OXYGEN-ISOTOPIC EVOLUTION OF THE SOLAR NEBULA

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Abstract. Studies of the three oxygen isotopes in chondrite meteorites demonstrate that diverse O reservoirs (characterized by their $\Delta^{17}O$ values) were present in the solar nebula. The discovery that some chondritic materials have O-isotopic compositions that cannot be explained by mass-dependent fractionation of an initially well mixed reservoir has important implications for the history of the solar nebula. On a plot of $\delta^{17}O$ versus $\delta^{18}O$ (or $^{17}O/^{16}O$ versus $^{18}O/^{16}O$), terrestrial samples (with the main exception of stratospheric ozone) fall along a single line (the terrestrial fractionation, or TF, line) having a slope ~0.52, an indication that the parental reservoir was homogenized. A convenient measure of O-isotopic heterogeneity is the deviation from the TF line, $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$. A popular model to explain the evolution of chondritic oxygen compositions during nebular and asteroidal aqueous alteration processes calls for the nebula to have formed from solids having $\delta^{18}O = -40‰$ and $\delta^{17}O = -41‰$ ($\Delta^{17}O = -20‰$) and a gas having a composition roughly estimated to be $\delta^{18}O = 30‰$ and $\delta^{17}O = 24‰$ ($\Delta^{17}O = 9‰$). This model encounters serious difficulties when examined in detail; in particular, it cannot readily account for the O-isotopic compositions of both chondrules and refractory inclusions from individual chondrite groups, or for the differences between groups, particularly in the compositions of chondrules. Magnetite (Fe_3O_4) is a key phase for O-isotope studies because during its formation by the oxidation of ferrous metal or FeS, all O comes from the oxidant, probably H_2O. It appears that most (and, possibly, nearly all) magnetite formed during aqueous alteration processes that occurred in asteroids. In all chondrite groups studied to date, $\Delta^{17}O$ of the magnetite is greater than or equal to that of the chondrule silicates. If the H_2O originated in the ambient (local) nebula, then at the time of accretion the $\Delta^{17}O$ of the nebular gas was generally higher than that of the solids. An alternative view is that the heterogeneity in the O-isotopic composition of chondrites indicates that the nebula formed from diverse batches of presolar materials, the precise O-isotopic composition of the mix varying during the accretion history of the nebula. The large compositional gaps between groups suggest that agglomeration of nebular dust to form chondrites did not proceed at a constant rate but that periods with turbulence levels low enough to allow agglomeration were punctuated by periods of high turbulence during which the composition of the inner nebula sampled by chondrites changed appreciably.

1. INTRODUCTION

The discovery of O-isotopic variations in primitive chondritic meteorites that could not be explained by fractionation processes was the first direct evidence of isotopic heterogeneity in the primitive solar nebula [*Clayton et al.*, 1973]. If a reservoir is initially homogeneous, mass-dependent fractionation produces arrays with slope 0.52 on plots of $\delta^{17}O$ versus $\delta^{18}O$. (Here $\delta^{18}O = [((^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{SMOW}) - 1] \times 1000$. Units are per mil. SMOW stands for standard mean ocean water, and $\delta^{17}O$ is defined analogously. A plot of $\delta^{17}O$ versus $\delta^{18}O$ can be thought of as a plot of normalized $^{17}O/^{16}O$ versus $^{18}O/^{16}O$ with the origin suppressed.) Terrestrial samples (with stratospheric ozone [*Schueler et al.*, 1990] and tropospheric ozone [*Krankowsky et al.*, 1995] being the main exceptions) form such an array called the terrestrial fractionation (TF) line.

Clayton et al. [1973] found that the minerals separated from the CV2 Allende formed an array with a slope near unity and that all samples had compositions below the TF line. (Chondrite groups are designated by one or two letters. The three main kinds are (1) carbonaceous chondrites, all of which have first letter C; (2) the ordinary chondrites H, L, and LL; and (3) the enstatite chondrites EL and EH. The petrographic type number follows the letter symbols without space. Type 3.0 is the most primitive; lower types have experienced aqueous alteration, and higher types have experienced thermal metamorphism.)

Later studies [e.g., *Clayton*, 1993] showed that it is the norm that meteoritic materials have O-isotopic compositions plotting below or above the TF line; only the enstatite meteorites (EH and EL chondrites and the differentiated meteorites called aubrites) plot within experimental uncertainty of that line (and, perhaps not a

coincidence, close to the composition of the Earth's mantle). The term $\Delta^{17}O$ offers a convenient way to quantify the vertical deviations of O-isotopic compositions from the TF line; $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$.

During the 2.5 decades since the discovery of O-isotopic anomalies, several groups have discussed how the large range ($\sim 60\%o$) in $\Delta^{17}O$ could have originated and what O-isotopic compositions tell us about the evolution of the solar nebula. The two-component model of *Clayton and Mayeda* [1984] (hereinafter referred to as CM84) has proven quite popular, perhaps because it allows numerical evaluation of various hypothetical O-isotope reservoirs and the relative fractions of these reservoirs incorporated into diverse meteoritic materials. The simple picture used in this model is that the solar nebula initially consisted of two reasonably uniform reservoirs, one gaseous and one consisting of solids. The O-isotopic composition of the gaseous component was well above the TF line, and that of the solid component was well below. More detailed two-component models of aqueous alteration in asteroids have recently appeared [*Clayton and Mayeda*, 1999; *Young et al.*, 1999].

Equilibrium calculations [e.g., *Wood and Hashimoto*, 1993] show that in a canonical nebula having solar [*Anders and Grevesse*, 1989] composition at a temperature of 500 K, at which most metals have condensed as solids, oxygen in gaseous form (e.g., CO and H_2O) is roughly 6 times more abundant than oxygen in solid form (e.g., silicates).

Although some low-temperature reactions involving gases (or gases and solids) produce $\delta^{17}O$-$\delta^{18}O$ arrays with slopes near unity [*Thiemens and Heidenreich*, 1983; *Morton et al.*, 1990], much larger variations in the $^{17}O/^{16}O$ and/or $^{18}O/^{16}O$ ratios are produced by stellar nucleosynthesis, and most researchers [e.g., *Clayton*, 1993] conclude that this is the main source of the meteoritic O-isotopic variations. *Wasson* [1988] noted that few, if any, astrophysical settings would have separated presolar materials into distinct, isotopically uniform gas and solid reservoirs that would have persisted through the accretion of the solar nebula. Presolar materials would have originated in numerous stars that produced the different O-isotopes in a variety of ways. Because the solar system formed late in the history of the galaxy, most matter was from second-generation stars containing moderate amounts of the common metals (e.g., Mg and Si) that condense as oxides; thus one would expect that the matter ejected from each stellar source (after cooling and condensation) would have included a more or less "normal" fraction of solid O together with the approximately 6 times more abundant gaseous fraction. Wasson therefore argued that each batch of presolar matter falling into the solar nebula had its own O-isotopic signature and that these were largely the same in the solid and gas. He suggested that the O-isotopic differences among chondrite groups reflected formation during different epochs of nebular history.

Wood [1981] considered the possibility of diverse sources of the O isotopes but concluded that such a model is unlikely to be correct, because each star would have imprinted other elements with unique isotopic compositions. He noted that few isotopic variations had been reported in other elements and that none had been shown to be ubiquitous, let alone to correlate with the observed variations in O.

Wiens et al. [1999] examined several simple models of solar nebula evolution based on CM84 in order to obtain predictions of the O-isotopic composition of the solar photosphere. A key goal of the NASA Genesis spacecraft mission is to obtain $\delta^{17}O$ and $\delta^{18}O$ values for the solar wind.

Choi et al. [1998b] recently reported $\Delta^{17}O$ values in the magnetite of the LL3.0 Semarkona chondrite that are higher than those in any other solid materials formed in the solar nebula (or by natural processes on Earth). They noted that the oxidant (probably H_2O) responsible for the oxidation of metal to form magnetite could be the same oxidant responsible for the correlation between $\Delta^{17}O$ and FeO/(FeO + MgO) through the ordinary chondrite (H-L-LL) sequence. This discovery stimulated me to reexamine the evidence for such correlations between degree of oxidation and O-isotopic composition within other groups of chondrites and to review the general issue of isotopic heterogeneities within the solar nebula. Although the differentiated meteorites also offer information about the solar nebula, the formation of these meteorites from their chondritic precursors has obscured the record, and I will therefore limit my consideration to the chondrites.

2. CLASSIFICATION OF CHONDRITES: INTERGROUP VARIATIONS IN THE ISOTOPIC COMPOSITION OF OXYGEN

Chondrites are classified into 12 groups having five or more members and a comparable number of grouplets having four or fewer members. Some sets of chondrite groups are closely related in composition and petrography and are collectively referred to as clans. The ordinary chondrite (OC) clan consisting of the H, L, and LL groups is the type example. In Figure 1 I show the positions of the chondrite groups on a plot of refractory-lithophile abundance versus $FeO_x/(FeO_x + MgO)$ ratio, which is an approximate measure of the degree of oxidation. (Refractory lithophiles are elements such as Ca and Al that condense from a cooling solar nebula at temperatures higher than the condensation of the common lithophiles Mg and Si. The term "abundance" generally refers to a normalized element/element ratio. In this case, the element/Mg ratio in a chondrite sample is normalized to the same ratio in CI chondrites. Refractory inclusions are millimeter- to centimeter-size nuggets that largely (>80%) consist of oxides of the refractory-lithophile elements.) The Mg-normalized and CI-
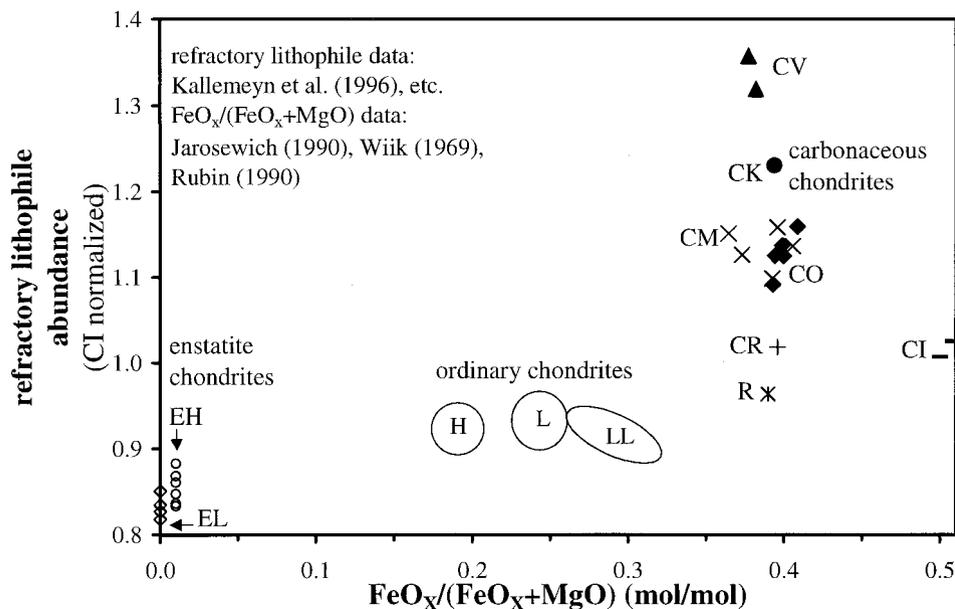
Figure 1. A traditional way to resolve the chondrite groups is a plot of the refractory-lithophile abundance versus $FeO_x/(FeO_x + MgO)$ ratio, which is an approximate measure of the degree of oxidation. Refractory-lithophile data are from *Kallemeyn et al.* [1996] and *Wasson and Kallemeyn* [1988]; $FeO_x/(FeO_x + MgO)$ units for whole-rock equilibrated ordinary chondrite (OC) are from *Rubin* [1994], and those for unequilibrated chondrites are from *Jarosewich* [1990] and *Wiik* [1969] (see text for details). All carbonaceous chondrites have higher refractory-lithophile abundances than ordinary and enstatite chondrites. Ordinary and enstatite chondrites have $FeO_x/(FeO_x + MgO) < 0.32$, but the ratio is 0.38–0.40 in their aqueously altered OC relatives, the R chondrites.

normalized refractory-lithophile abundances are calculated from Mg, Al, Ca, and Sc concentrations in whole-rock chondrites taken from the work of Kallemeyn and coworkers [e.g., *Kallemeyn et al.*, 1996].

The FeO_x values were obtained as follows: For chondrites having olivine and pyroxene that are equilibrated (or nearly so) I used compositions of the most abundant silicate (pyroxene in enstatite chondrites and olivine in ordinary and carbonaceous chondrites). For unequilibrated ordinary chondrites (UOC) I used bulk analyses, with emphasis given to those of *Jarosewich* [1990]. The data of *Wiik* [1969] were used only for carbonaceous-chondrite groups for which Jarosewich provided few analyses. To better reflect the degree of oxidation, I used the moles of O bound to Fe as FeO_x. These FeO_x values differed significantly from FeO only in CI, CR, and CM chondrites, in which an appreciable fraction of the Fe is present as magnetite, Fe_3O_4; in text and diagrams that do not involve these three groups I use FeO instead of FeO_x.

Unfortunately, because of experimental difficulties, all bulk analyses tend to have large errors in the assignment of Fe to FeO or $FeO_{1.5}$ (G. W. Kallemeyn, personal communication, 1989). In the specific case of the CM chondrites, which have small amounts of magnetite but for which *Wiik* [1969] did not provide $FeO_{1.5}$ data, I made the rough assumption that 5% of the Fe was in the +3 state. In the CI and CM chondrites the small fraction of Fe present as metal or sulfides was not estimated but

was included in the FeO total. This has a negligible effect on the plotting location on Figure 1.

The enstatite chondrites (EC) are highly reduced. I plot all EL chondrites at a $FeO_x/(FeO_x + MgO)$ of 0.0002, the value recommended by *Wasson et al.* [1994] as the best estimate of the composition of EL6 enstatite (the dominant mafic phase); these authors pointed out that all other published values are too high because of fluorescence of Fe metal or FeS during electron-probe studies. The EH chondrites are not equilibrium assemblages. Although, relative to EL chondrites, their silicates tend to have higher FeO contents, implying a higher degree of oxidation, their metal has higher Si contents than observed in EL chondrites, indicating a greater degree of reduction [*Keil*, 1968]. I arbitrarily plotted the EH chondrites at an $FeO_x/(FeO_x + MgO)$ ratio of 0.01.

Only a small fraction of compositional space in Figure 1 is occupied by the groups and clans, and although a few chondrite grouplets having one to four members are known, most grouplet members tend to plot relatively close to the group positions. Most plot in compositional space near the carbonaceous-chondrite (CC) groups.

As was noted in section 1, the remarkable discovery of *Clayton et al.* [1973] was that on plots of $\delta^{17}O$ versus $\delta^{18}O$, many meteorite samples do not plot on the TF line. Figure 2 shows O-isotopic whole-rock compositions of the meteorites from the major groups of chondrites.
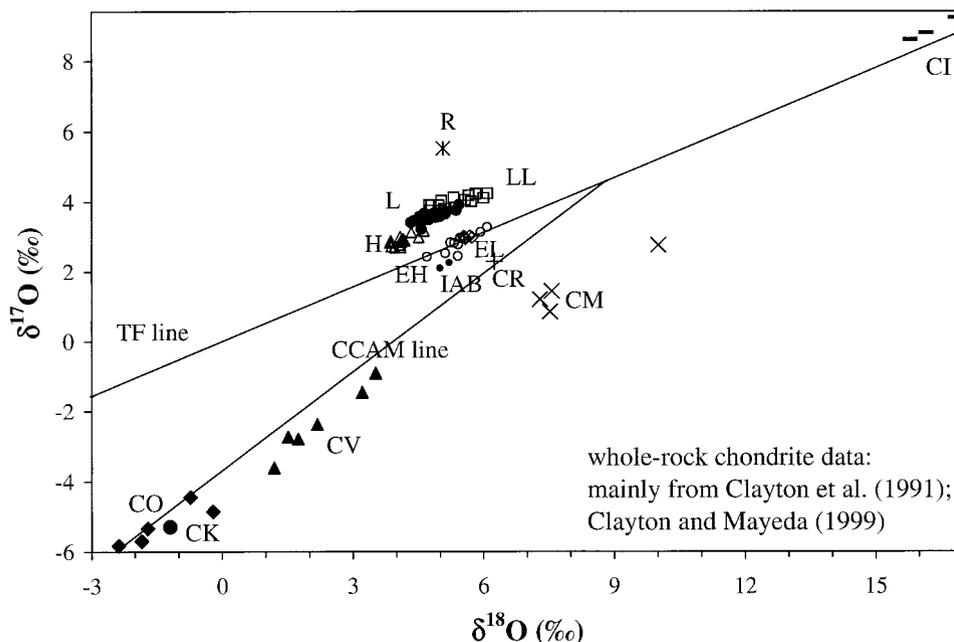
Figure 2. Whole-rock O-isotopic compositions of members of the major groups of chondrites are also excellent taxonomic parameters. All data are from Clayton and coworkers (*Clayton et al.* [1991], *Clayton and Mayeda* [1999], and references cited therein). Where duplicate data were available, arithmetic means are plotted. The R chondrites show strong links to the ordinary chondrites but are as oxidized as carbonaceous chondrites. The CI, CM, CR, and R chondrites have experienced aqueous alteration in asteroidal settings that seems to have reset their O-isotopic compositions.

Also shown in Figure 2 is another reference line, the carbonaceous-chondrites-anhydrous minerals (CCAM) line; this line was obtained by fitting data by Clayton and coworkers for separated minerals and mineral aggregates from carbonaceous chondrites, especially CV Allende.

All data in Figure 2 are from Clayton and coworkers (*Clayton et al.* [1991], *Clayton and Mayeda* [1999], and references therein) and were determined by fluorination techniques. Where duplicate data were available, arithmetic means are plotted. Figure 2 demonstrates that the O-isotope data yield the same groups as the chemical data plotted in Figure 1. Grouplets are not plotted; these mainly occupy the area near the carbonaceous chondrites.

The taxonomic record in the O isotopes can be characterized by two parameters: $\Delta^{17}O$, which indicates the mixing of different reservoirs, and $\delta^{18}O$, which offers information about the conditions present when mineral phases formed. In Figure 3, $\Delta^{17}O$ is plotted against the $FeO_x/(FeO_x + MgO)$ ratio. In Figure 3 the groups are again sharply delineated. "Stick" symbols (such as a plus sign or cross) are used for members of the four groups (CI, CM, CR, and R) that may have had their bulk compositions shifted by aqueous alteration in the parent asteroids. If these are ignored, the amount of compositional space occupied by the remaining chondrites is a tiny fraction of that in the entire diagram. If the nebular processes that produced the chondrites originally produced a continuous band across this diagram, only a tiny fraction of the original population has been sampled by

the Earth. The chondritic meteorites from Antarctica are clearly sampling many (my rough estimate is 100) asteroids, yet their compositions, if plotted, would result in only a minor diminution of the gaps. Thus it seems probable that the compositional gaps reflect nebular processes. Because these different reservoirs probably reflect different mixes of presolar materials, they appear to offer information about the nebular time and/or place where particular kinds of chondrites formed.

3. SOME EVOLUTIONARY MODELS OF THE SOLAR NEBULA

The composition of the solar nebula was closely related to that now preserved in the solar atmosphere. In Table 1 I list the 15 most abundant elements in the solar nebula based on the data compilation of *Anders and Grevesse* [1989]; these authors make the standard assumption that the CI chondrites offer the best estimates of the abundances of the condensable elements. The variations in chemical or isotopic composition discussed here represent minor variations on this composition, albeit the details of these variations can help constrain the process involved in the formation and evolution of the nebula.

The main cosmochemical scenarios differ in terms of temperatures experienced by the bulk of nebular matter. According to the low-temperature scenario, tempera-
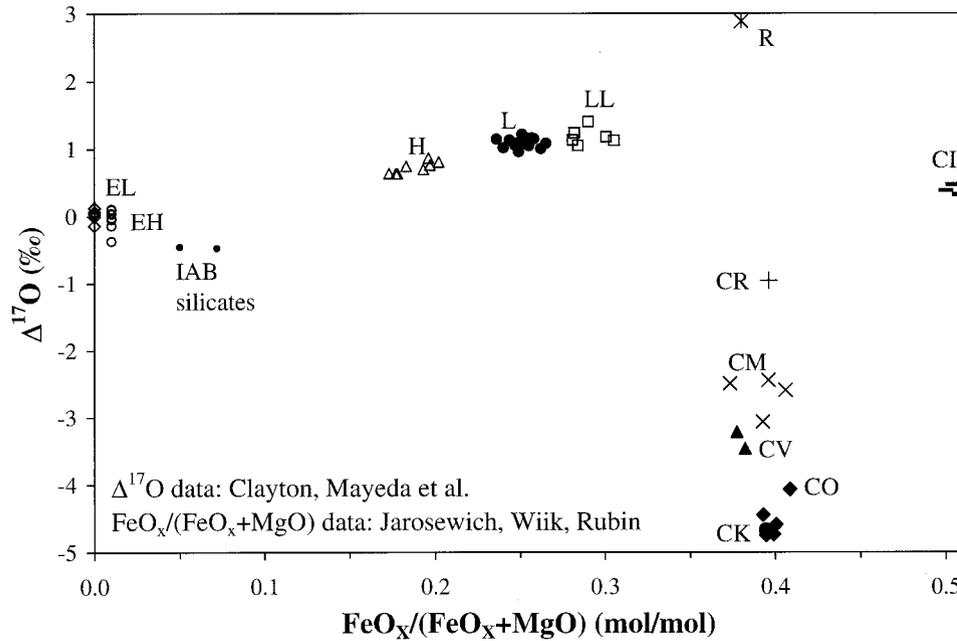
Figure 3. A plot of the $\Delta^{17}O$ versus $FeO_x/(FeO_x + MgO)$ ratio for samples of bulk chondrites gives even better resolution of the chondrite groups than do the chemical parameters plotted in Figure 1 or the $\delta^{17}O$-$\delta^{18}O$ distribution in Figure 2.

tures in large (scales of astronomical units) regions of the nebula were never high enough to vaporize the oxides of the common elements Si and Mg, whereas in the high-temperature scenario, most presolar materials vaporized, either during infall or in a later high-temperature (e.g., FU-Orionis-like) event. The FU-Orionis-like stars are young stars just moving onto the main sequence [*Hartmann et al.*, 1993; *Bell et al.*, 2000]. During quiescent periods these stars are similar to the more common T-Tauri stars, and they may represent an early stage in T-Tauri evolution. They undergo luminosity increases by factors of 80–200 within brief (1- to 10-year) periods, and then their brightness slowly decreases back down to steady state values.

Gibbs-free-energy data can be used to determine the temperatures at which phases condense from a slowly cooling canonical (i.e., solar composition) nebula. Listed in Table 2 are the temperatures at which 50% of certain elements condense. All listed elements condense as oxides, with the exception of Fe. In these calculations I

made the standard (and only partially correct) assumption that previously condensed phases remain in equilibrium with the gas and other condensates; for example, in the case of Ca, I assumed that the previously condensed phase Al_2O_3 readily reacts to allow Ca to condense as gehlenite, $CaAlSi_{0.5}O_{3.5}$. The condensation temperature of Si also depends on the amount of back reaction of previously condensed phases and on the nucleation of $MgSiO_3$; the listed value corresponds to 40% condensation of Si as Mg_2SiO_4 and more refractory phases and 10% as $MgSiO_3$. If, instead of cooling, the nebula was slowly heating up, these temperatures correspond to 50%-evaporation temperatures.

In a canonical (i.e., solar composition) nebula having $pH_2 = 10^{-5}$ atm, 50% vaporization of Mg_2SiO_4 requires a temperature of 1292 K (Table 2). The presence of refractory inclusions (or CAI, calcium-aluminum-rich inclusions) that appear to be evaporation residues [*Chou et al.*, 1976; *Wood*, 1981] sets an upper temperature limit of about 1484 K, the 50% vaporization temperature of Ca as gehlenite ($CaAlSi_{0.5}O_{3.5}$) at $pH_2 = 10^{-5}$ atm. Note that both these temperature estimates would be about 60 K lower at $pH_2 = 10^{-6}$ atm. The presence of interstellar grains in chondrites can be accommodated by the high-temperature scenario by having them fall into ("dust") the nebula after the last high-temperature event occurred.

Important in later discussions is the fraction of nebular O tied up as solids. In Table 3 I show that in a nebula with $pH_2 = 10^{-5}$ atm, the fraction of O in solids rises from 0.002 at 1600 K to 0.137 ($\sim$1/7) at 1200 K and to 0.158 ($\sim$1/6) at 400 K.

TABLE 1. Fifteen Most Abundant Elements in the Solar Nebula [After *Anders and Grevesse*, 1989]

Element	Abundance	Element	Abundance	Element	Abundance
H	27,900	N	3.13	Ar	0.10
He	2,720	Mg	1.07	Al	0.085
O	23.8	Si	1.00	Ca	0.061
C	10.1	Fe	0.90	Na	0.057
Ne	3.44	S	0.52	Ni	0.049

Abundances are relative to Si ≡ 1.00.

TABLE 2. Fifty Percent Condensation Temperatures of Several Oxide-Forming Elements From the Solar Nebula

Element	Compound	Condensation Temperature, K	Element	Compound	Condensation Temperature, K
Al	Al_2O_3 (s)	1610	Fe	Fe-Ni (s)	1260
Ti	$CaTiO_3$ (s)	1531	Si	Mg_2SiO_4 (s)[a]	~1260
Ca	$Ca_2Al_2SiO_7$ (s)	1484	O	H_2O (s)	164
Mg	Mg_2SiO_4 (s)	1292			

Here $pH_2 = 10^{-5}$ atm. See text for details.
[a]Also $MgSiO_3$.

4. INTRAGROUP VARIATIONS IN COMPOSITION: VARIATION OF OXYGEN-ISOTOPIC COMPOSITION AMONG PHASES AND COMPONENTS

A range in $\Delta^{17}O$ values is found in the components of unequilibrated chondrites. In the CC these ranges can be ~20‰, with the lowest values in refractory inclusions. In chondrites that have very low contents of refractory inclusions, the $\Delta^{17}O$ range in the common components is much smaller (e.g., 1.0‰ in H Dhajala chondrules and 1.4‰ in L/LL Chainpur chondrules). These data are discussed in more detail below.

There is increasing evidence that most groups of chondrites have experienced minor amounts of aqueous alteration. In two carbonaceous-chondrite groups (CI and CM), alteration is so severe that most of the nebular record has been erased. Some other groups also show moderate alteration, particularly the carbonaceous CR chondrites and the noncarbonaceous R chondrites. In the most altered materials, metal was largely oxidized, and during metamorphism, the FeO has been incorporated into mafic silicates. In the remaining, relatively anhydrous groups, aqueous alteration is variable although probably more extensive than has been recognized in the past. *Krot et al.* [1995] give a detailed discussion of aqueous-alteration effects in the CV chondrites; these include (1) evidence of the incorporation of Fe, alkalis, and halogens into low-temperature minerals in chondrules, matrix, and other assemblages; (2) formation of ferrous olivine rims; (3) formation of platy olivine

in the matrix; (4) formation of pure fayalite; (5) formation of phyllosilicates.

Magnetite is a key phase for enciphering the isotopic record of O involved in low-temperature processes. Although some researchers [*Rubin*, 1993; *Haggerty and McMahon*, 1979] have ascribed its formation to nebular processes, there appears to be a growing consensus [e.g., *Krot et al.*, 1995; *Choi et al.*, 1998b] that most, perhaps all, chondritic magnetite formed by aqueous alteration processes in asteroids. Most magnetite seems to have formed by the oxidation of metallic Fe (or possibly FeS), and the most plausible oxidant is H_2O in liquid or vapor form. Thus the probable chemical reaction is

$$3 \text{ Fe (s)} + 4 H_2O \text{ (l or g)} = Fe_3O_4 \text{ (s)} + 4 H_2\text{(g)} \quad (1)$$
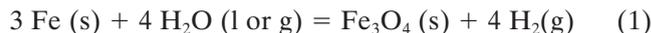
or a similar reaction involving FeS as a reactant. Because all the O in the magnetite originates in the H_2O and parent and daughter phases must lie along the same mass-fractionation line, the magnetite records the $\Delta^{17}O$ of the H_2O. Thus, in terms of $\Delta^{17}O$, the magnetite is a proxy for asteroidal H_2O [*Choi et al.*, 1998b].

There is, however, appreciable fractionation in $\delta^{18}O$ and $\delta^{17}O$ between the magnetite and its parental H_2O. The difference in $\delta^{18}O$ between two phases formed under equilibrium conditions is called the fractionation factor and is represented by $\Delta^{18}O$. Figure 4 shows the variation of the fractionation factor $\Delta^{18}O(\text{mgt} - \text{wtl})$ for the temperature range 300–1700 K (mgt is magnetite; wtl is liquid water and below; sil is silica; and ol is

TABLE 3. Fraction of O Atoms in Nebular Phases

T = 1600 K	Fraction	T = 1200 K	Fraction	T = 400 K	Fraction
CO (g)	0.424	CO (g)	0.424	CO (g)	0.000
H_2O (g)	0.574	H_2O (g)	0.439	H_2O (g)	0.842
Al_2O_3 (s)	0.002	$MgSiO_3$ (s)	0.107	Mg_2SiO_4 (s)	0.056
		Mg_2SiO_4 (s)	0.016	$MgSiO_3$ (s)	0.052
		$CaSiO_3$ (s)	0.008	Fe_2SiO_4 (s)[a]	0.038
		$MgAl_2O_4$ (s)	0.007	$NaAlSi_3O_8$– $CaAl_2Si_2O_8$	0.009
				$CaSiO_3$ (s)	0.004
Total solid O	0.002		0.137		0.158

Nebular $pH_2 = 10^{-5}$ atm.
[a]Fifty percent of total Fe is assumed to be in olivine.

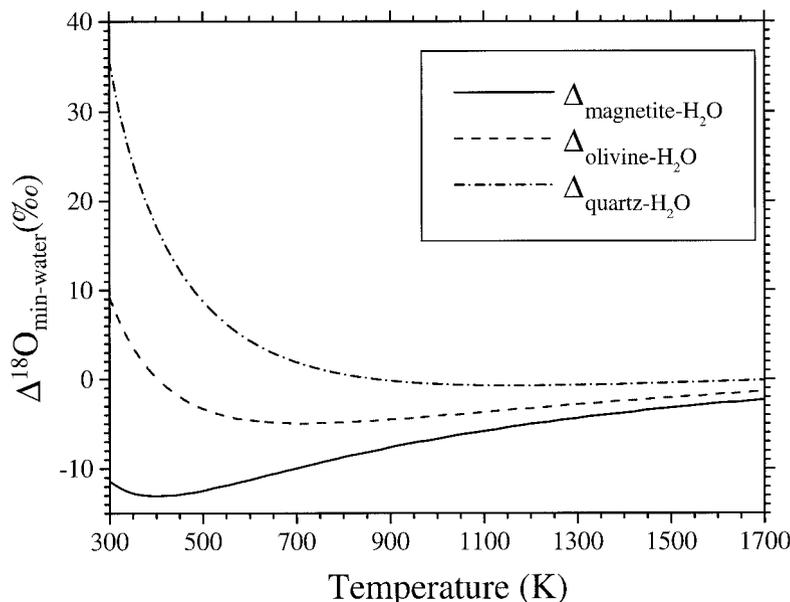**Figure 4.** Isotopic fractionation factors ($\Delta^{18}O$) between three solid phases (magnetite, olivine, and silica) and liquid water. These curves were compiled by B.-G. Choi from partition function information given by *Clayton and Kieffer* [1991] and *Hattori and Halas* [1982].

olivine). This diagram was prepared by B.-G. Choi (personal communication, 2000) based on reduced partition functions summarized by *Clayton and Kieffer* [1991] and *Hattori and Halas* [1982].

Another important low-temperature phase is fayalite. Although there is not yet a consensus, there are strong reasons for holding that the fayalite in chondrites was produced by aqueous alteration processes in asteroidal settings. In Figure 4, $\Delta^{18}O$ (ol-wtl) is also shown. There has not yet been much discussion of the origin of the silica polymorphs cristobalite and tridymite that are abundant in some chondrite nodules. *Bridges et al.* [1995] argue for an igneous origin for the occurrences of these phases in OC that they studied. I find the arguments for formation during aqueous alteration to also be tenable. The $\Delta^{18}O$ (sil-wtl) is also shown in Figure 4.

As is discussed in some detail in a later section, the nebular record is best preserved in meteoritic chondrules. Fine-grained materials (i.e., matrix grains) experienced much more extensive alteration. Because the chondrules are relatively coarse grained and nonporous, those present in the mildly altered chondrite groups seem to have passed through the asteroidal aqueous-alteration event with minimal change in O-isotopic composition.

5. ASTROPHYSICAL SOURCES OF THE OXYGEN ISOTOPES

Much of the material in the interstellar medium is ejected by medium-to-large-mass stars, particularly type 2 supernova and red giants, especially the asymptotic

giant branch (AGB) red giants (see, e.g., the introduction in the work by *Alexander and Nittler* [1999]). The range in $\delta^{18}O$ and $\delta^{17}O$ in whole-rock samples of chondrites is much smaller than the range encountered in interstellar grains or calculated to exist in stellar interiors.

In part because the slope of the CCAM line is so close to unity (and *Young and Russell* [1998] argue that it is exactly unity), most solar nebula models have been couched in terms of dilution of normal oxygen by a component very rich in ^{16}O [e.g., *Clayton*, 1993]. Calculations by *Woosley and Weaver* [1995] summarized by *Meyer et al.* [1995] indicate that nearly pure ^{16}O can be produced by ^4He burning in medium to large stars and be expelled from these during supernova explosions. In the O/Ne zone of a 25 $M_\odot$ type 2 supernova, there is a great overabundance of ^{16}O; the calculated $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios are 2000 and 63,000 times smaller, respectively, than those in SMOW. In contrast, in the He/N zone of this star the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios are 180 and 6 times larger, respectively, than those in SMOW. In the total 23.5 $M_\odot$ of ejecta from this star the calculated $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios are 1.4 and 1.7 times smaller, respectively, than the SMOW values. There are stars whose typical ejecta plot far above the TF line; AGB stars generate very high $^{17}O/^{16}O$ ratios, while the $^{18}O/^{16}O$ ratio remains largely the same as in the starting material [*Boothroyd et al.*, 1994].

Studies of interstellar grains isolated from unequilibrated chondrites confirm that stars produced a wide variety of O-isotopic compositions and thus that mixing lines having slopes $\neq 0.5$ can also be produced by admixing materials from interstellar reservoirs having $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios much higher than typical meteorite
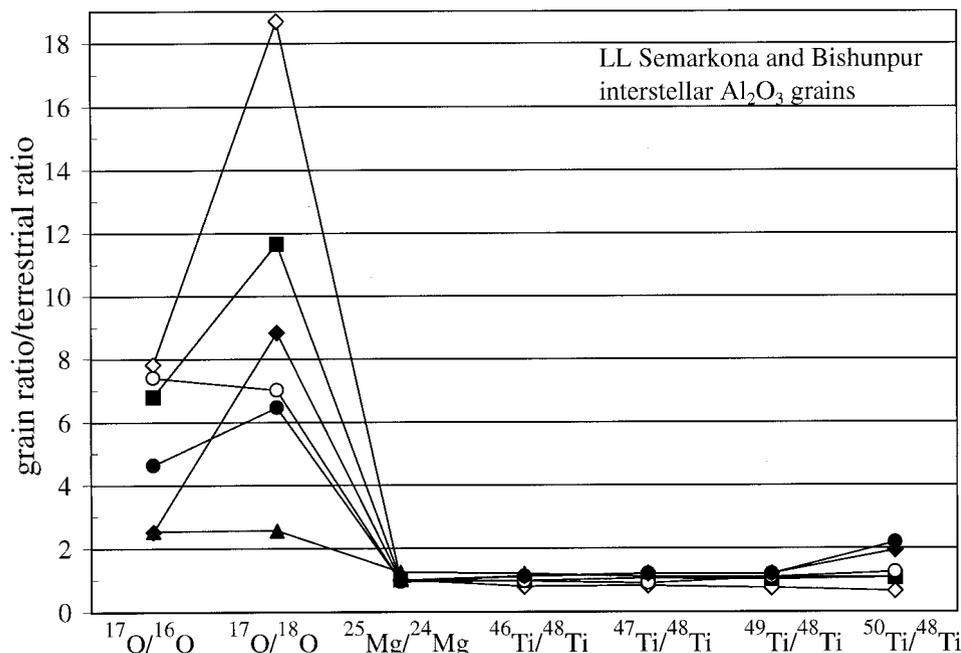
Figure 5. Isotopic ratios in six interstellar Al_2O_3 grains from the LL chondrites Semarkona and Bishunpur [*Choi et al.*, 1998b] show that $^{17}O/^{16}O$ ratios are much higher than the terrestrial ratio. The most extreme grain (the open diamond) is Semarkona C261. Ratios of Mg and Ti isotopes in the same grains also differ from terrestrial ratios, but the deviations are 1–2 orders of magnitude smaller than for O isotopes. Among the Mg and Ti isotopes, appreciable variations are found only for ^{50}Ti. These corundum grains appear to have originated in asymptotic giant branch (AGB) stars.

values. Also, the $^{17}O/^{18}O$ in these materials can also be grossly different from SMOW.

Choi et al. [1998a] isolated Al_2O_3-rich grains from LL3.0 Semarkona and Bishunpur; in Figure 5 I show results for six grains in which they measured isotopic ratios in O, Mg, and Ti. All ratios are normalized to terrestrial data provided by the authors. On the basis of their isotopic characteristics, the authors interpreted these grains to be condensates from AGB stars. The important point here is that the O isotopes deviate from terrestrial (SMOW) isotopic ratios by a much greater degree than do any of the ratios involving Mg or Ti isotopes. Thus, to resolve heterogeneities in these latter elements, much greater analytical sensitivity is needed. These studies also suggest that the largest effects should be seen in ^{50}Ti, consistent with the fact that ^{50}Ti is the isotope with mass number >24, for which the variations have been most consistently reported [e.g., *Niemeyer*, 1988]. A point of interest is that there are rare cases where Ti and O anomalies are large and similar, i.e., in hibonite-rich inclusions from CM chondrites [*Fahey et al.*, 1987].

Thiemens and Heidenreich [1983] demonstrated that in laboratory settings, mass-independent fractionation can occur under certain circumstances. Their original example was the formation of ozone at low temperatures in a spark discharge, but by now many additional processes have been found to show this effect [*Thiemens*, 1999]. Quite large mass-independent fractionations

(110‰ in returned samples, still larger in in situ measurements) occur during formation of ozone in the stratosphere [*Schueler et al.*, 1990].

Thiemens and Heidenreich [1983] suggested that such mass-independent fractionation processes could have been responsible for the fact that the slope of the CCAM array is near unity. However, it seems doubtful that these mass-independent processes could have been more important than mass-dependent processes at high (>1000 K) nebular temperatures [e.g., *Navon and Wasserburg*, 1985], particularly in a system rich in particles that can serve as substrates for reactions. *Morton et al.* [1990] carried out ozone syntheses at temperatures up to 360 K. Their results indicate that mass-independent fractionations persist up to ~500 K (and possibly higher) but are less important than mass-dependent effects above ~350 K.

It seems possible that mass-independent formation of O-bearing solids might occur at the cold (<50 K) temperatures of molecular clouds. If this does occur in an initially homogenous system, subsequent separation of gas and solids could form reservoirs having different $\Delta^{17}O$ values. As was discussed above, large O-isotopic variations and large differences in the metal/O ratio can be present in stellar ejecta; thus it is not unreasonable to expect parcels of interstellar material to have moderately different O-isotopic compositions in their gaseous and solid components, whatever the processes and locales associated with their production. Also, a wide
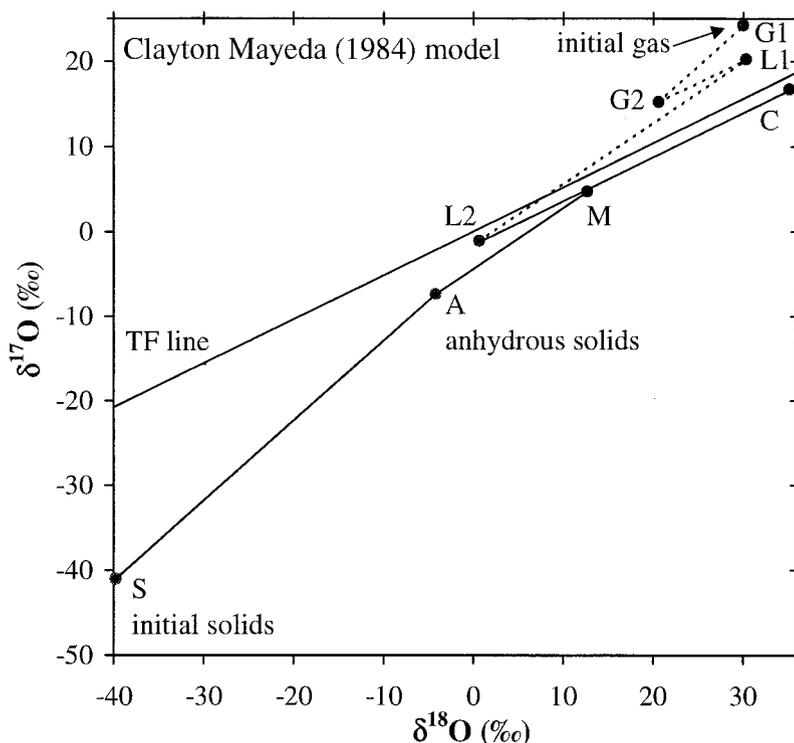
Figure 6. The tracks on this diagram illustrate the two-component O-isotopic evolution model first proposed by *Clayton and Mayeda* [1984] specifically to explain the $\delta^{17}O$-$\delta^{18}O$ systematics observed in CM chondrites. Shown here is a variant of this model published by *Rowe et al.* [1994] for CI chondrites. The various compositions observed within chondrites are modeled in terms of mixing and exchange processes between two initial nebular reservoirs, one gaseous at G1, the other solid at S, and by similar processes (nebular and asteroidal aqueous alteration) between the products resulting from the initial set of processes. See text for a detailed discussion.

($>100‰$) range in O-isotopic compositions may have been present in the solids.

6. EVOLUTION IN THE ISOTOPIC COMPOSITION OF THE NEBULAR GAS

6.1. Clayton-Mayeda Model for the Isotopic Evolution of O Reservoirs in the Nebula

Clayton and Mayeda [1984] (abbreviated CM84) proposed a simple model to account for the O-isotopic variations they observed in CM chondrites, particularly Murchison. Minor variants of this model for CI chondrites were proposed by *Rowe et al.* [1994] and *Leshin et al.* [1997]. The essential aspects of the model are illustrated in Figure 6, which is redrawn from the Rowe et al. paper. The solar nebula initially consisted of gas with a composition at G1 and solids with a composition at S. The latter was fixed at $\delta^{18}O = -40$, $\delta^{17}O = -41‰$ (hereinafter I follow the traditional O-isotope listing sequence of Clayton's group, first $\delta^{18}O$, then $\delta^{17}O$), representative of the most ^{16}O-rich composition found in the studies of refractory inclusions by Clayton and coworkers. Although not explicitly stated in the discussion of the model, it appears to have been assumed that these

solids included all condensable (at $T > \sim 400$ K) elements in solar proportions and that much of the Fe was present as FeO. It also seems to have been assumed that most of the solids had a composition near S rather than the alternative suggested above by the discussion of astrophysical sources, that this was a mean composition of solid grains having a large ($>100‰$) range in $\Delta^{17}O$ values.

A process described by *Rowe et al.* [1994] as "high-temperature exchange" between the solids (S) and gas G1 created solids having the composition A; this composition is based on the inexactly defined composition of anhydrous silicates, mainly chondrules, in carbonaceous chondrites. Mass balance during the exchange process results in the gas composition shifting from G1 down to G2. CM84 (p. 154) indicate that the O-isotope exchange that formed component A may have occurred during "a brief heating event that produced chondrules" and that "the exchange temperature was assumed to be 1800°C" (2073 K). Because the major and minor elements except Ca and Al are almost entirely in component A, it became far more abundant than the residual component S.

Component L1 is described by *Rowe et al.* [1994] to be liquid H_2O condensed from the nebula in equilibrium with gaseous H_2O having a composition close to G2.

These authors note that at the time of this condensation (which they suggest occurred at $T \approx 273$ K), CO, the dominant O-bearing compound present at high nebular temperatures, will have been converted to CH_4, the more stable form of C at low nebular temperatures. Thus nearly all the gaseous O was present as H_2O at the time the condensation occurred, and one can use $\Delta^{18}O$ ($H_2O(I)$-$H_2O(g)$) fractionation factors to assess the $\delta^{18}O$ value of the gaseous H_2O from the composition of condensed H_2O derived from their model.

Solids with mean composition A and H_2O with mean composition L1 agglomerated and accreted to form a parent asteroid; the O_{water}/O_{rock} atom ratio is called f. Temperatures were (or became) high enough to cause the water (liquid or vapor) to react with metal and silicates to form magnetite, hydrated minerals, and other low-temperature phases. During this aqueous alteration process, phyllosilicates formed with a mean composition at M. Mass balance required that the H_2O composition shift from L1 to L2, the precise value depending on the water/rock ratio. Trace amounts of carbonate having composition C also formed in equilibrium with this liquid. Because M and C plot along a line having the mass-fractionation slope of 0.52, they are inferred to have formed under equilibrium conditions, allowing the calculation of the position of L2 from the model at the assumed temperature.

The cosmochemical basis for this model has never been discussed in detail, either by the proponents or by those more skeptical. I will attempt to discuss how it fits into the general picture of processes and conditions in the solar nebula. There are several implausible details such as the condensation temperature of H_2O. In addition, two serious problems were found. (1) It appears impossible to formulate a plausible cosmochemical process to generate both common metal oxides having composition A and refractory metal oxides at composition S. If refractory inclusions are formed by near-complete evaporation, one cannot later generate A. If A formed by exchange with a solar mix of chondritic oxides, it is impossible to also produce residual refractory oxides having composition S. (2) There is strong evidence that some refractory inclusions having compositions near S formed by condensation, which requires the same $\Delta^{17}O$ (less than $-20‰$) in the gas.

It is clear that component S is based on the properties of CC refractory inclusions. The best studied are from CV Allende; the -40, $-41‰$ composition of these is well documented by fluorination studies [e.g., *Clayton et al.*, 1977]. Some ion-probe analyses [e.g., *Fahey et al.*, 1987; *Yurimoto et al.*, 1998] have yielded slightly more extreme values (e.g., $\delta^{18}O$ and $\delta^{17}O$ in the range $-60‰$ to $-50‰$), and thus these $\delta^{17}O$ and $\delta^{18}O$ values of -41.1, $-39.8‰$ used by CM84 should probably be treated as means with moderately large uncertainties.

In contrast to component S, there is no fraction of chondrites that preserves the composition of the hypothetical gaseous components G1 and G2. If, in a global

solar nebula model, these two components are to explain all chondrites (and although CM84, *Rowe et al.* [1994], or *Leshin et al.* [1997] have not claimed that one set of conditions can account for all classes of chondrites, the tenor of the discussion implies global models), it is clear that the $\Delta^{17}O$ of component G2 has to be at least as large as that of the highest preserved nebular solids. The current benchmark is the magnetite of LL chondrites which reaches values $>6‰$ [*Choi et al.*, 1998b]. CM84 obtained the G1 (and G2) compositions based on their assumption that component A formed by interaction of the gas with component S. Mass balance requires that the slope of the G2-G1 line must be the same as that of the S-A line, but the $\delta^{17}O$ intercepts of the two lines will differ because of the mass fractionation between the gas (CO and H_2O) and solids (Mg_2SiO_4 is the main constituent). According to CM84, at the assumed temperature of 2073 K, the $\delta^{17}O$ intercepts differ by $0.91‰$, the relatively small difference reflecting the fact that fractionation factors become small at high temperatures.

As emphasized by CM84, the remainder of the model is very dependent on the assumptions. The gas G1 condenses at 273 K to form H_2O (I) having composition L1. This liquid is incorporated into the CM parent body and interacts with a portion of the anhydrous silicates A to form phyllosilicate matrix having composition M. The residual parent-body water obtains the composition L2, estimated from the (poorly determined) fractionation factors ($\Delta^{18}O$) between H_2O (I) and phyllosilicates and from the (somewhat better determined) $\Delta^{18}O$ values between $CaCO_3(s)$ and H_2O (I). *Clayton and Mayeda* [1984] assessed fractionation factors at 273 and 293 K and preferred the fit obtained at 273 K. It is the composition of L1 that sets the composition of G2; the L1 composition is calculated from those of A and M and the assumed water/rock ratio f. CM84 adjusted f to improve the fits to the data and obtained values of 0.57 at 273 K and 0.92 at 293 K; units are (moles of O in H_2O)/(moles of O in rock).

To calculate the composition of G2, one needs to know the fractionation factor $\Delta^{18}O_{cond}$ (= $\delta^{18}O$(H_2O condensate)-$\delta^{18}O$ (gas)) and φ, the fraction of the nebular water that condensed. CM84 used $\Delta^{18}O_{cond} = 11.4‰$, corresponding to a liquid condensate at a temperature of 273 K. The $\delta^{18}O$ of G2 is then given by

$$\delta^{18}O(G2) - \delta^{18}O(L1) = \Delta^{18}O_{cond}(1 - \varphi). \quad (2)$$

If φ was very small, $\delta^{18}O_{G2}$ is $11.4‰$ lower than L1; if all the nebular water condensed ($\varphi = 1$), the two $\delta^{18}O$ values are the same.

CM84 set φ equal to $(21/79)$ f, where the 21/79 ratio reflects their mass-balance calculations that 21% of nebular O formed as solid metal oxides and 79% was, prior to H_2O condensation, in the gas phase. Thus, for the water/rock ratios estimated by CM84, the value of φ is ~ 0.2. Calculating φ in this way requires the unstated assumption that the efficiency of accretion of condensed

TABLE 4. Compositions From the *Clayton and Mayeda* [1984] (CM84) Model and the Composition of the Gas After Formation of the Refractory Component S

Component	$\delta^{17}O$, ‰	$\delta^{18}O$, ‰	$\Delta^{17}O$, ‰
CM84 initial gas (G1) (at 273 K)	24.2	30.0	8.6
CM84 initial solids (S)	−41.07	−39.79	−20.4
CM84 anhydrous component (A)	−7.4	−4.2	5.2
CM84 gas (G2) after interaction with S	15.2	20.6	4.5
Calculation, gas after 93% vaporization of S	14.5	19.7	4.3

H_2O and of nebular solids to the CM parent planet was the same and also that within the parent body, there was no subsequent physical separation between these phases prior to the aqueous alteration of the nebular materials that formed the CM chondrites. Both of these assumptions are questionable.

It seems clear that both temperature and gravity cause H_2O to migrate from the interior of asteroids toward the exterior and that any H_2O that was gaseous when it reached the surface will have escaped. The choice of 273 K as the nebular condensation temperature for H_2O is grossly high, and it seems certain that H_2O could only condense as a solid phase, not as a liquid. Many estimates for the condensation temperature of H_2O (s) exist in the literature; for example, *Lewis* [1972] depicts condensation temperatures in the range 150–180 K for nebular pH_2 in the range 10^{-3}–10^{-6} atm. My calculations (Table 2) indicate that 50% of nebular H_2O (g) should condense at 164 K at $pH_2 = 10^{-5}$ atm. Because the absolute values of fractionation factors tend to increase with decreasing temperature, the value of 11.4‰ used by CM84 is probably incorrect, perhaps by a large factor.

As indicated by (2), the separation between L1 and G2 is controlled by both $\Delta^{18}O$ and φ, and thus one can obtain the values used by CM84 even if $\Delta^{18}O_{cond}$ is large by increasing φ. However, this is implausible, because it requires the condensation to have occurred within a narrow range of temperatures. At $pH_2 = 10^{-5}$ atm the range in nebular temperatures between 1% and 90% condensation is only 10 K, and it is therefore questionable whether φ can be treated as a free parameter. Of course, if most of the nebular H_2O condensed, the composition of the condensate is essentially the same as the gas, and this part of the model becomes irrelevant.

As was noted above, the major cosmochemical problems faced by the CM84 model are how to produce refractory oxides by condensation that have a different $\Delta^{17}O$ than the gas and how to produce component A from solids having composition S and a gas having a composition well above the TF line. I see no way out of the first conundrum. There are fine-grained, often somewhat porous inclusions that show no evidence of having ever been fully molten; most researchers infer that these formed by condensation [e.g., *MacPherson et al.*, 1988]. In the least altered carbonaceous chondrites such as CO3.0 Colony, *Wasson et al.* [2000b] showed that all the

major phases in one of these inclusions had $\Delta^{17}O$ less than −20‰. Even in the heavily altered CV3 Allende meteorite, *Clayton et al.* [1977] found spinel in a pink, fine-grained inclusion with $\Delta^{17}O$ of −16‰. If these inclusions formed by condensation, the gas had a $\Delta^{17}O$ value ~25‰ lower than the G2 $\Delta^{17}O$ of 4.5‰ (see Table 4).

The other cosmochemical conundrum arises because the surviving refractory inclusions that preserve composition S can only be formed by near-complete evaporation of the precursor solids having the same mean $\Delta^{17}O$ values. This evaporation puts essentially all of the major elements Mg and Si and most minor and trace elements into the vapor. A convenient measure of the required completeness is the fraction of chondritic O (O now present as chondritic solids) that was bound to the evaporated metals; my estimate is 93%.

If I assume a solar composition in the CM-chondrite region, before evaporation the fraction of O in the solids is 0.158 (this is smaller than the CM84 value of 0.21 because the O/Si ratio in solar matter was revised upward by *Anders and Grevesse* [1989] following publication of CM84). After evaporation of the nonrefractory solids, the fraction of O present as solids (all Ti is assigned to perovskite ($CaTiO_3$), all remaining Ca is assigned to gehlenite ($Ca_2Al_2SiO_7$), and finally, all the remaining Al is assigned to spinel ($MgAl_2O_4$)) is only 0.0110. As summarized in Table 4, if the initial gas composition was 30.0, 24.2‰, the evaporation event causes the gas composition to decrease to $\Delta^{17}O = 4.5$‰ (CM84) or 4.3‰ (my calculation after 93% of preexisting solids at S have evaporated). From this time onward it is impossible to produce component A with $\Delta^{17}O = -5.2$‰ by condensation of the vaporized metals, since these will obtain the $\Delta^{17}O$ of the gas.

As was noted above, CM84 avoided the evaporation-condensation problem by producing component A by O-exchange with solids having composition S, "perhaps" during the "heating event that produced chondrules." No further details are provided. Exchange has the potential to move materials from A to S, but (1) without evaporation there is no mechanism to form the refractory inclusions, and (2) as discussed below, the amount of O-isotope exchange that could have occurred during the brief (1- to 10-s) lifetimes of chondrule melts would have fallen short of the wholesale (>50% of O atoms) exchange required to go from −40, −41‰ to −7.4, −4.2‰.

It is almost certainly impossible to diffuse O into the interior of a static melt (at $T = T_{melt} \approx 1900$ K) during such a brief period. Measurements by *Canil and Muehlenbachs* [1990] yield an O-diffusion coefficient in a basaltic melt at 1900 K of 1.8×10^{-6} cm^2 s^{-1}; thus during 10 s the maximum diffusion distance estimated from $(D \times t)^{1/2}$ is 4.10^{-3} cm, or 40 μm, a layer too thin to have a major impact on the composition of the melt of large chondrules. Also, because the surface of the chondrule melt is cooling by radiation and evaporation [see, e.g., *Wasson*, 1996], if the ambient nebular temperature is <1800 K, the surficial layer will quickly form a solid surface (e.g., the outer shell in barred-olivine chondrules) in which O diffusion is still lower by several orders of magnitude.

Despite the cosmochemical problems of the complete CM84 model, there is important information to be gleaned by using it to model asteroidal water-rock interactions in carbonaceous chondrites. *Clayton and Mayeda* [1999] made a more detailed examination of the interplay between the O_{water}/O_{rock} ratio, the fraction of anhydrous silicates that reacted with the water, and the initial (nebular) isotopic composition of the water. For large sets of samples (e.g., mineral separates from CM Murchison) they carried out regression fits of arrays on $\delta^{17}O - \delta^{18}O$ diagrams, and from these they calculated O_{water}/O_{rock} based on inferred fraction of the initial rock that had reacted. However, the fraction reacted is also model dependent; it derives from an assumed O-isotopic composition of the mean anhydrous solids at the onset of aqueous alteration, and these have uncertainties of at least 2‰ in $\Delta^{17}O$. As an example of the uncertainty, *Clayton and Mayeda* [1999] inferred that the composition of anhydrous solids in CM chondrites was −4.2, −7.4‰ ($\Delta^{17}O = -5.2$‰), 3‰ higher in $\Delta^{17}O$ than the composition inferred for CR chondrites, −1.0, −2.8‰ ($\Delta^{17}O = -2.3$‰).

Clayton and Mayeda [1999] used this model to calculate the $\Delta^{17}O$ of the water that produced the aqueous alteration. For CI, CM, and CR chondrites they first calculated regression lines along which loci of nebula water must lie and assumed that the (near) intersection of these at a single point corresponded to nebular water; this yielded a $\Delta^{17}O$ of +0.9‰. Then, noting that this is in conflict with higher $\Delta^{17}O$ values for the H$_2$O inferred from studies of ordinary and R chondrites (application of this constraint clearly indicates that their goal is to create a global model), they conclude that the true $\Delta^{17}O$ value must be greater than 2.7‰. Finally, they return to the CM84 approach and calculate a value of 3.1‰, slightly lower than the original +4.5‰ value. Both these latter values are much less than the +7‰ value *Choi et al.* [1998b] estimated for the water in asteroidal parent of the LL chondrites.

6.2. Well-Mixed Gas-Exotic Solid Models

As was mentioned in section 1, *Wasson* [1988] argued that there is no general basis to expect that the mean O-isotopic composition of the solid fraction of ejecta from a single star would differ in a major way from that of the gaseous fraction. This statement needs modification. As was discussed above, huge variations in the $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios are formed in the different layers of type 2 supernovae; the $^{16}O/Mg$ and $^{16}O/Si$ ratios also vary by orders of magnitude among these layers. Although the O-isotopic composition of gaseous O and (after cooling of ejecta) the solid condensate from each layer will have the same composition, mixing of materials originating in different layers can yield average solids with compositions that differ from the coexisting gas.

Mixing times in interstellar clouds are too long to allow homogenization of regions having dimensions of >10^4 AU. The scale is set equal to the minimum separation between young stars in the densest clusters [*Zinnecker et al.*, 1993], the scale of the feeding zone of the solar nebula. It is therefore probable that exotic O-isotopic compositions were preserved in unevaporated solids, with the solids accreting to the nebula at each chondrite formation location/time having somewhat different compositions.

Wasson [1988] noted that the more oxidized portions of carbonaceous chondrites had compositions near (but with the exception of CI chondrites, slightly below) the TF line and (based on fragmentary evidence) inferred that oxidized materials in OC were also closer to the TF line than more refractory materials. He incorporated these views into a model that called for the nebular gas to mix over distances of several astronomical units and suggested that the well-mixed gas would have had a composition on or near the TF line. He inferred that the carriers of oxygen having $\Delta^{17}O$ values ≠O were different batches of presolar solids. Because the ordinary chondrites plot above the TF line, Wasson suggested that the OC materials with the highest $\Delta^{17}O$ values were the unevaporated refractory residues of the presolar materials accreting to the OC formation location.

The study of LL3.0 Semarkona magnetite showed this model to be untenable. These results, discussed in more detail in the next section, show that magnetite has $\Delta^{17}O$ values in the range 4–7‰, far higher than whole-rock values and those measured in Semarkona silicate samples, mainly chondrules. Petrographic evidence (such as veins that cross chondrule boundaries) indicates that this magnetite formed by the oxidation of metallic Fe in the parent body. The oxidant was inferred to be water that had condensed from the nebular gas. This parental gas clearly had a $\Delta^{17}O$ value far above the TF line; the value estimated by *Choi et al.* [1998b] was 7‰.

7. THE EVOLUTION OF NEBULAR OXYGEN

7.1. Imprinting the Nebular O-Isotopic Record in Chondrules

I will take it as given that the chondrules formed in the solar nebula and that they were heated to the melt-

ing point relatively quickly [e.g., *Wasson*, 1993; *Boss*, 1996; *Jones et al.*, 2000]. I will also accept the consensus view that all or most formed locally, i.e., at the same nebular location where agglomeration later occurred. In this case, the question is not where the chondrules formed, but how they obtained the isotopic composition we observe in them today.

Clayton and Mayeda [1984] and *Rowe et al.* [1994] suggested that the chondrule melts exchanged O-isotopes with the nebular gas during the brief period that they were molten. If the melt is static, this would require a diffusion coefficient 6×10^{-5} cm^2 s^{-1} to penetrate 0.25 mm, half way to the center of a 1-mm-diameter chondrule, within 10 s. This is higher than the value for a basaltic melt at 1900 K by a factor of ~40 [*Canil and Muehlenbachs*, 1990]. As was also indicated above, the surface of the chondrule should solidify rapidly if $T_{neb} \ll T_{melt}$, resulting in a drop in O-diffusion coefficients by several orders of magnitude.

The more common alternative view is that chondrule compositions largely reflect those of the precursor solids that were melted. In particular, the retention of Na, an element that diffuses more than an order of magnitude faster than O in a basaltic melt [*Lowry et al.*, 1982], and S, a major element that forms a separate gaseous phase and would explosively escape if heated above the vaporization temperature long enough for bubbles to nucleate, is interpreted to indicate that the high-temperature period was too short to allow Na to diffuse or S$_2$ to nucleate.

Another argument for concluding that the chondrule-forming high-temperature period must have been brief is that chondrules at their 50%-solidification temperatures are far above their bulk evaporation temperatures. According to *Wasson* [1996], typical 50%-solidification temperatures are ~1750 K, whereas from Table 2 we see that the equilibrium 50%-condensation (=50%-vaporization) temperature of the relatively refractory mineral forsterite in a canonical nebula with pH$_2$ = 10^{-5} atm is only ~1260 K, 500 K lower. If chondrule melts had existed for long periods and been able to mix by convection, they should have distilled away their most volatile constituents. Rare chondrules that could be distillation residues are known [*Grossman and Rubin*, 1986], but the fraction is tiny. As will be discussed in more detail below, it is clear that some evaporation has to occur during chondrule formation. Even if the skin of the chondrule crystallizes, it will continue to evaporate until the temperature drops below ~1200 K, and small particles that are enveloped in the chondrule-forming "plasma" will evaporate completely.

I will assume that the flash melting chondrule-formation scenario is correct, in which case the O-isotopic composition of chondrules preserves the mean composition of O in each batch of precursor grains. Precursor grains can be condensates or relicts from earlier melting events. Precursors that were condensates record the composition they obtained during condensation; the

Δ^{17}O value of each grain is the same as that of the gaseous reservoir from which it formed.

There appear to be three different cooling environments that could lead to the condensation of metal oxides: (1) the cooling of gaseous stellar ejecta before accretion to the solar nebula; (2) the cooling of materials evaporated during large-scale heating events in the solar nebula; and (3) the cooling of materials flash evaporated during chondrule-forming events. If the solar nebula never got hot enough to evaporate most infalling presolar solids, then intergroup or interclan differences in the O-isotopic compositions of chondrules must reflect the differences between batches of infalling presolar solids. If extensive large-scale evaporation occurred at all chondrite-forming nebular locations, then the chondrule O-isotopic differences between groups or clans must reflect differences in the composition of the nebular gas at these locations or times.

Because the fraction of small particles evaporated during chondrule formation is unknown, it is impossible to assess whether evaporation during flash-melting chondrule formation exerted a large influence on the final compositions of chondrules. As summarized by *Wasson* [1996], the fraction that was evaporated during flash-melting events from typical chondrules having diameter of 0.2–2 mm appears to have been small, but appreciably smaller particles in the hot "plasma" would have completely evaporated. One argument showing that the heat source was limited is the fact that a large fraction of chondrules experienced incomplete melting, as indicated by the high fraction of porphyritic chondrules [*Wasson*, 1993] and relict grains [*Jones*, 1996]. However, because we do not know how many flash-melting/evaporation events were, on average, experienced by each chondrule, and because we also do not know what fraction of the materials enveloped in chondrule-forming "plasmas" was small enough to evaporate, we cannot rule out that a large fraction of nebular material was evaporated during the course of the period of chondrule formation at each nebular location. Chondrule formation may have spanned a wide range of ambient nebular temperatures, and evaporation at low nebular temperatures (<500 K) provides a natural way to condense low-temperature silicates that are FeO-rich and possibly also hydrated.

7.2. Interpreting the O-Isotopic Record in Chondrules

The most extensive whole-chondrule data sets are for carbonaceous chondrites (CC) and ordinary chondrites (OC), and I will simplify this review by focusing my discussion on these data sets. I will also limit my consideration to data on chondrules from petrographic type 3 chondrites. The chondrules in chondrites of types 1 and 2 have been heavily affected by aqueous alteration, and the record in types ≥4 may have been affected by isotopic exchange resulting from thermal metamorphism.

The data can be approached in two ways: comparison (1) between the observed composition ranges in the two
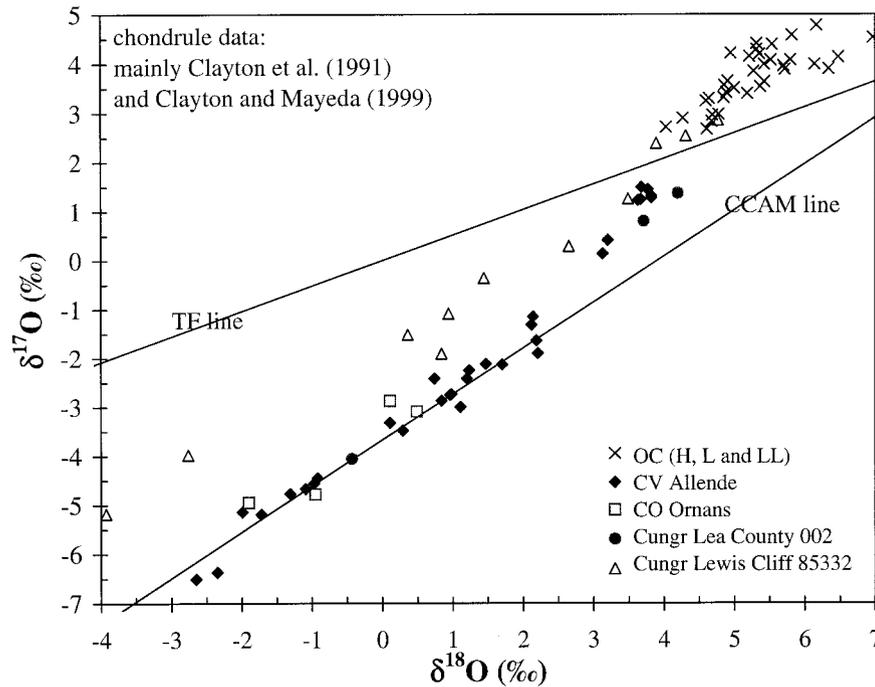
Figure 7. Bulk chondrule whole-rock data obtained by fluorination techniques in the Clayton laboratory for ordinary chondrites [*Clayton et al.*, 1991] and for carbonaceous chondrites (*Clayton and Mayeda* [1999] and other sources cited in the text) plotted on a $\delta^{17}O$-$\delta^{18}O$ diagram. Symbols identify different data sets. With the exception of three chondrules from LEW85332, all CC chondrule data plot below the terrestrial fractionation (TF) line, and all OC chondrule data plot above the TF line. As is discussed in the text, chondrules appear to record the composition of the precursor materials and thus probably the O-isotopic composition of the nebula at the time these precursor materials formed.

sets of chondrites; and (2) within chondrules from a single chondrite or a single chondrite group, to search for correlations between the O-isotopic composition and other compositional or petrographic parameters.

Chondrules separated from type 3 CC and OC and analyzed by fluorination techniques by Clayton and co-workers [*Clayton et al.*, 1991; *Clayton and Mayeda*, 1999; *Prinz et al.*, 1991; *Rubin et al.*, 1990; *Wasson et al.*, 2000a] are plotted in Figure 7. Additional data for individual chondrule minerals [e.g., *Choi et al.*, 1998b; *Greenwood et al.*, 2000] have been obtained by ion-probe analysis; with rare exceptions, these data are fully consistent with the whole-chondrule data. One interesting feature in Figure 7 is the trend through the data of Lewis Cliff 85332 (LEW85332), which are offset from the well-defined CV Allende trend. This seems to be an effect produced in the solar nebula, but alteration effects are pulling the compositions in opposite directions. Asteroidal aqueous alteration of Allende produced phyllosilicates that moved mean compositions toward high $\delta^{18}O$ values [*Young and Russell*, 1998; *Ash et al.*, 1999], and contamination of LEW85332 chondrules by terrestrial oxides produced by weathering in Antarctica pulls compositions toward lower $\delta^{18}O$ values. The magnitudes of these effects are not well determined, but they appear to be smaller than the 1–2‰ offset between the Allende chondrules and those from LEW85332.

The main observation to be gleaned from Figure 7 is that the CC and OC chondrules occupy very different parts of the diagram. On the basis of arguments given in the previous section, the most probable reason for this difference is that the nebular gas at the locations/times where the CC chondrules (and precursors) formed was different from that at the locations/times where the OC chondrules formed or that the compositional signatures are of precursor materials that were presolar relicts that differed because the infalling mixes of interstellar grains varied with time (or, less likely, nebular location at the same time).

Figure 8 gives details regarding the ordinary chondrite chondrules. The data as a whole show a positive trend with a slope of ~0.7. The chondrules separated from individual meteorites do not deviate significantly from the general trend independent of which group (H, L, or LL) they belong to.

Unfortunately, detailed compositional data are not available for most of these OC chondrules. There are several studies that show evidence of a relationship between CC chondrule composition and O-isotopic composition; that observed in Cungr 3.0–3.1 LEW85332 is shown in Figure 9a. *Wasson et al.* [2000a] showed that low-FeO and high-FeO (with the border at FeO/(FeO + MgO) = 8 mol %) chondrules exhibit very different siderophile-element abundance-ratio patterns, with low-
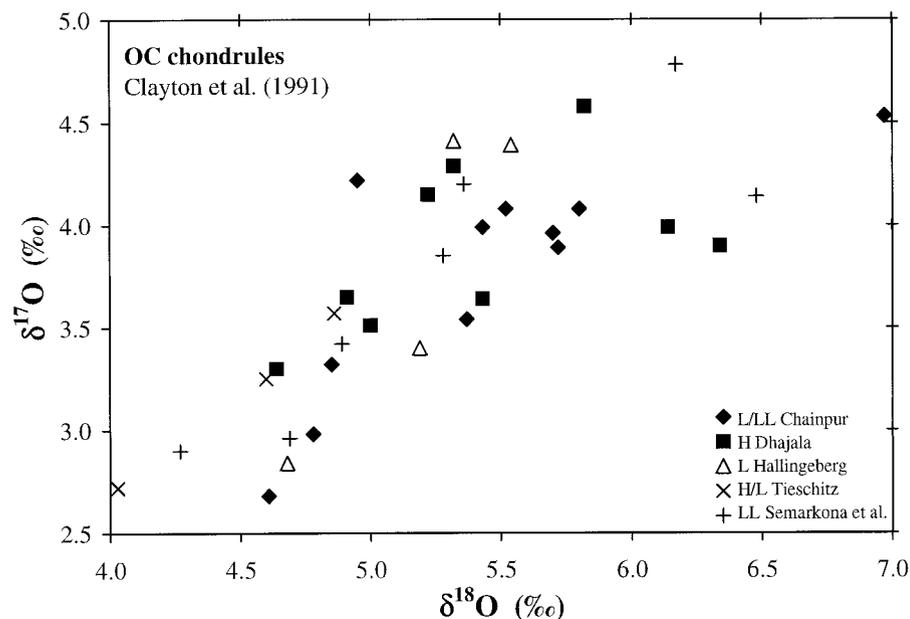
Figure 8. Chondrules separated from unequilibrated ordinary chondrites span a wide range in O-isotope compositions, independent of chondrite group assignments. Note, for example, that the ranges in H Dhajala (squares), L/LL Chainpur (diamonds), and LL chondrites (plus signs) are quite similar. Four LL chondrules are from Semarkona, two are from Krymka, and one is from Bishunpur. Data are from *Clayton et al.* [1991].

FeO chondrules having largely unfractionated patterns. The difference in these two classes also showed up in the O-isotopic compositions, with low-FeO chondrules having lower $\Delta^{17}O$ values than high-FeO chondrules (Figure 9a). There is a monotonic increase in $\Delta^{17}O$ with increasing FeO/(FeO + MgO).

A similar pattern is observed in olivine grains separated from CI chondrites by *Leshin et al.* [1997]; these are believed to be the remnants of chondrules that experienced extensive alteration. As shown in Figure 9b, these also show a trend of $\Delta^{17}O$ increasing with the FeO/(FeO + MgO) ratio of the olivine.

In the next section I discuss high $\Delta^{17}O$ values associated with the formation of oxidized phases (magnetite, fayalite) during asteroidal aqueous alteration processes. During metamorphism, such phases could exchange Fe, Mg, and O with more reduced phases, but because LEW85332 shows no evidence of such exchange (it is type 3.0–3.1), there is no reason to doubt that the trend among LEW85332 chondrules reflects nebular processes. If we accept the common cosmochemical view that the mean FeO contents of nebular silicates increased as time passed and mean nebular temperatures decreased, then the correlation of $\Delta^{17}O$ with FeO/(FeO + MgO) may indicate that the $\Delta^{17}O$ of the nebular gas was increasing with the passage of time.

An interesting question essentially not dealt with in published papers is why refractory inclusions, with $\Delta^{17}O \leq -20‰$, are so far removed in composition from the most ^{16}O-rich chondrules (e.g., $-6.5‰$ in Figure 9b). Stimulated by this and also by the remarkably narrow range in initial $^{26}Al/^{27}Al$ ratios (with $\pm 10\%$ of $4.5 \times$

10^{-5}) inferred in these objects, I [*Wasson*, 1999] suggested (in an abstract) that they formed at a distant place or time, perhaps in a neighboring stellar system. Young stars have strong polar outflows that could both form the refractory inclusions and eject them with velocities exceeding the escape velocity.

7.3. Evidence for an Upward Drift in $\Delta^{17}O$ Recorded in Chondrite Alteration Products

As was discussed above, most (and perhaps all) chondritic magnetite seems to have formed by aqueous alteration of metal and FeS in asteroidal settings. Fayalite (FeO/(FeO + MgO) > 0.9) also appears to have formed by similar processes.

Magnetite studies in unequilibrated OC and CC have produced data indicating high $\Delta^{17}O$ in H_2O, the presumed oxidant that converted metal to magnetite. In the previous section I noted that $\Delta^{17}O$ correlated with FeO/(FeO + MgO) in sets of separated chondrules and that one possible interpretation is that chondrules formed during an extended period during which the mean nebular temperature decreased and the $\Delta^{17}O$ of the nebular gas increased. Recondensation of dust flash evaporated during chondrule formation led to a gradual increase in FeO/(FeO + MgO) in the precursor materials.

This idea that $\Delta^{17}O$ increased with time finds support in the discovery by *Choi et al.* [1998b] that (with one exception) $\Delta^{17}O$ values in magnetite in LL3.0 Semarkona and LL3.5 Ngawi ranged from 4 to 7‰. These values are far higher than $\Delta^{17}O$ in the coexisting silicates, which (with one exception) are $\leq 2‰$. The data are shown in Figure 10.

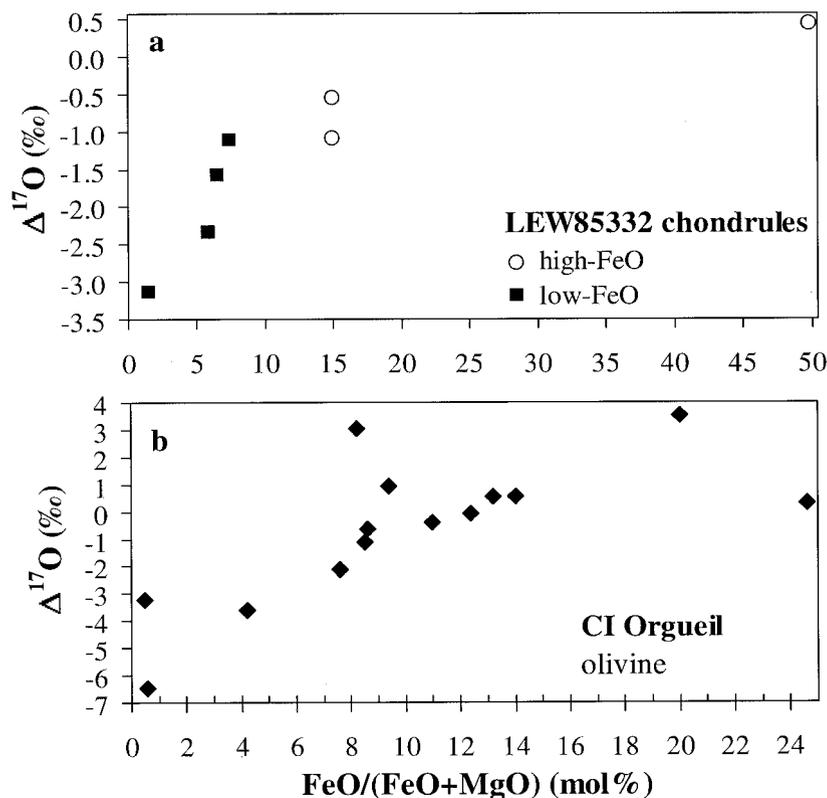**Figure 9.** Chondrules separated from different chondrite groups show similar trends: $\Delta^{17}O$ increases with increasing FeO/(FeO + MgO) in the mafic minerals (generally olivine). (a) Chondrules from type 3.0–3.1 ungrouped C Lewis Cliff 85332 (Reprinted from *Wasson et al*. [2000a] with permission from Elsevier Science). (b) Olivine grains, probably from chondrules from CI1 Orgueil [*Leshin et al*., 1997]. Simple arguments suggest that the FeO/(FeO + MgO) of nebular silicates increased and the mean temperature decreased as time passed. In this case, the observed trend indicates that the $\Delta^{17}O$ of the nebular gas was increasing with the passage of time.

As was discussed earlier in connection with (1), all O in magnetite is from the oxidant, which in this case appears to be H_2O incorporated into the LL parent body. At temperatures ≥ 270 K this water would have been able to migrate through the body. *Krot et al.* [1997] discuss petrographic observations suggesting that H_2O moving through millimeter-size channels reacted with adjacent metal to form magnetite. The large range in $\delta^{18}O$ in the LL magnetite implies that the H_2O reservoir experienced isotopic fractionation during the period when the magnetite formed and thus that the amount of H_2O was limited.

The slope of the LL magnetite array is 0.70. That this is ≠0.52 implies mixing of reservoirs. The scenario suggested by *Choi et al.* [1998b] is that the $\Delta^{17}O$ of the H_2O decreased as a result of minor amounts of exchange with the silicates during the period when magnetite was forming. It then follows that the initial $\Delta^{17}O$ of the H_2O was ≥ 7‰ and that the magnetite with the highest $\Delta^{17}O$ (and $\delta^{18}O$) was the first to form. As is shown in Figure 4, magnetite has a much lower $\delta^{18}O$ than does the H_2O from which it forms, resulting in an increase in $\delta^{18}O$ of the residual H_2O. If only magnetite were forming, the

$\delta^{18}O$ of the H_2O (and the magnetite it produced) would gradually increase. For this reason, *Choi et al.* [1998b] hypothesized that phyllosilicates were also forming in sufficient quantities to cause $\delta^{18}O$ in the residual H_2O to decrease with time. The phyllosilicate fractionation factor [*Savin and Lee*, 1988] is not shown in Figure 4; it lies between olivine and quartz but closer to olivine. Thus, at a temperature of 300 K, the O-isotopic fractionations of phyllosilicates and magnetite from H_2O are similar in magnitude but opposite in sign.

This study thus provides strong evidence that the H_2O in the LL parent body had $\Delta^{17}O \geq 7$‰. The highest $\Delta^{17}O$ values that have been reported in silicates or silica from the UOC are 2.7–3.0‰ in silica-rich clasts from LL Parnallee [*Bridges et al*., 1995]. The highest $\Delta^{17}O$ values reported in UOC chondrules are 1.5–1.65‰ in H Dhajala, L Hallingeberg, L/LL Chainpur, and LL Krymka [*Clayton et al*., 1991]. Thus either the H_2O was from another part of the solar system or recycling during chondrule formation was not able to bring chondrule compositions into isotopic equilibrium with the ambient gas. I will show in the next section that although the
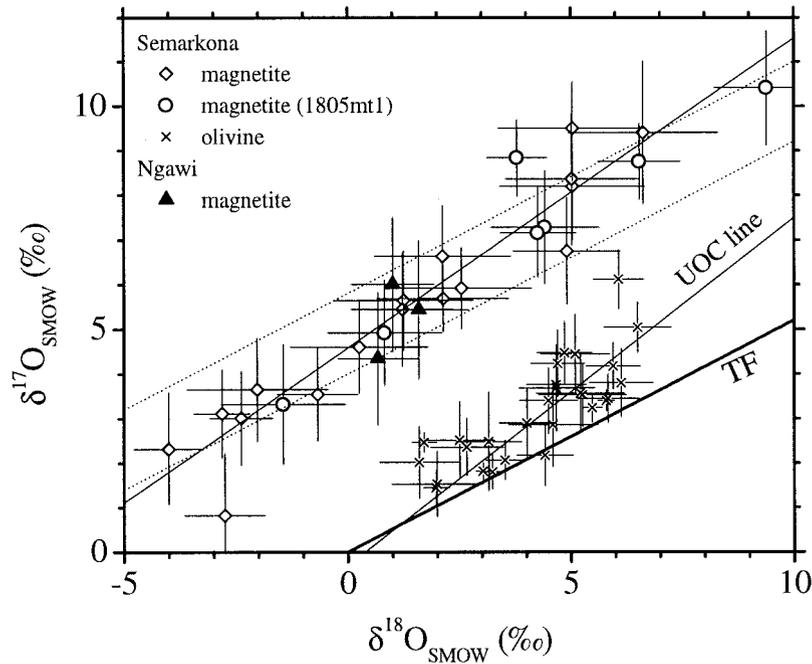
Figure 10. In this $\delta^{17}O$ versus $\delta^{18}O$ diagram from *Choi et al.* [1998b] we see that magnetite $\Delta^{17}O$ values determined by ion probe in unequilibrated LL chondrites Semarkona and Ngawi are about 4‰ higher than those in the olivine of coexisting Semarkona chondrules. A trend line through the magnetite has a slope of ~0.7, similar to that defined on the basis of fluorination studies of whole-rock samples of UOC. The ion-probe data on Semarkona chondrules also form a trend with slope >0.5 that is adequately fitted by the UOC line. The dotted lines that enclose most of the magnetite points correspond to $\Delta^{17}O$ values of 4 and 6‰. Reprinted with permission from *Nature*.

evidence is not definitive, there is good reason to believe that the H_2O was of local origin.

7.4. The Correlation Between $\Delta^{17}O$ and FeO/(FeO + MgO) in Bulk Ordinary-Chondrite Samples

As was noted earlier in the discussion of Figure 3, there is an obvious correlation between $\Delta^{17}O$ and the FeO/(FeO + MgO) ratio in bulk samples of equilibrated ordinary chondrites; Figure 11 shows the trend in more detail. The O-isotope data are from *Clayton et al.* [1991], and the FeO/(FeO + MgO) ratios are olivine compositions of *Rubin* [1990]. This correlation may extend to the unequilibrated members of these groups, but there is too much scatter in the available FeO/(FeO + MgO) data to determine whether this is true.

The OC appear to be an incompletely sampled continuum, with the H, L, and LL groups having been produced by the disruption of three asteroids, but it seems probable that there are (largely unsampled by the Earth) OC asteroids whose constituent materials would fill out the compositional continuum. Also, a few OC having compositions intermediate between H and L chondrites are designated H/L chondrites. Because the compositional gap between H and L is so large, some or all of these might originate on a parent asteroid that is neither H nor L.

Another set of chondrites is designated L/LL, but the taxonomic situation is different. *Kallemeyn et al.* [1989] and *Rubin* [1990] carried out detailed petrographic and bulk-compositional studies but were unable to find a hiatus between the L and LL groups. They therefore chose a boundary band that maximized the differences in the U, Th-He ages between L and LL. The meteorites designated L/LL have compositions within the boundary band, but most or all may be from the L or LL parent bodies.

Two competing hypotheses regarding the process that produced the positive H-L-LL trend in Figure 11 are (1) that it originated in the nebula including the possibility that the fraction of hydrated minerals increased through the sequence, and (2) that it reflects parent-body alteration by ices [e.g., *McSween and Labotka*, 1993], presumably from comets. If the trend is of nebular derivation, one would expect it to also show up in representative sets of UOC chondrules. However, as shown in Figure 7, chondrules from individual meteorites show large ranges in $\delta^{18}O$ and $\Delta^{17}O$, and in the published studies, no attempt was made to ensure that these sets of chondrules were representative of the host chondrites. On the basis of these limited data it is not possible to determine whether mean chondrule compositions follow the trend toward higher $\Delta^{17}O$ through the H-L-LL sequence.
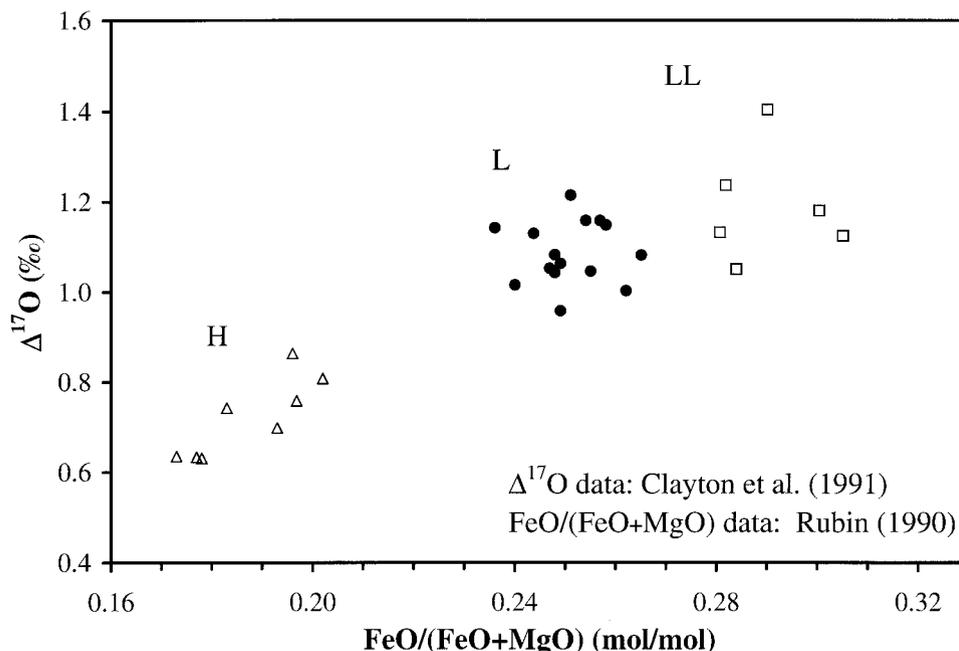
Figure 11. This enlargement of a portion of Figure 3 shows that in bulk samples of equilibrated ordinary chondrites, $\Delta^{17}O$ increases with increasing FeO/(FeO + MgO). Because there are well-resolved differences in elemental ratios among these three groups (e.g., in Fe/Mg or Au/Mg ratio), the trend cannot be explained by asteroidal alteration of a common starting material. A possible nebular model to account for this trend involves the sequential formation of H, L, and LL chondrites in the same part (e.g., neighboring regions) of the nebula. O-isotope data are from *Clayton et al.* [1991], and olivine composition data are from *Rubin* [1990].

If the only resolvable difference between the OC were in terms of O isotopes, then the hypothesis that the three parent bodies happened to accrete different amounts of a high $\Delta^{17}O$ oxidant would be appealingly simple. However, there are several compositional and textural properties that change systematically through the H-L-LL sequence. Among those mentioned by *Kallemeyn et al.* [1989] are Mg (or Si) normalized siderophile abundances, volatile/refractory interelement ratios among siderophiles (e.g., Au/Ir or Ge/Ir), and the mean sizes of chondrules. Given these systematic compositional changes of unquestioned nebular origin, it is not implausible that the systematic change in O-isotope composition is also of nebular derivation. Because the cometary-ice model offers no mechanism to produce an increase in H_2O from H to L to LL that parallels the metal-silicate fractionation, the observed trend in Figure 11 would be a fortuitous result. Also, if the oxidant in the OC parent bodies was heterogeneously distributed cometary ice, one would expect to see more scatter in $\Delta^{17}O$ and FeO/(FeO + MgO) within the individual groups.

Thus the weight of the evidence favors the conclusion that the $\Delta^{17}O$-FeO/(FeO + MgO) trend through the OC is best attributed to nebular processes including recycling during chondrule formation. There is no reason to believe that the nebular temperatures fell to 160 K as required to condense H_2O ice, which is slightly lower than the current equilibrium temperature of a spinning blackbody at 2.5 AU. Because when agglomeration oc-

curred, the nebula was probably still accreting and thus not fully transparent, one would expect temperatures higher than those present today. Thus it seems more likely that the water was incorporated as hydrous silicates and that the abundance of these increased through the H-L-LL sequence. This seems possible if, as suggested in other studies [e.g., *Wasson*, 1972], the H chondrites were the first to agglomerate and (at somewhat lower temperatures) the LL chondrites were last.

7.5. A Simple (but Speculative) Scenario: An Upward Drift of $\Delta^{17}O$ in the Nebular Gas

There is some evidence that the different groups of chondrites formed at different times. The evidence is based on observed variations in the abundance of isotopes such as ^{53}Cr or ^{26}Mg formed by the decay of extinct radionuclides and on highly precise formation ages based on the U, Th-Pb system. The problem is that the continuing accretion of materials to the solar nebula discussed in this paper brings with it the potential that the isotopic compositions of the chronometric elements (e.g., Al or Mn) may have had different isotopic abundances in the different parcels of materials accreting to the nebula.

In particular, *Lugmair and Shukolyukov* [1998] have shown that the initial $^{53}Mn/^{55}Mn$ ratio was different at different chondrite formation locations. They even infer that the initial ratio varied monotonically with distance from the Sun.

Isotopic variations are also found in the nonradiogenic isotopes. Variations of the $^{54}Cr/^{52}Cr$ in carbonaceous chondrites have been known for some time [*Rotaru et al.*, 1992; *Podosek et al.*, 1997], and variations in $^{54}Cr/^{52}Cr$ and $^{53}Cr/^{52}Cr$ ratios in LL3.0 Semarkona fractions were recently reported by *Dougherty et al.* [1999].

As was discussed above, in each of the well-studied chondrite groups there is evidence that can be interpreted as indicating that during the period that chondritic materials were forming in the solar nebula, the continuing accretion of interstellar matter to the nebula was causing the mean $\Delta^{17}O$ of the gas to increase monotonically. Although much more evidence must be assembled in order to confirm this interpretation, it is nonetheless interesting to examine some of the implications of this scenario.

The scenario would need to be relatively complex. Consider, for example, what would be required to produce the type 3.0–3.1 chondrule set present in the carbonaceous chondrite LEW85332 (Figure 8a). When the first generation of chondrules formed, the precursor grains were FeO-poor, presumably because they formed at moderately high (>600 K) nebular temperatures when most Fe was present as metal or FeS. Perhaps the simplest model is that the $\Delta^{17}O$ of these precursor grains reflects that of the nebular gas when they formed. In that case, Figure 8a shows that the $\Delta^{17}O$ of the gas was −3.2‰ at that time. Following the same simple model, the nebular gas was +0.5‰ when the most oxidized chondrule formed. If we assume that the gas changed only as a result of dilution by accreting matter, and that there was no loss of the original gas, then we can estimate the fraction of additional gas required. For example, if we assume that the accreting gas had $\Delta^{17}O$ of 10‰, then to change the $\Delta^{17}O$ of the gas by 3.7‰ would require the accretion of a mass of ~40% as large as that initially present. This seems implausibly high and suggests that this model requires a more extreme (perhaps $\Delta^{17}O > 100‰$) diluent. As was discussed in section 5, this is not out of the question. However, it does not seem worthwhile to try to develop more detailed models given the limited set of constraints that currently exist.

In any case, the "quantized" distribution of chondrite groups and clans in compositional space (Figures 1–3) seems to indicate either (1) that the meteorites falling to the Earth represent only a tiny fraction of the materials originally produced, or (2) that chondrites were able to form only during a small fraction of nebular history and that during most of nebular history the level of turbulence was too high to permit agglomeration. Because the mix of infalling materials was changing, during each of the agglomeration periods the nebula had a somewhat different composition. Thus the old cosmochemical assumption that the composition of the nebula was "solar" does not hold in a strict sense.

8. SUMMARY

The isotopic composition of oxygen shows large non-mass-dependent effects in the components of the most primitive chondritic meteorites. Almost certainly, these reservoirs reflect differences in the astrophysical sources of the O isotopes. Although isotopic differences are also observed in heavier elements, the effects are much smaller and thus more difficult to resolve. For this reason, O-isotopic studies currently provide the most important constraints on the nature of these astrophysical sources.

There are resolvable differences in O-isotopic composition both between groups (or clans) of chondrites and among the components separated from an individual chondrite. These whole-rock intergroup differences demonstrate that two or more O-isotope reservoirs were present at the formation locations of each of the chondrite groups and that the relative contributions from these reservoirs varied from location to location. As used here, the term location can refer to different distances from the Sun or to different times or to both.

As data from individual chondrite components or phases become available, there is increasing evidence that $\Delta^{17}O$ tends to be higher in the most oxidized chondritic components. For example, in chondrites separated from the type 3.0–3.1 grouped carbonaceous chondrite LEW85332, $\Delta^{17}O$ increases by 3.5‰ as the FeO/(FeO + MgO) ratio increases from 2 to 50 mol‰ (Figure 8a). The consensus view is that chondrules in highly unequilibrated chondrites that have avoided appreciable aqueous alteration preserve the compositions of their precursor solids. As was discussed in some detail above, high-FeO solids reflect formation at low (<600 K) nebular temperatures; low-FeO solids formed at high temperatures. Thus, if these solids were (at least partially) able to track the composition of the nebular gas, $\Delta^{17}O$ of the gas was not constant but evolved upward. As was also discussed above, if the nebula did not get hot enough to evaporate most interstellar solids, then the observations are also consistent with initial differences between solids and gas and a gradual evolution of chondrule compositions as a result of recycling associated with flash evaporation during chondrule formation.

There is also evidence that the H_2O incorporated into the chondritic parent bodies (and by now, aqueous alteration effects have been recognized in most chondrite groups) had $\Delta^{17}O$ values higher than those in the (chondrite) silicates. The $\Delta^{17}O$ of this H_2O is preserved in magnetite (Fe_3O_4) which, when formed from metal or FeS, obtains all of its O atoms from the oxidant (probably H_2O). In the LL chondrites, magnetite $\Delta^{17}O$ values are about 4‰ higher than those in chondrule mafic silicates. Although this H_2O could be cometary (and thus have $\Delta^{17}O$ different from that of the ambient gas at the time the chondrites agglomerated), the weight of the evidence implies that the H_2O is of local derivation, probably condensed from the nebula as hydrated sili-

cates. Thus the magnetite record supports and amplifies the evidence that at the time of agglomeration of chondrites, the $\Delta^{17}O$ of nebular H_2O (g) was significantly higher than that recorded in most chondrules.

There is also evidence that H_2O accreted at the various chondrite formations locations differed. The $\Delta^{17}O$ of magnetite in ordinary chondrites seems to have been ~7‰, that at the CV formation location seems to have been ~−1‰, and that at the CI formation location seems to have been ~1‰.

This leads to a simple interpretation that the $\Delta^{17}O$ of nebular materials changed with time. There is some evidence that carbonaceous chondrites formed earlier than ordinary chondrites, suggesting the simple (and oversimplified) model that the $\Delta^{17}O$ of nebular materials drifted up in time. The timescale involved (~1 Ma) would make this idea testable by dating based on short-lived radionuclides, but there is increasing evidence that the key isotopic ratios (e.g., $^{26}Al/^{27}Al$ or $^{53}Mn/^{55}Mn$) may not have been the same in all batches of interstellar materials falling into the solar nebula [e.g., *Nichols et al.*, 1999].

Independent of models, the O-isotopic data seem most consistent with the view that the placental interstellar cloud that provided materials to the accreting solar nebula was not well stirred. As a result, each batch of infalling matter differed in composition. The oxygen isotopes provide the strongest evidence for this source heterogeneity, but support is now accumulating in the form of isotopic anomalies in minor and trace elements.

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