What were the spatial and temporal extents of these more oxidizing and reducing regions of the solar nebula?

A. Oxidized Nebular Gas

1. Enhancement of the Dust/Gas and Ice/Gas Ratios. One possible mechanism for production of oxidizing conditions in the solar nebula is enhancement of the dust/gas ratio, the ice/gas ratios, or both. In a solar gas,

oxygen is partitioned between CO (48 at%), H_2O (37 at%), and rock-forming minerals (15 at%). The oxygen in CO is essentially locked up and unavailable for reactions because of the very strong triple bond in CO, whereas the oxygen in water vapor and rock-forming minerals can potentially take part in other chemistry. We know that the dust/gas and ice/gas ratios were enriched over the solar values during accretion of planets, satellites, asteroids, and comets. It is also possible that dust- and/or ice-enriched parcels of presolar material fell into the nebula during earlier stages of nebular evolution. Furthermore, laboratory studies of CAI and chondrule cooling rates indicate that some of these objects cooled more slowly than if they had radiated into free space. Dust-enriched regions of the nebula are needed to provide the slow cooling rates.

Table 5 of Fegley and Palme (1985) illustrates how enrichments of ice and dust lead to higher fO_2 in the solar nebula. The H_2O/H_2 ratios are tabulated there because this ratio is a temperature-independent indicator of how oxidizing (or reducing) the nebular gas was. The respective fO_2 at a given temperature can be calculated from the H_2O/H_2 ratio using equation (3). The H_2O/H_2 ratios inferred from the Mo and W depletions in CAIs correspond to dust (or ice enrichments) in the range of 50–500 times the solar dust/gas or ice/gas ratios. Similar enrichments are needed to explain the high-temperature formation of fayalitic olivines (if high-temperature model of fayalitic olivine formation is correct; for discussion see section III.G).

Dust and ice enrichments have other consequences in addition to increasing the nebular oxygen fugacity. These include increases in the opacity, viscosity, and coagulation rates in the dust- or ice-enriched regions. Furthermore, dust and ice enrichments also lead to changes in the condensation chemistry of the major rock-forming elements, although condensation calculations by different groups give different predictions (Wood and Hashimoto 1993; Yoneda and Grossman 1995). In this respect the difference between dust and ice enrichments is that dust enrichments also lead to enrichments in Mg, Si, Fe, and so on, whereas ice enrichments lead only to increases in fO_2.

2. Nebular Photooxidation. Alternatively, the Mo and W depletions found in CAIs may be the result of photooxidation of nebular water vapor in x-winds (Shu et al. 1996) or in low opacity regions of the inner solar nebula, such as the nebular photosphere, where backscattered solar H I Lyα (121.6 nm), He I (58.4 nm), and He II (30.4 nm) UV radiation may drive nebular photochemistry (Gladstone 1993; Gladstone and Fegley 1997). Photolysis of water vapor and hydroxyl radicals via the reactions

$$H_2O + h\nu \rightarrow OH + H \tag{16}$$

$$OH + h\nu \rightarrow O + H \tag{17}$$

may produce OH radical and O atom concentrations significantly higher than the thermochemical equilibrium values in a solar gas, while the H atoms recombine with each other via

$$H + H + M \rightarrow H_2 + M \tag{18}$$

where M is any third body (statistically H_2, He, or H). The enhanced OH and O concentrations could then drive reactions exemplified by

$$Mo(g) + O \rightarrow MoO(g) \tag{19}$$

$$W(g) + O \rightarrow WO(g) \tag{20}$$
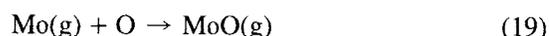
which increase the Mo and W oxide vapor concentrations above the thermochemical equilibrium values in a solar gas. Shu et al. (1996) note that this general concept is supported by observations of atomic O in the outflows from young T Tauri stars. However at present, no quantitative modeling has been done to work out the details of a photochemical oxidation scheme for Mo and W, and this must be done to test this model.

B. Reduced Nebular Gas

There are two principal mechanisms to reduce the solar nebula gas: addition of C-rich dust or removal of water from the inner solar system (Larimer 1968, 1975; Larimer and Bartholomay 1979). A measure of the redox state is the C/O ratio, which is ~0.5 for a solar gas (Grevesse and Noels 1993). At high temperatures and low pressures in a solar gas, all carbon is in CO while oxygen is about evenly divided between CO and H_2O, and oxide condensation occurs via net reactions such as

$$2 Al(g) + 3 H_2O = Al_2O_3(s) + 3 H_2 \tag{21}$$
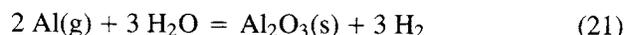
An increase in C/O ratio leads to the formation of more CO, so less H_2O is available for oxide forming reactions. Oxides then form at lower temperatures when reaction (4) proceeds to the right and supplies H_2O. Therefore, equilibrium condensation temperatures of oxides decrease with increasing C/O ratio. At some critical C/O ratio, the suite of initial condensates for the major elements switches from oxides and silicates to carbides, nitrides, and sulfides.

We used the CONDOR code (Lodders and Fegley 1993) to study the effect of increasing the C/O ratio (by either pathway) on types of condensates and condensation temperatures and computed the condensation temperatures for major elements at a total pressure of 10^{-3} bar.

Major element condensations as a function of C/O ratio as the O abundance is systematically decreased from the solar value are illustrated in Fig. 7. Initial condensates from a solar gas (C/O ~ 0.5) are corundum; hibonite; grossite, $CaAl_4O_7$; perovskite, $CaTiO_3$; melilite,
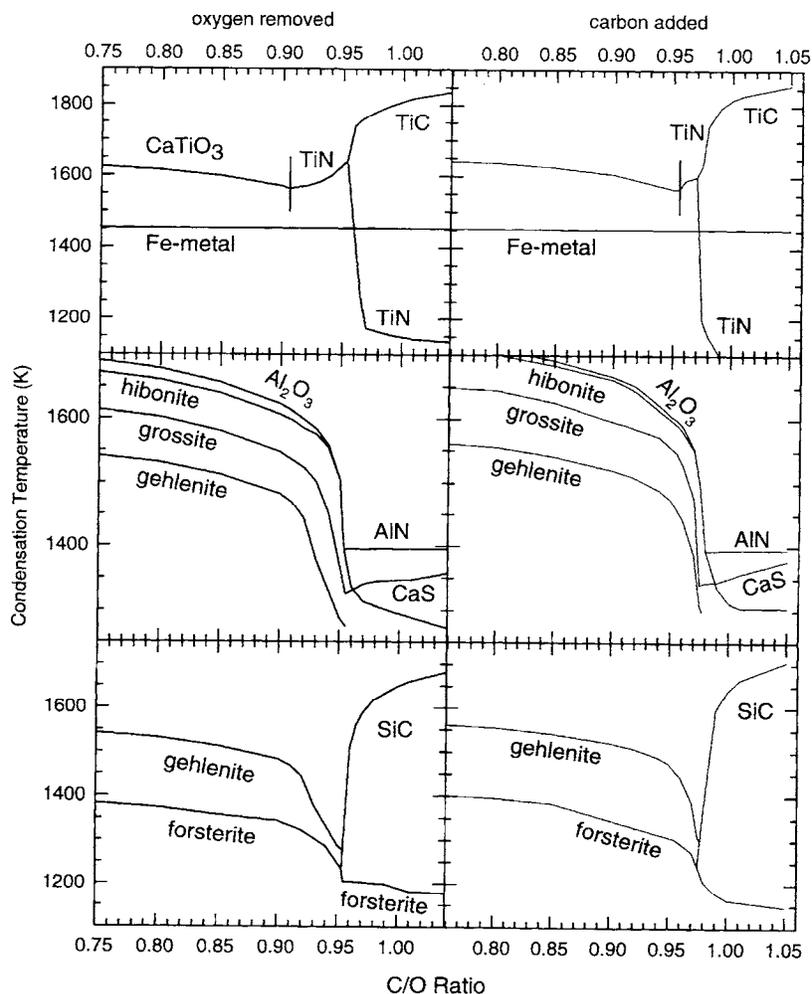
Figure 7.   Condensation temperatures for initial major element condensates as a
    function of C/O ratio at a total pressure of 10^{-3} bar. The left panel shows the
    condensation temperatures as the C/O ratio is increased by removing oxygen
    from a solar-composition gas, and the right panel shows the respective conden-
    sation temperatures as the C/O ratio is altered by adding carbon (from Lodders
    and Fegley 1997).

$(Ca,Na)_2(Al,Mg)(Si,Al)_2O_7$ [shown by gehlenite, $Ca_2Al(Si,Al)_2O_7$];
spinel $(MgAl_2O_4)$; forsterite; and enstatite. Iron metal condensation is
independent of C/O. However, as the C/O ratio increases, the condensa-
tion temperatures of the oxides and silicates decrease. At C/O ~ 0.91 to
~0.95, osbornite forms instead of perovskite. Oxides of Al, Ca, and Si
remain the initial condensates of these elements, because enough H_2O is
still available for reactions such as equation (21). At C/O > 0.95, TiC

replaces TiN as an initial condensate, AlN and CaS replace Ca-Al oxides, and SiC replaces gehlenite. Graphite and cohenite [(Fe,Ni)$_3$C] condensation requires C/O > 1.

The condensation temperatures for major element-forming minerals as a function of C/O ratio for the case in which carbon is increased above solar values are shown in the right panel in Fig. 7. In general, the condensation temperatures are somewhat higher, and the new suite of reduced condensates appears at higher C/O ratios than in the case of oxygen removal. Osbornite appears at C/O ~ 0.95, and TiC, AlN, and CaS start forming at C/O ~ 0.98.

The C/O range over which enstatite chondrites (ECs) may have formed is constrained by their mineralogy. Graphite and cohenite are not very abundant in these meteorites, indicating that the upper bound in C/O was ~1, because graphite and cohenite form at C/O > 1. The occurrence of CaS puts the lower bound at C/O ~ 0.95 if the C/O ratio was altered by oxygen removal from the solar gas. On the other hand, the lower bound of the C/O ratio necessary for the suite of reduced condensates is 0.98 if carbon was added to a solar gas; this is very close to the assumed upper bound of C/O ~ 1.

How were reducing conditions obtained in the solar nebula? Removal of oxygen by oxide condensation increases C/O in the gas from 0.48 to ~0.57, but this is too small an increase to produce reduced condensates. Another problem with removal of oxygen into silicates is that the major elements are then also condensed and are no longer available to form the reduced minerals by direct condensation. It is necessary to reduce the nebular gas before the onset of condensation to obtain enstatite chondrite minerals (e.g., CaS) as primary condensates. Plausible mechanisms to increase the C/O ratio are injection of carbonaceous dust or removal of water (Larimer 1968, 1975; Larimer and Bartholomay 1979; Baedecker and Wasson 1975). As seen above, both cases (i.e., O removal from and C addition to a solar gas) lead to reduced condensate formation, and thermodynamics alone does not unambiguously constrain which alternative is responsible for the reduction of the solar gas.

1. Adding Carbonaceous Dust to Solar Gas. Isotopic variations in chondrites indicate that the solar nebula was not homogeneous, and it is not inconceivable that there may have been "pockets" enriched in carbonaceous interstellar dust. Heating and evaporation of such carbon-rich pockets during their infall to the nebular midplane could have locally produced more reducing conditions than those obtained from evaporation of the standard presolar cloud material. Condensation from a solar gas reduced by carbonaceous dust would then produce the reduced minerals observed in ECs. The larger abundances of presolar SiC in the enstatite chondrite Qingzhen (EH3) than in the carbonaceous chondrite Orgueil (CI) (Huss and Lewis 1995) may indicate that larger amounts of carbonaceous dust, which could raise the C/O ratio, were present in the EC-forming region.

An indication that carbonaceous dust (including SiC dust) may have been responsible for the reducing conditions in the EC-forming region is the Si/Mg mass ratio of $\sim$1.5 in enstatite chondrites, which is higher than in CI chondrites (Si/Mg $\sim$ 1.1). The increased Si/Mg ratio in ECs could thus reflect the addition of Si from SiC. However, enstatite chondrites have normal Si isotopic compositions (Molini-Velsko et al. 1986), which argues against large amounts of SiC and, by implication, also against larger amounts of other carbonaceous dust in the formation region of enstatite chondrites.

Larimer (1988) has pointed out that the higher Si/Mg ratio in ECs points toward Mg fractionation rather than enhancement of Si, because the Si/Fe ratio in EH and CI chondrites is very similar. If so, the argument that Si was added from carbonaceous dust to ECs is weakened. The amount of carbonaceous dust required to reduce the nebular gas is very high. For example, mass returned to the interstellar medium (ISM) in our galaxy by evolved intermediate-mass stars is estimated to be 0.35 solar masses per year and 10–50% of that mass is reduced dust from carbon stars (Thronson et al. 1987). Although we do not have any observations of the ratio of carbon dust and SiC dust in the ISM, the major sources of the reduced dust are cool carbon stars, which preferentially show SiC dust emission, and there is evidence in only a few cases for carbon dust in their stellar outflows to the ISM (Lodders and Fegley 1997). The reduced dust may undergo processing in the ISM, but the survival of presolar SiC and carbon dust in meteorites suggests that SiC is not "lost" and is expected to be present in any carbonaceous dust pocket in the nebula. We may reasonably expect Si isotopic anomalies in ECs if the nebula gas were reduced by carbonaceous dust in the EC formation location.

Thus, although the presence of reduced presolar dust is ubiquitous in all chondrites, there is no clear evidence that enhanced carbonaceous dust addition was responsible for the increased C/O ratio in the solar nebula that is required for the condensation of EC minerals. Another drawback of dust addition to solar nebula gas is that the C/O range over which EC minerals form is very narrow ($\sim$0.98 to $\sim$1; see above), and it may appear as mere coincidence that enstatite chondrites ever formed. In the case of oxygen removal, the range in C/O ratios over which reduced EC minerals can form (C/O $\geq$ 0.95) is somewhat wider and possibly more favorable than in the case of carbonaceous dust addition (C/O $\geq$ 0.98).

2. *Removing Oxygen from Solar Gas.* Oxygen removal from the EC formation region is an alternative pathway to increase the C/O ratio (Baedecker and Wasson 1975). About half of the oxygen had to be lost to increase the C/O ratio from solar to about 1, possibly by H_2O ice condensation. Solar nebula models place water ice condensation at 5.2 AU and beyond (Cameron 1995). Early accretion of ice and rock is believed to have caused a runaway accretion of Jupiter (Lissauer 1987), so that the jovian planets served as cold traps for water ice (Stevenson and Lunine 1988).

In the case of water removal from the inner to the outer solar system, the jovian planets should be relatively enriched in water. One indication of water enrichment comes from the observed CO concentrations in the atmospheres of the jovian planets. For example, about 0.6 parts per million by volume (ppmv) CO is observed on Neptune. About 440 times the solar abundance of oxygen as water is required to explain this CO, which is formed by the reaction of water and methane in Neptune's deep atmosphere and subsequent upwelling (see Lodders and Fegley 1994). Similarly, the upper limit of ~0.01 ppmv CO on Uranus implies an overabundance of oxygen as water of up to 260 times solar. However, other heavy elements such as carbon (as CH_4) are only 41 and 32 times solar abundance in Uranus and Neptune, respectively. Thus, Neptune and (possibly) Uranus have an overabundance of water as compared to carbon, and their amount of water is also larger than that available from a solar-composition gas. Interior structure models and atmospheric chemistry models indicate that water abundances in Jupiter, Saturn, Uranus, and Neptune increase as a function of heliocentric distance. This trend may reflect more efficient cold trapping in the coolest regions of the nebula, which also implies that water was redistributed within the solar system.

Water removal from the inner to the outer solar nebula constrains the formation location of the ECs to be closer to the sun. In contrast, C dust addition could have happened anywhere in the solar system. The large enrichments of water on the outer planets also implies that the removal of water from the inner solar system was quite efficient. Early accretion of reduced matter in the inner solar nebula is also consistent with the two-component accretion models for the terrestrial planets, which postulate that terrestrial planet accretion started from material as reduced as enstatite chondrites (e.g., Wänke 1981; see also Lodders 1995). Water removal from the inner solar system could have been an efficient mechanism to produce this reduced component. The terrestrial planets now clearly do not appear to be as reduced as enstatite chondrites (with the possible exception of Mercury); this fact indicates that after accretion of the reduced components, more oxidized matter was accreted and current oxidation states of the terrestrial planets evolved.

In fact, the production of highly oxidizing and highly reducing regions in the solar nebula may be linked. During the infall of presolar gas and grains into the solar nebula, icy grains and grain mantles evaporated, first producing local enrichments of water vapor. Mixing of this water- enriched gas into the hotter inner nebula then produced highly oxidized regions. As nebular evolution and heating continued, all (or at least most) of the icy grains evaporated, and the H_2O/H_2 ratio decreased back to the solar value.

Later cooling of the nebular cloud eventually led to recondensation of icy material in outer regions of the nebula (the snowline). The position of the nebular snowline must have varied with nebular cooling, but it is generally believed that formation of ice at about 5.2 AU was responsible for the runaway accretion of Jupiter. During the cooling of the nebula,

water-bearing gas from the inner nebula was desiccated as it was transported outward and ice condensed at the snowline (e.g., Stevenson and Lunine 1988). As a consequence, water depletion in the inner solar nebula led to more reducing conditions and to the formation of the highly reduced enstatite chondrites (e.g., Larimer and Bartholomay 1979) and to reduced planetesimals later accreted by the proto-Earth (e.g., Lodders 1995). The formation of highly reduced material was plausibly limited by the smaller extent of hotter regions in the inner nebula during this stage of nebular evolution. However, more theoretical modeling is needed to quantitatively address the timing and dynamics of this model for formation of highly oxidized and highly reduced regions.

V. CONCLUSIONS AND SUMMARY

Chondritic meteorites show a wide spectrum of oxidation states, ranging from highly oxidizing relative to solar gas (e.g., Mo and W depletions in CAIs and fayalitic rims in carbonaceous chondrites) to highly reducing relative to solar gas (the mineralogy of enstatite chondrites). At present it is possible to recognize (at least partially) the signatures of nebular and planetary processing in chondritic meteorites. In the carbonaceous chondrites, chemical indicators generally preserve the nebular record with greater fidelity than do mineralogical indicators (such as valence state ratios and colors). Several mineralogical indicators in carbonaceous chondrites indicate that thermal metamorphism and fluid/rock interactions have altered the original nebular signatures and left an overprint of planetary processing. However, in the enstatite chondrites, the existence of highly reduced minerals, which would be destroyed by fluid/rock and thermal processing on parent bodies, provide the best evidence of nebular processes and of the nebular oxidation state in the enstatite chondrite formation region.

Although the origin of fO_2 variations in the nebula is unknown, several plausible mechanisms have been proposed. It may be that the production of highly oxidizing regions (relative to a solar gas) is linked to the initial evaporation of icy presolar grains and that the production of highly reducing regions (relative to a solar gas) is linked to the later recondensation of icy grains and to the runaway accretion of Jupiter. However, the relative timing of fO_2 variations in the solar nebula, as well as the spatial extents of highly oxidized and highly reduced regions, remain matters of conjecture and cannot be quantified. The issue of timing is difficult to resolve because of inherent limitations in the time intervals that can be distinguished using different short-lived radionuclides (about 50% of a half-life), which are generally long relative to the estimates of 0.1–10 million years for the nebular lifetime (Podosek and Cassen 1994).

Further studies along the following lines may help to understand better the origin of oxidized components in carbonaceous chondrites and allow better estimates of fO_2 variations in the solar nebula:

1. Study of the time required at various temperatures (1000–300°C) for the blue-to-orange color transition in hibonite, to constrain alteration conditions experienced by hibonite-bearing CAIs.
2. Laboratory studies of iron transport and incorporation into olivine and enstatite at low temperatures in the presence of aqueous solutions and in dry systems.
3. Good quantitative models of oxidizing regions and reducing regions in the solar nebula.
4. More detailed theoretical models of nebular radial mixing and thermal evolution.
5. Absolute dating of secondary and primary mineralization in chondrules and CAIs using short-lived nuclides (^{53}Mn, ^{26}Al, ^{129}I), to constrain the time interval between primary and secondary mineralization and the duration of alteration.

REFERENCES

Allen, J. M., Grossman, L., Davis, A. M., and Hutcheon, I. D. 1978. Mineralogy, textures and mode of formation of a hibonite-bearing Allende inclusion. *Proc. Lunar Planet. Sci. Conf.* 9:1209–1233.

Allen, J. M., Grossman, L., Lee, T., and Wasserburg, G. J. 1980. Mineralogy and petrography of HAL, an isotopically-unusual Allende inclusion. *Geochim. Cosmochim. Acta* 44:685–699.

Anders, E. 1971. Meteorites and the early solar system. *Ann. Rev. Astron. Astrophys.* 9:1–34.

Armstrong, J. T., Meeker, G. P., Huneke, J. C., and Wasserburg, G. J. 1982. The Blue Angel: I. The mineralogy and petrogenesis of a hibonite inclusion from the Murchison meteorite. *Geochim. Cosmochim. Acta* 46:575–595.

Armstrong, J. T., El Goresy, A., and Wasserburg, J. T. 1985. Willy: A prize noble UR-Fremdlinge: Its history and implications for the formation of Fremdlinge and CAI. *Geochim. Cosmochim. Acta* 49:1001–1022.

Armstrong, J. T., Hutcheon, I. D., and Wasserburg, G. J. 1987. Zelda and company: Petrogenesis of sulfide-rich Fremdlinge and constraints on solar nebula processes. *Geochim. Cosmochim. Acta* 51:3155–3173.

Baedecker, P. A., and Wasson, J. T. 1975. Elemental fractionations among enstatite chondrites. *Geochim. Cosmochim. Acta* 39:735–765.

Beckett, J. R., and Grossman, L. 1986. Oxygen fugacities in the solar nebula during crystallization of fassaite in Allende inclusions (abstract). *Lunar Planet. Sci.* 17:36–37.

Beckett, J. R., Live, D., Tsay, F.-D., Grossman, L., and Stolper, E. 1988. Ti^{3+} in meteoritic and synthetic hibonite. *Geochim. Cosmochim. Acta* 52:1479–1495.

Bischoff, A., and Palme, H. 1987. Compositions and mineralogy of refractory-metal-rich assemblages from a Ca-, Al-rich inclusion in the Allende meteorite. *Geochim. Cosmochim. Acta* 51:2733–2748.

Blum, J. D., Wasserburg, G. J., Hutcheon, I. D., Beckett, J. R. and Stolper, E. M. 1989. Origin of opaque assemblages in C3V meteorites: Implications for nebular and planetary processes. *Geochim. Cosmochim. Acta* 53:483–489.

Boynton, W. V. 1975. Fractionation in the solar nebula: Condensation of yttrium and the rare earth elements. *Geochim. Cosmochim. Acta* 39:569–584.

Boynton, W. V. 1978. Rare-earth elements as indicators of supernova condensation (abstract). *Lunar Planet. Sci.* 9:120–122.

Boynton, W. V., and Cunningham, C. C. 1981. Condensation of refractory lithophile trace elements in the solar nebula and in supernovae (abstract). *Lunar Planet. Sci.* 12:106–108.

Boynton, W. V., Wark, D. A., and Ulyanov, A. A. 1986. Trace elements in Efremovka fine-grained inclusion E14: Evidence for high temperature, oxidizing fractionations in the solar nebula (abstract). *Lunar Planet. Sci.* 17:78–79.

Brearley, A. J. 1996. Nature of matrix in unequilibrated chondrites and its possible relationship to chondrules. In *Chondrules and the Protoplanetary Disk*, ed. R. H. Hewins, R. H. Jones, and E. R. D. Scott (Cambridge: Cambridge University Press), pp. 137–153.

Brearley, A. J. 1997. Disordered biopyriboles and talc in chondrules in the Allende meteorite: Possible origins and formation conditions (abstract). *Lunar Planet. Sci.* 28:153–154.

Brearley, A. J., and Duke, C. L. 1998. Aqueous alteration of chondritic meteorites: Insights from experimental low temperature hydrothermal alteration of Allende (abstract). *Lunar Planet. Sci.* 28:CD-ROM 1274.

Brearley, A. J., and Prinz, M. 1996. Dark inclusions in the Allende meteorite: New insights from transmission electron microscopy (abstract). *Lunar Planet. Sci.* 28:153–154.

Brigham, C. A., Yabuki, H., Ouyang, Z., Murrell, M. T., El Goresy, A., and Burnett, D. S. 1986. Silica-bearing chondrules and clasts in ordinary chondrites. *Geochim. Cosmochim. Acta* 50:1655–1666.

Cameron, A. G. W. 1995. The first ten million years in the solar nebula. *Meteoritics* 30:133–161.

Connolly, H. C., Jr., and Love, S. G. 1998. The formation of chondrules: Petrologic tests of the shock wave model. *Science* 280:62–67.

Connolly, H. C., Jr., Hewins, R., Ash, R. D., Zanda, B., Lofgren, G. E., and Bourot-Denise, M. 1994. Carbon and the formation of reduced chondrules. *Nature* 371:136.

Davis, A. M., and Grossman, L. 1979. Condensation and fractionation of rare earths in the solar nebula. *Geochim. Cosmochim. Acta* 43:1611–1632.

Davis, A. M., Grossman, L., and Allen, J. M. 1978. Major and trace element chemistry of separated fragments from a hibonite-bearing Allende inclusion. *Proc. Lunar Planet. Sci. Conf.* 9:1235–1247.

Davis, A. M., Tanaka, T., Grossman L., Lee, T., and Wasserburg, G. J. 1982. Chemical composition of HAL, an isotopically-unusual Allende inclusion. *Geochim. Cosmochim. Acta* 46:1627–1651.

Davis, A. M., Hashimoto, A., Clayton, R. N., and Mayeda, T. 1995. Isotopic and chemical fractionation during evaporation of $CaTiO_3$ (abstract). *Lunar Planet. Sci.* 26:317–318.

Dohmen, R., Chakraborty, S., Palme, H., and Rammensee, W. 1998a. Solid-solid reactions mediated by a gas phase: An experimental study of reaction progress and the role of surfaces in the system olivine + Fe-metal. *Am. Mineral.* 83:970–984.

Dohmen, R., Palme, H., Chakraborty, S., and Rammensee, W. 1998b. Experimental evidence for gas phase transport of siderophile elements in the solar nebula (abstract). *Lunar Planet. Sci.* 29:CD-ROM 1588.

Eisenhour, D. D., and Buseck, P. R. 1992. Transmission electron microscopy of RMNs: Implications for single-phase condensation of the refractory siderophile elements (abstract). *Meteoritics* 27:217–218.

Ekambaram, V., Kawabe, I., Tanaka, T., Davis, A. M., and Grossman, L. 1984. Chemical compositions of refractory inclusions in the Murchison C2 chondrite. *Geochim. Cosmochim. Acta* 48:2089–2105.

El Goresy, A., Nagel, K., and Ramdohr, P. 1978. Fremdlinge and their noble relatives. *Proc. Lunar Planet. Sci. Conf.* 9:1279–1303.

Fegley, B., Jr. 1986. A comparison of REE and refractory metal oxidation state indicators for the solar nebula (abstract). *Lunar Planet. Sci.* 25:220–221.

Fegley, B., Jr., and Kong, D. 1989. Mo and W depletions in CAIs in carbonaceous chondrites: A theoretical study of the effects of nebula total pressure (abstract). *Lunar Planet. Sci.* 20:279–280.

Fegley, B., Jr., and Lodders, K. 1994. Chemical models of the deep atmospheres of Jupiter and Saturn. *Icarus* 110:117–154.

Fegley, B., Jr., and Palme, H. 1985. Evidence for oxidizing conditions in the solar nebula from Mo and W depletions in refractory inclusions in carbonaceous chondrites. *Earth Planet. Sci. Lett.* 72:311–326.

Fegley, B., Jr., and Prinn, R. G. 1989. Meteoritic evidence for oxidizing conditions in the solar nebula. Presented at the Intl. Geologic Congress, Washington, D.C.

Floss, C., El Goresy, A., Zinner, E., Kransel, G., Rammensee, W., and Palme, H. 1996. Elemental and isotopic fractionations produced through evaporation of the Allende CV chondrite: Implications for the origin of HAL-type hibonite inclusions. *Geochim. Cosmochim. Acta* 60:1975–1997.

Gladstone, G. R. 1993. Photochemistry in the primitive solar nebula. *Science* 261:1058.

Gladstone, G. R., and Fegley, B., Jr. 1997. Lyα photochemistry in the primitive solar nebula. *EOS Trans. AGU* 78:F538–F539.

Greenwood, R. C., Lee, M. R., Hutchison, R., and Barber, D. J. 1994. Formation and alteration of CAIs in Cold Bokkeveld (CM2). *Geochim. Cosmochim. Acta* 58:1913–1935.

Grevesse, N., and Noels, A. 1993. Cosmic abundances of the elements. In *Origin and Evolution of the Elements*, ed. N. Prantzos, E. Vangioni-Flam, and M. Cassé (Cambridge: Cambridge University Press), pp. 14–25.

Grossman, J. N. 1988. Formation of chondrules. In *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), pp. 680–696.

Grossman, J. N. 1996. Chemical fractionations of chondrites: Signatures of events before chondrule formation. In *Chondrules and the Protoplanetary Disk*, ed. R. H. Hewins, R. Jones, and E. R. D. Scott (Cambridge: Cambridge University Press), pp. 243–256.

Grossman, L. 1972. Condensation in the primitive solar nebula. *Geochim. Cosmochim. Acta* 36:597–619.

Grossman, L. and Ganapathy, R. 1976a. Trace elements in the Allende meteorite. I. Coarse-grained, Ca-rich inclusions. *Geochim. Cosmochim. Acta* 40:331–344.

Grossman, L. and Ganapathy, R. 1976*b*. Trace elements in Allende meteorite. II. Fine-grained, Ca-rich inclusions. *Geochim. Cosmochim. Acta* 40:967–977.

Hanon P., Chaussidon, M., and Robert, F. 1996. The redox state of the solar nebula: C and H concentrations in chondrules (abstract). *Meteorit. Planet. Sci.* 31:A57.

Hartmann, L. 1996. Astronomical observations of phenomena in protostellar disks. In *Chondrules and the Protoplanetary Disk*, ed. R. H. Hewins, R. H. Jones, and E. R. D. Scott (Cambridge: Cambridge University Press), pp. 13–21.

Hashimoto, A. 1992. The effect of H_2O gas on volatiles of planet-forming major elements: I. Experimental determination of thermodynamic properties of Ca-, Al-, and Si-hydroxide gas molecules and its application to the solar nebula. *Geochim. Cosmochim. Acta* 56:511–532.

Hashimoto, A. and Grossman, L. 1987. Alteration of Al-rich inclusions inside amoeboid olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta* 51:1685–1704.

Hewins, R.H., Jones, R. H., and Scott, E. R. D., eds. 1996. *Chondrules and the Protoplanetary Disk* (Cambridge: Cambridge University Press).

Hewins, R. H., Yu, Y., Zanda, B., and Bourot-Denise, M. 1997. Do nebular fractionations, evaporative losses or both, influence chondrule compositions? *Antarct. Meteorite Res.* 10:275–298.

Hua, X. and Buseck, P. R. 1995. Fayalite in the Kaba and Mokoia carbonaceous chondrites. *Geochim. Cosmochim. Acta* 59:563–578.

Hua X., Adam, J., Palme, H., and El Goresy, A. 1988. Fayalite-rich rims, veins, and halos around and in forsteritic olivines in CAIs and chondrules in carbonaceous chondrites: Types, compositional profiles and constraints of their formation. *Geochim. Cosmochim. Acta* 52:1389–1408.

Huang, S., Jie L., Prinz, M., Weisberg, M. K., Benoit, P. H., and Sears, D. W. G. 1996. Chondrules: Their diversity and the role of open-system processes during their formation. *Icarus* 122:316–346.

Huss, G. R., and Lewis, R. S. 1995. Presolar diamond, SiC, and graphite in primitive chondrites: Abundances as a function of meteorite class and petrologic type. *Geochim. Cosmochim. Acta* 59:115–160.

Hutcheon, I. D., and Newton, R. C. 1981. Mg isotopes, mineralogy, and mode of formation of secondary phases in C3 refractory inclusions (abstract). *Lunar Planet. Sci.* 12:492–493.

Hutcheon, I. D., Krot, A. N., Keil, K., Phinney, D. L., and Scott, E. R. D. 1998. [53]Mn-[53]Cr dating of fayalite formation in the CV3 chondrite Mokoia: Evidence for asteroidal alteration. *Science* 282:1865–1867.

Ihinger, P. and Stolper, E. 1986. The color of meteoritic hibonite: An indicator of oxygen fugacity. *Earth Planet. Sci. Lett.* 78:67–79.

Ireland, T. R., Zinner, E. K., Fahey, A. J., and Esat, T. M. 1992. Evidence for distillation in the formation of HAL and related hibonite inclusions. *Geochim. Cosmochim. Acta* 56:2503–2520.

Jones, R. H. 1990. Petrology and mineralogy of type II, FeO-rich chondrules in Semarkona (LL3.0): Origin by closed-system fractional crystallization, with evidence for supercooling. *Geochim. Cosmochim. Acta* 54:1785–1802.

Jones, R. H. 1996. FeO-rich, porphyritic pyroxene chondrules in unequilibrated ordinary chondrites. *Geochim. Cosmochim. Acta* 60:3115–3138.

Keil, K. 1968. Mineralogical and chemical relationships among enstatite chondrites. *J. Geophys. Res.* 73:6945–6976.

Keller, L. P. 1997. A transmission electron microscope study of the matrix mineralogy of the Leoville CV3 (reduced-group) carbonaceous chondrite: Nebular and parent-body features (abstract). In *LPI Tech. Rep. No. 97-02*, part 1 (Houston: Lunar and Planetary Institute), pp. 31–33.

Kerridge, J. F., and Matthews, M. S., eds. 1988. *Meteorites and the Early Solar System* (Tucson: University of Arizona Press).

Kimura, M., and Ikeda, Y. 1995. Anhydrous alteration of Allende chondrules in the solar nebula. II: Alkali-Ca exchange reactions and formation of nepheline, sodalite and Ca-rich phases in chondrules. *Proc. NIPR Symp. Antarct. Meteorites* 8:123–138.

Köhler, A. V., Palme, H., Spettel, B., and Fegley, B., Jr. 1988. Fractionation of refractory metals by high temperature oxidation. *Lunar Planet. Sci.* 19:627–628.

Kornacki, A. S., and Fegley, B., Jr. 1984. Origin of spinel-rich chondrules and inclusions in carbonaceous and ordinary chondrites. Proc. 14th Lunar Planet. Sci. Conf. *J. Geophys. Res.* 89:B588–B596.

Kornacki, A. S., and Wood, J. A. 1985. Mineral chemistry and origin of spinel-rich inclusions in the Allende CV3 chondrite. *Geochim. Cosmochim. Acta* 49:1219–1237.

Krot, A. N., and Wasson, J. T. 1994. Silica- and merrihueite/roedderite-bearing chondrules and clasts in ordinary chondrites: New occurrences and possible origin. *Meteoritics* 29:707–717.

Krot, A. N., Scott, E. R. D., and Zolensky, M. E. 1995. Mineralogical and chemical modification of components in CV3 chondrites: Nebular or asteroidal processing? *Meteoritics* 30:748–776.

Krot, A. N., Scott, E. R. D., and Zolensky, M. E. 1997. Origin of fayalitic olivine rims and lath- shaped matrix olivine in the CV3 chondrite Allende and its dark inclusions. *Meteorit. Planet. Sci.* 32:31–49.

Krot, A. N., Brearley, A. J., Ulyanov, A. A., Biryukov, V. V., Swindle, T. D., Keil, K., Mittlefehldt, D. W., Scott, E. R. D., Clayton, R. N., and Mayeda, T. K. 1998a. Mineralogy, petrography and bulk chemical, I-Xe, and oxygen isotopic compositions of dark inclusions in the reduced CV3 chondrite Efremovka. *Meteorit. Planet. Sci.*, in press.

Krot, A. N., Petaev, M. I., and Meibom, A. 1998b. Mineralogy and petrography of Ca-Fe-rich silicate rims around heavily altered Allende dark inclusions. *Lunar Planet. Sci.* 29:CD-ROM 1555.

Krot, A. N., Petaev, M. I., Scott, E. R. D., Choi, B.-G., Zolensky, M. E., and Keil, K. 1998c. Progressive alteration in CV3 chondrites: More evidence for asteroidal alteration. *Meteorit. Planet. Sci.* 33:1065–1085.

Krot, A. N., Petaev, M. I., Zolensky, M. E., Keil, K., Scott, E. R. D., and Nakamura, K. 1998d. Secondary Ca-Fe-rich minerals in the Bali-like and Allende-like oxidized CV3 chondrites and Allende dark inclusions. *Meteorit. Planet. Sci.* 33:623–645.

Larimer, J. W. 1967. Chemical fractionation of meteorites. I. Condensation of the elements. *Geochim. Cosmochim. Acta* 31:1215–1238.

Larimer, J. W. 1968. An experimental investigation of oldhamite, CaS, and the petrologic significance of oldhamite in meteorites. *Geochim. Cosmochim. Acta* 32:965–982.

Larimer, J. W. 1975. The effect of C/O ratio on the condensation of planetary material. *Geochim. Cosmochim. Acta* 39:389–392.

Larimer, J. W. 1988. The cosmochemical classification of the elements. In *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), pp. 375–390.

Larimer, J. W., and Bartholomay, M. 1979. The role of carbon and oxygen in cosmic gases: Some applications to the chemistry and mineralogy of enstatite chondrites. *Geochim. Cosmochim. Acta* 43:1453–1466.

Lewis, J. S., and Prinn, R. G. 1980. Kinetic inhibition of CO and N_2 reduction in the solar nebula. *Astrophys. J.* 238:357–364.

Lewis, J. S., Barshay, S. S., and Noyes, B. 1979. Primordial retention of carbon by the terrestrial planets. *Icarus* 37:190–206.

Lissauer, J. J. 1987. Timescales for planetary accretion and the structure of the protoplanetary disk. *Icarus* 69:249–265.

Live, D., Beckett, J. R., Tsay, F. D., Grossman, L., and Stolper, E. 1986. Ti^{3+} in meteoritic and synthetic hibonite: A new oxygen barometer (abstract). *Lunar Planet Sci.* 17:488–489.

Lodders, K. 1995. Alkali elements in the Earth's core: Evidence form enstatite meteorites. *Meteoritics* 30:93–101.

Lodders, K., and Fegley, B., Jr. 1993. Lanthanide and actinide chemistry at high C/O ratios in the solar nebula. *Earth Planet. Sci. Lett.* 117:125–145.

Lodders, K., and Fegley, B., Jr. 1994. The origin of carbon monoxide in Neptune's atmosphere. *Icarus* 112:368–375.

Lodders, K., and Fegley, B., Jr. 1995. The origin of circumstellar silicon carbide grains found in meteorites. *Meteoritics* 30:661–678.

Lodders, K., and Fegley, B. Jr. 1997. Condensation chemistry of carbon stars. In *The Astrophysical Implications of the Laboratory Study of Presolar Materials*, AIP Conf. Proc. Vol. 402, ed. E. Zinner and T. Bernatowicz (Woodbury, NY: The American Institute of Physics), pp. 391–423.

Lodders, K., and Fegley, B., Jr. 1998. *The Planetary Scientist's Companion.* (New York: Oxford University Press).

MacPherson, G. J., Grossman, L., Allen, J. M., and Beckett, J. R. 1981. Origin of rims on coarse-grained inclusions in the Allende meteorite. *Proc. Lunar Planet. Sci. Conf.* 12B:1079–1091.

MacPherson, G. J., Hashimoto, A., and Grossman, L. 1985. Accretionary rims on inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* 49:2267–2279.

MacPherson, G. J., Wark, D. A., and Armstrong, J. T. 1988. Primitive material surviving in chondrites: Refractory inclusions. In *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), pp. 746–807.

Mason, B., and Taylor, S. R. 1982. Inclusions in the Allende meteorite. *Smithsonian Contrib. Earth Sci.* 25:30.

McGuire, A. V. and Hashimoto, A. 1989. Origin of zoned fine-grained inclusions in the Allende meteorite. *Geochim. Cosmochim. Acta* 53:1123–1133.

McSween, H. Y., Jr. 1977. Petrographic variations among carbonaceous chondrites of the Vigarano type. *Geochim. Cosmochim. Acta* 41:1777–1790.

Meeker, G. P., Wasserburg, G. J., and Armstrong, J. T. 1983. Replacement textures in CAI and implications regarding planetary metamorphism. *Geochim. Cosmochim. Acta* 47:707–721.

Molini-Velsko, C., Mayeda, T. K., and Clayton, R. N. 1986. Isotopic composition of silicon in meteorites. *Geochim. Cosmochim. Acta* 50:2719–2726.

Nagahara, H. 1984. Matrices of type 3 ordinary chondrites; primitive nebular records. *Geochim. Cosmochim. Acta* 48:2581–2595.

Nagahara, H., Kushiro, I., Mysen, B. O., and Mori, H. 1988. Experimental vaporization and condensation of olivine solid solution. *Nature* 331:516–518.

Nagahara, H., Kushiro, I., and Mysen, B. O. 1994. Evaporation of olivine: Low pressure relations of the olivine system and its implication for the origin of chondritic components in the solar nebula. *Geochim. Cosmochim. Acta* 58:1951–1963.

Palme, H., and Boynton, W. V. 1993. Meteoritic constraints on conditions in the solar nebula. In *Protostars and Planets III*, ed. E. Levy and J. I. Lunine (Tucson: University of Arizona Press), pp. 979–1004.

Palme, H., and Fegley, B., Jr. 1990. High-temperature condensation of iron-rich olivine in the solar nebula. *Earth Planet. Sci. Lett.* 101:180–195.

Palme, H., and Wlotzka, F. 1976. A metal particle from a Ca-Al-rich inclusion from the meteorite Allende, and condensation of refractory siderophile elements. *Earth Planet. Sci. Lett.* 33:45–60.

Palme, H., Hutcheon, I., and Spettel, B. 1994. Composition and origin of refractory-metal-rich assemblages in a Ca, Al-rich Allende inclusion. *Geochim. Cosmochim. Acta* 58:495–513.

Peck, J. A., and Wood, J. A. 1987. The origin of ferrous zoning in Allende chondrule olivine. *Geochim. Cosmochim. Acta* 51:1503–1510.

Petaev, M. I., and Wood, J. A. 1998. The condensation with partial isolation (CWPI) model of condensation in the solar nebula. *Meteorit. Planet. Sci.*, in press.

Podosek, F., and Cassen, P. 1994. Theoretical, observational, and isotopic estimates of the lifetime of the solar nebula. *Meteoritics* 29:6–25.

Prinn, R. G., and Fegley, B., Jr. 1989. Solar nebula chemistry: origin of planetary, satellite, and cometary volatiles. In *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. K. Atreya, J. B. Pollack, and M. S. Matthews (Tucson: University of Arizona Press), pp. 78–136.

Rubin, A. E., Fegley, B., Jr., and Brett, R. 1988. Oxidation state in chondrites. In *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), pp. 488–511.

Ruden, S. P., and Lin, D. N. C. 1986. The global evolution of the primordial solar nebula. *Astrophys. J.* 308:883–901.

Russell, S. S., Huss, G. R., Fahey, A. J., Greenwood, R. C., Hutchison, R., and Wasserburg, G. J. 1998. An isotopic and petrologic study of calcium-aluminum-rich inclusions in CO3 meteorites. *Geochim. Cosmochim. Acta* 62:689–714.

Shu, F. H., Shang, H., and Lee, T. 1996. Toward an astrophysical theory of chondrites. *Science* 271:1545–1552.

Stevenson, D. J., and Lunine, J. I. 1988. Rapid formation of Jupiter by diffusive redistribution of water vapor in the solar nebula. *Icarus* 75:146–155.

Stolper, E., and Ihinger, P. 1983. The color of meteoritic hibonite: An indicator of oxygen fugacity (abstract). *Lunar Planet. Sci.* 14:749–750.

Stolper, E., Paque, L., and Grossman, G. R. 1982. The influence of oxygen fugacity and cooling rate on the crystallization of Ca-Al-rich inclusions from Allende (abstract). *Lunar Planet. Sci.* 13:773–774.

Thronson, H. A., Latter, W. B., Black, J. H., Bally, J., and Hacking, P. 1987. Properties of evolved mass-losing stars in the Milky Way and variations in the interstellar dust composition. *Astrophys. J.* 322:770–786.

Wänke, H. 1981. Constitution of terrestrial planets. *Philosoph. Trans. Roy. Soc. Lond.* A303:287–302.

Wänke, H., Baddenhausen, H., Palme, H., and Spettel, B. 1974. On the chemistry of the Allende inclusions and their origin as high-temperature condensates. *Earth Planet. Sci. Lett.* 23:1–7.

Wasson, J. T., and Krot, A. N. 1994. Fayalite-silica association in unequilibrated ordinary chondrites—evidence for aqueous alteration on a parent body. *Earth Planet. Sci. Lett.* 122:403–416.

Weinbruch, S., Palme, H., Müller, W. F., and El Gorsey, A. 1990. FeO-rich rims and veins in Allende forsterite: Evidence for high temperature condensation at oxidizing conditions. *Meteoritics* 25:115–125.

Wood, J. A., and Hashimoto, A. 1993. Mineral equilibrium in fractionated nebular systems. *Geochim. Cosmochim. Acta* 57:2377–2388.

Wood, J. A., and Holmberg, B. B. 1994. Constraints placed on the chondrule-forming process by merrihueite in the Mezö-Madaras chondrite. *Icarus* 108:309–324.

Wood, J. A., and Morfill, G. E. 1988. A review of solar nebular models. In *Meteorites and the Early Solar System*, ed. J. F. Kerridge and M. S. Matthews (Tucson: University of Arizona Press), pp. 329-348.

Wulf, A. V. 1990. Experimentelle Untersuchungen zum Flüchtigkeitsverhalten von Spurenelementen in primitiven Meteoriten. Ph.D. Thesis, Universität Mainz.

Yoneda, S., and Grossman, L. 1995. Condensation of $CaO-MgO-Al_2O_3-SiO_2$ liquids from cosmic gases. *Geochim. Cosmochim. Acta* 57:3413–3444.

Zanda, B., Bourot-Denise, M., Perron, C., and Hewins, R. H. 1994. Origin and metamorphic redistribution of silicon, chromium and phosphorous in the metal of chondrites. *Science* 265:1846–1849.

Zolensky, M. E., Krot, A. N., and Scott, E. R. D., eds. 1997. *Workshop on Nebular and Asteroidal Modification of Chondritic Components*, LPI Technical Report Number 97-02, Part I (Houston, TX: Lunar and Planetary Institute).