Stable Isotope Variations in Extraterrestrial Materials

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Introduction

The materials of the planets and the small bodies of the solar system contain a rich record of isotope variations in the light stable elements. As in isotope geochemistry, this record reflects physical and chemical processes involving isotopic mixing among different reservoirs as well as fractionations arising in chemical reactions. The processes that influence the isotopic records of extraterrestrial materials range widely in environmental conditions from very high-energy events such as formation of refractory inclusions and chondrules by evaporation, condensation and melting in the solar nebula to lower temperature fluid-rock interactions in asteroids and planets.

In extraterrestrial stable isotope cosmochemistry, however, the bounds are expanded into issues that are generally not considered in terrestrial isotope geochemistry. For example, in the terrestrial sphere one is not concerned with absolute isotope ratios but rather with differences (usually relatively small) between reservoirs or mineral pairs; the existence of an initially homogeneous terrestrial reservoir is assumed and the actual isotope compositions of the bulk earth do not need to be known in order to exploit the differences in stable isotope compositions that have been generated subsequently by various geochemical processes. The reason is of course that the formation and early thermal evolution of the earth has acted as a highly effective grand homogenizing event as far as the stable isotopes are concerned. This assumption of homogenization cannot be made for extraterrestrial samples. In fact, the stable isotopes preserve some of the most dramatic evidence for the incomplete nature of the mixing of distinct presolar materials during formation of the solar system. Such ‘isotopic anomalies’ are present in the isotopic distributions of H, C, N, and especially, O on all spatial scales – from microscopic zoning in certain meteoritic minerals to the bulk compositions of asteroids and planets. Thus, some of the isotopic heterogeneities of ‘primitive’ solar system materials represent vestiges of primordial differences that could not be fully erased during the processing of presolar materials. In other cases, isotopic heterogeneities reflect the preservation of unique clues to processes occurring during formation of the solar system and planetary accretion, including early ‘geologic activity’ on planetesimals and even pre-biotic chemistry. Deciphering whether an isotopic signature is primordial
or has been modified or even generated by solar system processes is often possible, but is sometimes fraught with ambiguity.

The most extreme example of isotopic anomalies is provided by the laboratory analyses of individual preserved presolar dust grains extracted from primitive meteorites (ANDERS and ZINNER, 1993). These micron or smaller grains of SiC, graphite, and (less commonly analyzed) refractory oxides formed in the outflows of evolved stars and their isotopic compositions of C, N, O and other major and even trace elements quantitatively reflect the unique nucleosynthetic environment of that particular star, which may differ from average solar system compositions by one or more orders of magnitude. That such materials could have survived the journey from star, through the interstellar medium, the solar accretion disk and residence in the asteroidal parent bodies of meteorites, and finally to terrestrial laboratories is one of the most remarkable discoveries in all of twentieth century astronomy. The isotopic compositions of these particles have great importance for constraining models of stellar evolution and nuclear astrophysics, but because these materials are so rare and are distinctive by virtue of their lack of interaction with average solar materials, their study gives little indication of the nature of the most important processes that transformed primordial materials into the stuff that built the planets. Hence the subject of isotopic variations in presolar grains is beyond the scope of this chapter, and the reader is directed to Zinner (1998), Ott (1998), and Hoppe and Zinner (2000) for excellent reviews of this rapidly evolving subject.

This chapter concentrates on the isotopic records of H and O, with some additional discussion of C and N (ie., CHON), in materials that formed within the solar system (see PILLINGER, 1984 for a review of the earliest history of this subject). As alluded to above, even though these materials formed ‘locally’, their isotopic records may preserve, with varying degrees of fidelity, memories of primordial heterogeneities that were established in presolar matter from various astrophysical sources. With the possible exception of oxygen, one type isotopic memory that we do not discuss are those associated with demonstrably nucleosynthetic processes (e.g., in n-rich isotopes of Ca, Ti, Cr, etc.) (see, e.g., BEGEMANN, 1980; IRELAND, 1990; LEE, 1979) or with ‘anomalies’ due to decay of short-lived radioisotopes (see PODOSEK and NICHOLS, 1997; WASSERBURG and PAPANASTASSIOU, 1982). We also choose to focus on laboratory analyses as these
measurement methods are most similar to what isotope geochemists are familiar with, although the fine-grained nature and limited supply of some types of extraterrestrial samples has stimulated new instrumental developments. Some of these methods, e.g. stable isotope analysis by ion microprobe, have been increasingly finding application in the terrestrial sphere. We begin by considering the general behavior of these isotope systems from an astrophysical point of view.

**Isotope cosmochemistry of the light stable isotopes**

The volatile elements H, C, N, and O are incompletely condensed in meteorites and planetary bodies, and thus their abundances are fractionated throughout the solar system (see discussion in ANDERS and GREVESSE, 1989). It is therefore not unreasonable to expect that the isotopic compositions of these elements may also be variable on a solar-system-wide scale. Large isotopic variations are known on planetary scales for H and N, and more subtle, but nevertheless very significant variations occur in C and O as well. These variations reflect heterogeneities inherited from presolar materials or established during planetary accretion, as well as those developed by specific planetary processes (e.g., hydrodynamic escape of an early atmosphere). In any discussion of extraterrestrial stable isotopes it is important, and sobering, to note that the average (or solar) isotopic composition is not necessarily well determined for any of these elements, where by ‘well determined’ we mean something close to the levels of precision that isotope geochemists tend to consider. Here we briefly summarize the main astrophysical sources of each isotope system, current estimates of their solar values, and the ranges encountered in both remote and in situ observations of various solar system objects.

**Hydrogen** The stable isotopes of hydrogen, \(^1\)H and \(^2\)H (Deuterium), are truly primordial, having been essentially completely produced in the big bang (BURBIDGE et al., 1957; EPSTEIN et al., 1976). They are the only isotopes considered here that lack the potential for specific stellar input into presolar materials. That is not to imply that there do not exist significant presolar isotope variations in D/H. On the contrary, because of the very low temperatures in molecular clouds, and the large differences in vibrational frequency levels between deuterated and protonated molecules, huge mass fractionations occur in condensed phases (e.g., organic ices) in these environments. As we shall see, a
memory of these presolar D/H enrichments is preserved in organic phases of chondritic meteorites, in interplanetary dust particles (IDPs), and in cometary volatiles and, possibly, even in water from chondrites (ROBERT et al., 2000).

It has long been known that the terrestrial D/H ratio of $\approx 1.5 \times 10^{-4}$ (or 150 ppm) is highly enriched relative to cosmic values (see review by (GEISS and REEVES, 1981)). The original solar system D/H value cannot be determined by direct observations of the Sun because D was completely burned by the convecting proto-Sun as it contracted toward an interior density where stable H fusion was achieved (the main sequence). Estimates of D/H in protosolar matter are instead based on $^{3}\text{He}/^{4}\text{He}$ abundances in the solar wind and astronomical observations of galactic hydrogen (GEISS and REEVES, 1981). Within relatively large uncertainties ($\approx 25\%$), the average protosolar D/H ratio is calculated to have been $\approx 20$ ppm (GEISS and GLOECKLER, 1998), leading to the conclusion that Earth’s oceans are enriched by a factor of about 8 in D/H relative to cosmic values.

With the exception of the gaseous giants Jupiter and Saturn, variable enrichments of D/H relative to the protosolar reservoir is a general characteristic of the planets, although the mechanisms responsible for this fractionation are not known definitively and may be different in each case (see YUNG and DISSLY, 1992 for a review). The terrestrial planets exhibit the highest D/H values: spacecraft and ground-based observations of the atmospheres of Venus and Mars show D/H ratios of $\approx 2 \times 10^{-2}$ and $\approx 8 \times 10^{-4}$, respectively, probably reflecting the loss of primordial hydrogen by Jeans escape or similar mass-fractionating processes (YUNG and DISSLY, 1992 and references therein). These values are much higher, by factors of 100 and 5, respectively, than the terrestrial D/H which is thought to have not been much affected by atmospheric loss of H over geologic time (ROBERT et al., 2000). The D/H values on Mars may be considered to be known in much greater detail than remote observations permit owing to laboratory analyses of the SNC meteorites, which are igneous rocks that are highly likely to have been derived from Mars. These analyses offer insights into planetary process that may have affected D/H ratios in different martian reservoirs (atmosphere, crust, mantle) and have important implications for understanding the sources and evolutionary history of water on the planet (e.g., FARQUHAR and THIEMENS, 2000; LESHIN, 2000).
Spectroscopic observations of Jupiter and Saturn made with the Infrared Space Observatory are consistent with other estimates of protosolar D/H (see ROBERT et al., 2000 and references therein), as is the D/H value determined by the Galileo atmospheric entry probe mass spectrometer \([26±7 \text{ ppm}; \text{Mahaffy, 1998 #1084}].\) This result is expected as the jovian planets are thought to have formed by quantitative capture of gas from the solar nebula. On the other hand, the outer solar system planets Uranus and Neptune appear to be significantly enriched in D/H by factors of \(~3\) compared to the protosolar value (FEUCHTGRUBER et al., 1999). This enrichment is interpreted to reflect the mixing of material from the icy cores of these planets, which constitutes a significant fraction of their mass (as opposed to the jovian case where the planetary mass is dominated by the gaseous envelope). The ice is thought to have been enriched in D by isotope exchange reactions at low temperature in the solar nebula (BEZARD et al., 1999).

Much larger D/H enrichments are observed in comets. The hydrogen isotopic composition of water has been determined with about \(10 – 30\%\) precision in 3 comets: P/Halley (EBERHARDT et al., 1995), Hyakutake (BOCKELÉE-MORVAN et al., 1998), and Hale-Bopp (MEIER et al., 1998b). All 3 have \(\text{D/H} \sim 3\times10^{-4}\) or \(\delta D \approx 1000 \text{‰}\). Measurements of DCN/HCN in Hale-Bopp (MEIER et al., 1998a) suggest that organic species might be more highly enriched in deuterium by as much as an order of magnitude, but it is not yet known how representative this single result might be. The D/H value for methane in the atmosphere of Titan, Saturn’s largest satellite, is close to the terrestrial value (DE BERGH et al., 1988), suggesting that a cometary component to Titan’s atmosphere is present but is of limited abundance (OWEN, 2000).

**Carbon** Carbon has 2 stable isotopes, \(^{12}\text{C}\) and \(^{13}\text{C}\), which have distinct nucleosynthetic origins. The former, abundant, isotope is produced during He-burning by the triple-alpha reaction \((3 \, ^4\text{He} \rightarrow ^{12}\text{C} + \gamma)\) whereas \(^{13}\text{C}\) requires seed nuclei and hence was not initially present in the first generation of stars. As further generations of stars process interstellar materials in their nuclear furnaces, the relative abundances of such secondary isotopes increase (e.g., BRILEY et al., 1997; BUSSO et al., 1999). This chemical evolution of the galaxy resulted in a \(^{12}\text{C}/^{13}\text{C}\) ratio of \(~90\) in the molecular cloud fragment from which the solar system formed.
Little precise information is available regarding the carbon isotopic composition in major planetary reservoirs in the solar system, or even in the Sun. Determination of isotopic abundances from photospheric observations is difficult; a high resolution study of CO molecular lines yields $^{12}\text{C}/^{13}\text{C} = 84 \pm 5$ (HARRIS et al., 1987). Lacking a precise and meaningful reference value for average solar system, by tradition carbon isotope ratios in extraterrestrial materials are defined relative to the Pee Dee Belemnite with $^{13}\text{C}/^{12}\text{C} = 0.011237$ (CRAIG, 1957).

**Nitrogen** The abundances of the two stable isotopes of nitrogen, $^{14}\text{N}$ and $^{15}\text{N}$, are modified by hydrogen burning in various types of stars during their life-cycles. Both isotopes can also be produced by He-burning, but $^{15}\text{N}$ is additionally produced by explosive H-burning in type II supernovae. Thus, with various distinct stellar sources, it is perhaps not surprising that N exhibits very large isotope heterogeneities, reaching more than 3 orders of magnitude in the $^{15}\text{N}/^{14}\text{N}$ ratio of circumstellar SiC grains wherein N is a major impurity (ZINNER, 1998). In addition to nucleosynthetic effects (of which the SiC grains are an extreme example), the $^{15}\text{N}/^{14}\text{N}$ relative abundances can be affected by mass fractionation at low-T in interstellar clouds and by planetary atmospheric processes in much the same manner as hydrogen isotopes. As pointed out by Kerridge in a recent review (1995), the result of these various effects is that nitrogen isotopic records among different solar system reservoirs are quite variable and it is not possible to precisely define a representative solar system mean initial value. Consequently, the $\delta^{15}\text{N}$ scale is referenced to the terrestrial atmosphere, $^{15}\text{N}/^{14}\text{N} = 3.68 \times 10^{-3}$.

The $^{15}\text{N}/^{14}\text{N}$ of the Sun would serve as an appropriate reference point from which to interpret isotopic variations observed in the meteorites and planetary bodies. As with C, direct spectroscopic or spacecraft observations suffer from lack of precision, e.g., the Solar and Heliospheric Observatory (SOHO) mission determined $^{15}\text{N}/^{14}\text{N}$ ratios compatible with the terrestrial atmosphere within errors of 300 to 500‰ [Kallenbach et al, 1998]. High precision measurements can best be made in terrestrial laboratories on returned samples, and indeed analyses of the noble gas contents of soils returned by the Apollo missions demonstrated that the lunar regolith provides an effective capture medium for solar material. However, in the case of nitrogen, the interpretation of the record of surface-correlated material in lunar soils is complex. The $^{15}\text{N}/^{14}\text{N}$ ratios of
different lunar samples are highly variable, and it has been argued that the variations in $\delta^{15}$N exhibit a secular trend with soil ‘antiquity’ implying that the nitrogen isotopic composition of the solar wind has systematically become heavier over the past several aeons [Kerridge, 1993; Becker and Pepin 1989]. However, the Sun is not the only source of N on the lunar surface, and mixing of isotopically distinct reservoirs may also explain the observed $\delta^{15}$N variability [Wieler et al., 1999]. An important advance in this long-standing problem has recently been made by Hashizume and co-workers who utilized an ion microprobe to perform direct depth-profiling analyses of $\delta^{15}$N in individual lunar minerals that were exposed on the Moon’s surface at epochs differing by ~ 10$^9$ years (Hashizume et al., 2000). These analyses provide convincing evidence for a solar-wind component of nitrogen that is highly depleted in $^{15}$N ($\delta^{15}$N < -240‰) in a sample irradiated between 1 and 2 Ga, suggesting that the solar $^{15}$N/$^{14}$N ratio has not changed markedly over time but that the terrestrial nitrogen isotopic composition is significantly different than the average solar system value.

**Oxygen** Among the elements considered in this chapter, oxygen is unique by virtue of its having 3 stable isotopes, $^{16}$O, $^{17}$O, and $^{18}$O. This typically allows the possibility to distinguish between processes that partition isotopes from a common isotopic reservoir according to the usual thermodynamically-driven mass-dependent fractionation and processes involving the mixing of isotopically distinct reservoirs that had never been previously equilibrated. (This is possible with the other elements having only one stable isotope pair only when the degree of isotopic heterogeneity greatly exceeds the plausible range of possible mass-dependent isotopic fractionation given other circumstantial evidence regarding temperature, etc.) On the three-isotope plot of $\delta^{17}$O vs. $\delta^{18}$O, the former set of processes, which include physical changes of state and most chemical reactions, result in a series of isotopic compositions that are related by a straight line of slope ~0.52 for the normally observed small degrees of isotopic fractionation of a few percent or less (Fig. 1a). In contrast, partial isotopic exchange between two unequilibrated reservoirs results in compositions lying on the tie-line between the two reservoirs which can, in principle, result in any slope on the three-isotope diagram (Fig. 1a) depending on the initial compositions. Slight deviations from a strictly linear relation
between two such reservoirs can occur due to the superposition of slope ~½ mass-
dependent fractionation effects on the overall mixing line.

The oxygen isotopic compositions of nearly all (see next paragraph) terrestrial
samples fall along a single correlation line of slope ~0.52, as expected, because of the
highly effective initial homogenization of the terrestrial reservoir. This empirically
defined relationship is called the terrestrial fractionation line (TF in subsequent figures)
and by definition it passes through the reference composition for oxygen, which is
Standard Mean Ocean Water (SMOW) with a composition \(^{18}\text{O}/^{16}\text{O} = 0.0020052\)
[Baertschi, 1976 #1074] and \(^{17}\text{O}/^{16}\text{O} = 0.0003845\) (FAHEY et al., 1987). It is useful to
characterize deviations from this line by the quantity \(\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}\)
(CLAYTON et al., 1991), which is a constant for any suite of samples that are related by
mass-dependent fractionation from a common reservoir (Fig. 1b). Samples with \(\Delta^{17}\text{O} < 0\)
are therefore depleted in \(^{17}\text{O}/^{16}\text{O}\) compared to terrestrial samples having the same \(^{18}\text{O}/^{16}\text{O}\)
values, which (as will be seen be seen below in the discussion of isotope records of
nebular components of chondrites) is best interpreted as reflecting an excess of \(^{16}\text{O}\) in
these materials compared to terrestrial values. Note that the addition or depletion of \(^{16}\text{O}\)
only follows a trajectory of slope of 1.0 on the three-isotope diagram (Fig. 1a).

The first observations of any samples with \(\Delta^{17}\text{O} \neq 0\) were for anhydrous mineral
separates from carbonaceous chondrites measured by Clayton and colleagues (CLAYTON
et al., 1973). This remarkable discovery was considered prima facie evidence for the
preservation of a distinctive nucleosynthetic component, rich in \(^{16}\text{O}\), in these meteoritic
phases (CLAYTON et al., 1973; CLAYTON et al., 1977) and it stimulated the discovery of
many isotope anomalies of nucleogenetic origin in primitive refractory phases of
chondrites (e.g., LEE, 1979). A decade later, however, it was demonstrated by laboratory
experiment that it is possible to produce non-mass dependent isotopic fractionations in
certain gas-phase chemical reactions, leading to changes in \(\Delta^{17}\text{O}\) of the products from
initially isotopically equilibrated (i.e., constant \(\Delta^{17}\text{O}\)) reactants (THIEMENS and
HEIDENREICH, 1983). Chemically-produced non-mass dependent isotopic signatures
have now been recognized in natural terrestrial atmospheric samples (THIEMENS et al.,
1995) and in certain minerals formed by interactions with isotopically anomalous
atmospheric species (BAO et al., 2000), and have also been posited to have affected
minerals formed near the martian surface (e.g., FARQUHAR and THIEMENS, 2000). Thus, an unambiguous assignment of departures from mass-dependent isotopic fractionation of oxygen isotopes as due to nuclear, as opposed to chemical, effects is not possible, and arguments regarding the origin of the premier isotopic anomaly discovered by Clayton must rely on interpretations of circumstantial, often complex evidence. A quarter century after its discovery, the interpretation of the origin of oxygen isotopic anomalies in solar system materials remains as arguably the most important outstanding problem in cosmochemistry.

An excellent summary of the cosmochemically significant properties of oxygen is given by Clayton (CLAYTON, 1993). Of prime importance is the fact that oxygen in the solar nebula is more abundant than carbon, allowing it to exist simultaneously as a significant gas-phase species (primarily CO and H₂O) and as the major constituent of rocks. In addition, the nucleosynthetic sources that are responsible for producing the primary isotope, ¹⁶O, are distinct from those synthesizing the secondary, rare isotopes ¹⁷O and ¹⁸O, which have abundances of only about 400 and 2000 ppm, respectively. The abundance of these secondary isotopes ought to increase with the chemical evolution of the galaxy, so that if there exists a difference in mean age between interstellar dust and gas, it could be expected that the older component (i.e., the dust) would, on average, be ¹⁶O-rich compared to the younger component (CLAYTON, 1988). The potential for distinct isotopic signatures of oxygen in dust compared to gas, regardless of whether they be inherited from presolar materials or generated by solar system gas-phase chemistry, combined with oxygen’s unique chemical abundance properties, make the distribution oxygen isotope anomalies a powerful tracer of high-temperature gas-dust interactions in the solar nebula (CLAYTON, 1993).

The interpretation of oxygen isotope records in differentiated planetary bodies (Earth, Mars, asteroidal sources of achondritic meteorites), as well as in distinct nebular components of chondrites, would be more straightforward if an average solar system composition could be defined. However, as with the other stable isotopes, the solar composition cannot be directly determined with anything approaching a precision useful for planetary science purposes. An estimate of the solar oxygen isotope composition has been constructed by Wiens et al. (1999), but it is based on model-dependent
interpretations of meteoritic data (discussed further below). The Genesis Discovery mission, to be launched in summer of 2001, is designed to capture and return (in 2004) a solar wind sample to terrestrial laboratories for analysis of its oxygen isotopic composition (see discussion in Wiens et al., 1999).

To date, there exists very little quantitative information concerning oxygen isotope compositions in major solar system reservoirs that is obtained by remote (spectroscopic) observation or spacecraft measurements. A measurement of water ice from comet P/Halley, made by the Giotto mission, yields $\delta^{18}$O = 12 ± 75‰ (Balsiger et al., 1995; Eberhardt et al., 1995) but no measurement of $\delta^{17}$O is available. Precise data are obtained for the Moon, of course, from returned Apollo samples, and the oxygen isotope composition of Mars and the largest asteroid, Vesta, may be inferred from laboratory mass spectrometric measurements of meteorites that are thought to derive from these bodies. These data are discussed in detail below in the section on isotope records in planetary materials.

Analysis methods

Measurements of stable isotope abundances have traditionally been accomplished by means of gas-source mass spectrometry. In the ‘conventional’ method, gases are evolved by either thermal or chemical means from ‘bulk samples’ to produce on the order of micromoles of purified analyte for high-precision isotope-ratioing mass spectrometry. For C and N, mass spectrometry is sometimes done in the ‘static mode’ to improve sensitivity to the sub-nanomole regime (Pillinger, 1984). Accuracy and precision are both very high by these gas-source methods, and for most types of sufficiently large samples are in the few ‰ range for $\delta$D, better than ~0.1‰ for $\delta^{13}$C and $\delta^{15}$N, and <0.2‰ for $\delta^{17}$O and $\delta^{18}$O. For oxygen isotopes, mineral separates (often < 100 % purity) may be analyzed on suitably coarse-grained materials (e.g., Clayton et al., 1977). Differential dissolution or other chemical means are sometimes utilized for studying specific components of meteorites (e.g., H, C, N in soluble organic matter, or C and O in carbonates). Stepped combustion or pyrolysis may be employed for H, C, and N to discriminate among different carrier phases.
In the last decade, lasers have been used to assist in the chemical extraction of stable isotopes from individual mineral samples (see chapter by Eiler). Most of the laser analyses of extraterrestrial materials concern oxygen isotope measurements (e.g., Young et al., 1998a; Young et al., 1998b), where there are significant advantages over conventional methods because of the reduction in system blank. The resulting increase in sensitivity allows sub-μmole quantities of O₂ to be analyzed which can be obtained from individual mineral grains in favorable circumstances. The IR laser method is used for physically isolated samples and can improve precision and accuracy of analyses of some difficult-to-react minerals, such as olivine, to sub-ε levels [e.g., <0.05‰ in Δ¹⁷O; Franchi, 1999 #1043]. For in situ work, a UV laser is utilized because it does not suffer from the partial reaction aureoles that limit IR laser in situ work. Typical spot sizes analyzed are ~100 μm in lateral dimension and ~50 μm deep. Precision and accuracy are also very high (~±0.3‰) for in situ O isotope work (Young et al., 1998a).

Because of its high sensitivity and spatial resolution, the ion microprobe has become a key instrument for the analysis of stable isotopes in a wide variety of extraterrestrial materials. Analyses can be made on very small samples, e.g., individual interplanetary dust grains (McKeegan et al., 1985), and other samples can be examined in thin-section with a spatial resolution of ~10 μm. The ion microprobe is used for measurements of all isotopes considered in this review, although N is only measured in C-rich materials (because of the high yield of the CN⁻ molecular ion). Analytical methods for ion microprobe isotopic measurements have been reviewed by Zinner (1989) and Ireland (1995); developments (relevant to this chapter) since that time involve primarily analyses of D/H in hydrous phases (Deloule et al., 1991; Deloule et al., 1998), of oxygen isotope compositions measured in situ in insulating minerals (Hiyagon and Hashimoto, 1999; Leshin et al., 1998; Lorin et al., 1990; Simon et al., 2000; Yurimoto et al., 1994), and of large D/H anomalies with approximately micron spatial resolution by ion microscope imaging techniques (Aléon et al., 2001; Messenger and Walker, 1997). Precision and accuracy obtained by ion microprobe is considerably poorer than that achievable by gas mass spectrometric methods (on much larger samples) and is somewhat dependent on sample characteristics. When good standards are
available, and analyses are not counting statistic limited, precision and accuracy of one to several % is typically realized for H, C, N, or O isotopic analyses.

Stable isotope records in primitive materials

The record of variability in primordial isotopic reservoirs, i.e., those inherited from the presolar molecular cloud, and of the isotopic compositions and interactions between important components of the solar nebula is preserved only in so-called ‘primitive’ materials. These materials are also referred to as having a ‘chondritic’ composition, a term which originally denoted chondrule-bearing, but which has evolved to encompass any chemically-undifferentiated material having approximately solar concentrations of all but the most volatile elements (ANDERS and GREVESSE, 1989).

Three types of primitive, chondritic extraterrestrial materials are distinguished on the basis of size, which determines modes of collection and is possibly indicative of distinctive origins. Chondritic interplanetary dust particles (IDPs) are decelerated in the upper atmosphere without melting owing to their small sizes (< ~30 µm) and are collected by high-flying aircraft (e.g., BROWNLEE, 1981). In the next size range (~ 50 µm to ~200 µm) are cosmic dust particles which constitute the dominant fraction of the total extraterrestrial material presently accreted by the Earth (LOVE and BROWNLEE, 1993). Depending on their velocity, these dust particles are either melted during atmospheric entry becoming cosmic spherules or suffer only modest levels of heating insufficient to cause total melting. The latter are termed micrometeorites, and are efficiently collected from Antarctic ice (MAURETTE et al., 1994). While the cosmic spherules have generally undergone either chemical differentiation and/or sufficient mass loss so that most are no longer chondritic, many Antarctic micrometeorites (AMMs) are totally unmelted and retain chondritic compositions. Macroscopic meteorites are also found efficiently in Antarctica (e.g, CASSIDY et al., 1992) and other desert environments (e.g., FOLCO et al., 2000) and, occasionally, they are observed to fall (e.g., BROWN et al., 2000). A small percentage (~15%) of observed meteorite falls are samples of chemically-differentiated objects, but most are chondrites and are thought to derive from remnant planetesimals in the asteroid belt (e.g, WETHERILL and CHAPMAN, 1988).
The chondrites may be conveniently thought of as cosmic sediments, formed by aggregation and compaction of a hodge-podge of rocky and (sometimes) icy materials existing near the midplane of the solar nebula (most likely at several AU). Most chondrites consist primarily of chondrules, whence their name, and fine-grained dust. The chondrules are typically rounded, mm-sized solidified melt droplets consisting of ferromagnesian silicate minerals and glass, often with minor amounts of FeNi-metal and sulfides. The astrophysical sites and processes responsible for chondrule formation are enigmatic, but the most widely-accepted models involve some form of flash-heating mechanism (Rubin, 2000). Chondritic meteorites are generally not strong rocks and are lithified only by a ‘matrix’ of chondrule fragments and fine-grained dust grains (which includes a tiny fraction of dust grains from other stellar systems). In addition to chondrules, an important component of some chondrites are inclusions containing refractory oxide and silicate minerals that also formed as free-floating objects within the solar nebula. These Ca-Al-rich inclusions (CAIs) are most abundant (~5%) and the largest (up to several cm) in the CV3 carbonaceous chondrites (GROSSMAN, 1980), but a wide spectrum of size ranges and mineralogical types exist among the various chondrite classes (e.g., MacPherson et al., 1988). CAIs occur only rarely in meteorites outside the carbonaceous chondrite class (e.g., Bischoff and Keil, 1984; Fagan et al., 2000).

Some chondrites have been thermally metamorphosed while resident on an asteroidal parent body, and others (especially the volatile-rich carbonaceous chondrites) have undergone variable degrees of interaction with low-temperature aqueous fluids (see Brearley and Jones, 1998 for a comprehensive review of chondrite chemical and mineralogical properties and classification). While thermal and aqueous alteration generally have not appreciably altered bulk chemical compositions of chondrites, both types of processes are imprinted on the mineral chemistry and stable isotope compositions of chondritic components. Thus, even among chondrites, there exists varying degrees of ‘primitiveness’ which is reflected in their isotope compositions. Those meteorites which exhibit the best preserved nebular records are considered to be the most primitive; these include the unequilibrated ordinary chondrites and enstatite chondrites of petrologic type 3, as well as various classes of carbonaceous chondrites (e.g., reduced CV3, CH, CB, CR). Based primarily on mineralogical and petrographic
observations, it is thought that particles of the anhydrous subset of IDPs are in some sense even more ‘primitive’ than any solar nebula components of macroscopic meteorites (i.e., excluding circumstellar dust grains), and may even be comprised of true presolar materials (e.g., BRADLEY, 1994). Stable isotopic evidence (see below) has been found to support a view of the extremely primitive nature of certain IDPs which, in turn, bolsters the hypothesis that many of these types of (anhydrous, low density) particles are derived from comets.

**Hydrogen**

Hydrogen isotopic compositions of various components of primitive extraterrestrial materials preserve evidence of extreme isotopic heterogeneity among presolar carriers, and track the processes associated with the partial equilibration of these materials in the formation of the solar system. The hydrogen isotopic compositions of these materials have recently been reviewed by Robert et al. (2000). Bulk D/H analyses of chondrites are useful for interpreting the relative contributions of these materials to the hydrogen budgets of the Earth and other terrestrial planets. Such analyses show a relatively restricted range of D/H values (Kerridge, 1985; Kolodny et al., 1980; McNaughton et al., 1981; Robert and Epstein, 1982; Robert et al., 1987; Robert et al., 1979), with 2/3 of the samples falling between -165 and +90 ‰, and a mean value of -100 ‰ (Robert et al., 2000), essentially identical the composition estimated for the bulk Earth (Lécuyer et al., 1998). Put another way, many chondrites have D/H values ver similar to Earth, and do not show evidence for significant internal isotopic variation.

The relatively homogenous hydrogen isotopic compositions of bulk chondrites belies the complexity of the distribution of deuterium in some extraterrestrial materials. Analyses of separated components from chondrites (e.g., matrix, organic matter) reveal isotopic variations from ~ -500 to +6000 ‰. Organic matter in meteorites consistently
shows D-enrichment at levels which are extreme for compared to terrestrial values, but still well below observed compositions of molecular clouds (summarized by Robert et al., 2000). As discussed in the Introduction, the high D/H values in molecular clouds are interpreted to reflect very low T ion-molecule reactions. The D/H values of the organic matter in meteorites most likely reflects the partial isotopic equilibration of precursor organic species with hydrogen during solar system formation (which occurs at higher temperatures). The organic matter in meteorites can be broadly divided into a soluble component (which includes amino and carboxylic acids and other hydrocarbons) and an insoluble component with a complex structure, often referred to as "kerogen" (e.g., Kerridge, 1999 and references therein). D/H analyses of amino acids separated from the soluble portion of the organic matter from the Murchison meteorite (the best studied sample in this respect) show δD values of ~+1700 ‰, and hydrocarbons and carboxylic acids show somewhat lower δD values (Cronin and Chang, 1993; Cronin et al., 1993; Pizzarello et al., 1994; Pizzarello et al., 1991). The bulk kerogen from carbonaceous chondrites has δD values of ~+1400–3000 ‰, with CR chondrite Renazzo showing the highest D-enrichment, while kerogen from LL3 ordinary chondrites studied shows even higher δD values of ~+4000–6000 ‰ (Kerridge et al., 1987; Robert and Epstein, 1982; Yang and Epstein, 1983).

Water in components of chondrites also shows large isotopic variation, whether analyzed from physically separated phyllosilicate, or in situ using an ion microprobe. The values range from ~-400–+3700 ‰ (Deloule and Robert, 1995; Deloule et al., 1998; McNaughton et al., 1981; Robert et al., 1979). The most striking feature of these data is that almost the entire range is observed on the scale of single chondrules from LL3
chondrites when traverses are performed with a 10 µm ion probe beam (Deloule and Robert, 1995; Deloule et al., 1998). The isotopic variations are too large to be caused by isotopic fractionation at variable nebular temperatures associated with chondrite formation, and thus imply mixing of water with variable histories in the nebula and on meteorite parent bodies. Specifically, Robert et al. (2000) have recently proposed that the range in D/H values results from variable sampling of water as it isotopically evolves from a high-δD "presolar water" component with time and space in the nebula through progressive isotopic exchange with protosolar H$_2$ (Deloule et al., 1998; Robert et al., 2000). The data upon which this model is based are somewhat limited, however, and confirmation of the large isotopic effects in meteoritic water is worth pursuing.

Ion probe analyses of Antarctic micrometeorites (AMMs) show a relatively restricted range in δD values from ~-300 to +200 ‰ (Engrand et al., 1999). These data support the idea that AMMs are related to heavily altered carbonaceous chondrites, which also show a similar restricted range in D/H. Interplanetary dust particles (IDPs) collected in the stratosphere, on the other hand, show the largest range in D/H of any Solar System materials analyzed, from ~-500 to >+15000‰ (McKeegan et al., 1985; Messenger, 2000; Messenger and Walker, 1997). Many particles have elevated D/H ratios, but these are most dramatically observed in so-called "cluster IDPs" which are anhydrous, fine-grained, highly porous, carbon-rich objects (Messenger, 2000). The carriers of the D-enrichments in IDPs are not well constrained, as particles are analyzed in "bulk" with the ion microprobe. However, observation of the most extreme D-enrichment in very C-rich IDPs is suggestive of an organic carrier. In the case of cluster IDPs, the D/H ratios approach those observed in molecular clouds, suggesting that the IDPs are carriers of some of the most unaltered presolar material (Messenger, 2000). This is consistent with the notion that at least some IDPs are samples of relatively unprocessed comets (e.g., Bradley, 1994). However, the average IDPs have D/H values more consistent with meteorite (and terrestrial) compositions than cometary values, suggesting that IDPs sample both asteroids and comets.
**Oxygen**

*The premier isotope anomaly*  In 1973, R. Clayton and co-workers (CLAYTON et al., 1973) discovered correlated variations in $\delta^{18}O$ and $\delta^{17}O$ in anhydrous minerals from the Allende carbonaceous meteorite that indicated mixing of isotopically "normal" oxygen with an "exotic" component enriched in $^{16}O$. By disaggregating the meteorites and analyzing individual components, it was quickly learned (CLAYTON et al., 1977) that the anomalous oxygen was most prevalent in the CAIs of carbonaceous chondrites, many of which are highly enriched in $^{16}O$ by values approaching 5% relative to terrestrial minerals (Fig. 2). Subsequent analyses, performed by Clayton, Mayeda and colleagues demonstrated a systematic trend in the oxygen isotopic compositions of the nebular constituents of the various chondrite groups (see CLAYTON, 1993 and references therein). As can be seen in Fig. 2, the chondrules and CAIs of carbonaceous chondrites are variably enriched in $^{16}O$, sometimes (for CAIs) to a large degree, compared to either terrestrial minerals or other classes of primitive or evolved meteorites. On the other hand, individual chondrules from the ordinary chondrites plot above the TF line ($\Delta^{17}O > 0$) indicating that they have small relative depletions in $^{16}O$ compared to terrestrial minerals. The oxygen isotopic compositions of chondrules separated from the highly reduced enstatite chondrites lie within error of the TF line ($\Delta^{17}O = 0$) and thus are intermediate in this sense between their CC and OC counterparts.

The preponderance of the data plotting approximately along a single linear trend strongly suggests that, to first order, oxygen isotope compositions of primitive (i.e., unequilibrated) solar system materials are determined by variable degrees of mixing and isotopic exchange between (only) two dominant reservoirs (CLAYTON et al., 1977). Three independent lines of evidence have been utilized to argue that these major reservoirs consist of an $^{16}O$-rich dust source and the solar nebula gas which is characterized by an oxygen isotopic composition near or above the TF line. The first is a simple appeal to mass balance – although we will discuss heterogeneities in detail below, in the first approximation most of the samples of planetary bodies that we have measurements for (Earth, Moon, and probably Mars and Vesta) plot near the TF line, as do most of the ordinary chondrites, and even (roughly speaking) the bulk carbonaceous
chondrites. The relative abundances of oxygen and the major rock-forming elements dictates that most (~80-85%) of oxygen in the solar nebula was sequestered in gas-phase molecules, and thus it would have to be the minor dusty component that was anomalous. As discussed above, this circumstantial argument would be even more compelling if the solar composition were known with better precision (Wien et al., 1999).

A second line of evidence for a gaseous composition that is somewhat $^{16}$O-depleted relative to the Earth comes from the analysis of secondary minerals in both carbonaceous and ordinary chondrites that are considered, on very strong petrographic grounds, to have formed by interaction with aqueous fluids, presumably on an asteroidal ‘meteorite parent body’. Several classes (CI, CM) of carbonaceous chondrites have been extensively mineralogically altered by chemical reaction with relatively large amounts of aqueous fluids at low temperatures, resulting in the formation of hydrous minerals (phyllosilicates), carbonate, and magnetite which exhibit elevated $\Delta^{17}$O values relative to the precursor anhydrous minerals in the same meteorites (Clayton and Mayeda, 1984; Rowe et al., 1994). A quantitative estimate of the isotopic composition of the solar nebula gas from which these fluids condensed can be derived based on a model of the coupled evolution of the fluid and the mineral phases of CM (Clayton and Mayeda, 1984) and CI (Leshin et al., 1996; Rowe et al., 1994) chondrites during the partial approach to equilibrium at low temperatures in an asteroidal setting. The gas itself is assumed to have evolved from an initial composition due to partial isotopic exchange with $^{16}$O-enriched dust at high temperatures in the nebula. If the $^{16}$O-rich component is modeled as having a starting composition of $\delta^{18}$O $\sim$ $\delta^{17}$O $\sim$ -40‰, then the mass balance calculations yield compositions in the range $\delta^{18}$O $\sim$ +25-30‰ and $\delta^{17}$O $\sim$ +20-25‰ ($\Delta^{17}$O $\sim$ +7-9‰) for the initial solar nebula gas, which is remarkably consistent with an estimate of fluid composition ($\Delta^{17}$O $\sim$ +7‰) derived from ion microprobe analyses of small magnetite nodules from the highly unequilibrated ordinary chondrite, Semarkona (Choi et al., 1998). Magnetite is a useful probe of volatile reservoirs because it results from the oxidation of Fe-Ni metal, which likely occurs by reaction with aqueous fluids in an asteroidal parent body, and hence all the oxygen in magnetite is derived from the fluid (with little temperature dependence of the fractionation factors in the temperature range of interest). The magnetite data of Choi et al. (1998) represent the highest $\Delta^{17}$O values
measured in solar system materials (~ +5‰); this comes about essentially because of the very small degree of fluid-rock interaction in Semarkona which leads to the preservation in the magnetite of a vestige of the high $\Delta^{17}\text{O}$ values of the solar nebula gas from which the fluid is derived.

A third line of evidence regarding the isotopic compositions of the initial dust and of the dominant gaseous reservoir in the solar nebula was actually historically the first to be developed, but perhaps ironically it is the most complicated to understand and fundamental aspects of this model remain enigmatic to this day. One of the more astounding features of Clayton’s discovery is that most of the extreme range of O isotopic variations among nebular components (Fig. 2) can be spanned by the internal isotopic distributions among the various minerals of an individual CAI. This remarkable result was first observed for the large (~cm-sized) CAIs from the CV3 carbonaceous chondrites (e.g., Allende) which are sufficiently coarse-grained that mineral separates of several CAIs could be obtained for analysis (CLAYTON et al., 1977). Spinel and Ti-bearing clinopyroxene were always found to be highly $^{16}$O-enriched, down to values of $\delta^{18}\text{O} \sim -40\%_\circ$, $\delta^{17}\text{O} \sim -41\%_\circ$, whereas melilite was invariably much closer to the TF line in composition (Fig. 3a). Such extreme O isotopic heterogeneity (up to ~20% in $\Delta^{17}\text{O}$) in objects that formed by crystallization from a melt at high temperatures (> 1400 ºC) can only be understood as reflecting open-system behavior, most plausibly post-crystallization isotopic exchange with an external reservoir which is presumably nebular gas (CLAYTON, 1993). Because spinel is an early crystallizing phase (STOLPER, 1982), and because the same extreme composition of spinel could be found whether the spinel was enclosed within $^{16}$O-rich pyroxene or $^{16}$O-poor melilite (CLAYTON et al., 1977), it can be concluded that the initial isotopic composition of the melt had to have been $^{16}$O-enriched and thus the second reservoir (solar nebula gas) was $^{16}$O-poor. The higher crystallization temperatures for melilite compared to pyroxene place important and difficult constraints on the physical processes driving the isotopic exchange between these reservoirs; this is discussed in further detail below within the context of in situ isotopic measurements on individual CAI minerals.

Two further results are obtained by BrF$_5$ analyses that have had a large significance for estimating the composition of the initial dust reservoir prior to isotopic
exchange with the gas and for confirming the general nature of the dust-gas fractionation that characterized the early solar nebula. The first is the O isotopic composition of a spinel mineral separate obtained by acid-dissolution of the CM2 Murchison meteorite (CLAYTON and MAYEDA, 1984). Although it is now recognized as an average composition, slightly contaminated by a minor population of $^{16}$O-poor spinel (McKEEGAN, 1987; SIMON et al., 1994; SIMON et al., 2000), the close agreement of this value ($\delta^{18}$O = $-40%$e, $\delta^{17}$O = $-42%$e) with the most $^{16}$O-enriched spinel compositions determined from mineral separates of individual Allende CAIs (Fig. 3a), suggested this as an appropriate composition for the end-member of the mixing line corresponding to refractory solar system dust. Additional evidence for the existence of an important reservoir near this $-40%$e value is provided by a model of the internal distributions of O isotopes within the rare CAIs that do not fall on the Allende mixing line (Fig. 2). These so-called FUN inclusions are isotopically (but not chemically or mineralogically) unique in that they have strongly mass-fractionated compositions of their major elements (e.g., Mg and Si) accompanied by correlated and unusually large apparent nuclear (i.e., nucleosynthetic) isotopic anomalies in several minor and trace elements (LEE and PAPANASTASSIOU, 1974; LEE et al., 1978; WASSERBURG et al., 1977). The melilite in EK-1-4-1, one of the ‘classical’ FUN inclusions for which mineral separations were possible, has essentially the same oxygen isotopic composition as ‘normal’ Allende CAIs (CLAYTON and MAYEDA, 1977) which is also the case for the rim phases of a unique Allende hibonite inclusion called HAL (LEE et al., 1980). These data can be understood as resulting from an overprint of the same post-solidus isotopic exchange process that affected the non-FUN type B CAIs in Allende and other CV3 chondrites, except in the FUN case operating on a starting composition that is mass fractionated from the $-40%$e endmember (Fig. 4a). The degree of mass fractionation inferred for oxygen correlates in a semi-quantitative fashion with that measured for Mg and Si in several of the classical FUN CAIs (CLAYTON, 1986).

The hypothetical mass fractionation trajectory on the O three-isotope plot for the FUN CAIs was recently confirmed by ion microprobe analyses (DAVIS et al., 2000) of primary minerals in a forsterite-rich inclusion from CV3 Vigarano (Fig. 4b). This CAI apparently was crystallizing while still suffering large amounts of mass loss and kinetic
isotope fractionation accompanying evaporation from a molten state (Rayleigh distillation). Isotopic exchange of the melilite followed after crystallization of the CAI. An extrapolation of the mass fractionation trend intercepts the CCAM line at a composition $\delta^{18}O \sim \delta^{17}O \sim -45$ to $-50\%e$. Although somewhat more $^{16}O$-enriched compositions ($\Delta^{17}O \sim -25\%e$ or more) can be found among oxide minerals, such as hibonite and corundum, that are still more refractory than the silicate-dominated CAIs typical of CV chondrites (Fahey et al., 1987; Virag et al., 1991), this composition of $-45$ to $-50\%e$ seems to characterize the extreme values found in a sufficiently large number of the refractory inclusions found in CV chondrites (including the FUN CAIs) that it must constitute an important solar system reservoir.

Thus, there is abundant evidence that confirms the basic systematics of the two reservoir mixing model with analyses of individual phases by microprobe techniques providing slightly modified estimates of the end-member compositions: $^{16}O$-enriched dust with $\Delta^{17}O \sim -25\%e$ and $^{16}O$-depleted nebular gas with $\Delta^{17}O \sim +7\%e$. The isotopic compositions of chondrules also exhibit variable degrees of $^{16}O$-enrichments (Clayton, 1993 and references therein), however falling in a more restricted range between the end-members reflecting their greater degree of processing and equilibration with solar compositions. The greatest degree of inter-chondrule and intra-chondrule isotopic heterogeneity documented thus far is exhibited by Al-rich chondrules from ordinary chondrites (Russell et al., 2000). These objects, while not representing simple mixtures of CAIs and precursor materials of typical ferromagnesian chondrules, nevertheless provide evidence for partial isotopic exchange between refractory precursors with moderate $^{16}O$-enrichments and nebular gas in a manner similar to that proposed for type B CAIs. Additionally, it is recognized that the interpretation of the isotopic mixing patterns in chondrules such as these is complicated by an overprinting due to multiple events, some involving aqueous processing. The complexities in interpreting nebular records due to secondary effects, which probably originate on the parent body, has been the focus of high precision laser fluorination analyses (Ash et al., 1998; Ash et al., 1999; Bridges et al., 1998). As of this writing, a consensus on the relative importance of precursor heterogeneity vs. isotopic exchange during chondrule formation, as well as the confounding effects of secondary alteration in determining the preserved $O$ isotopic
records in chondrules from both CC and OC has not yet emerged, and much recent in situ work utilizing new developments in both laser and ion microprobe analyses has not yet appeared in the reviewed literature [e.g., Leshin, 1998 #417; Leshin, 2000 #836; Young, 2001 #1166] although some has (Jones et al., 2000; Saxton et al., 1998; Sears et al., 1998). Given this situation, we defer a detailed discussion on oxygen isotope compositions of chondrules and in the remainder of this review concentrate on new constraints obtained by spatially resolved analyses since the last comprehensive review by Clayton (1993). As is often the case, observations made on the microscopic scale provide the proper perspective for understanding the large scale issues relating to the origin and distribution of the oxygen isotopic anomaly within the solar system.

The nature of dust-gas isotopic exchange: a microscopic view

The first phases to be investigated by high spatial resolution methods were coarse-grained type B Allende CAIs similar those that Clayton and colleagues had previously demonstrated preserve a record of extraordinary isotopic heterogeneity. The ion microprobe and UV-laser fluorination results broadly confirm the inferences from mineral separate data, but also provide new constraints that point to the complexity of the isotope exchange process(es). The pattern of mineral-controlled isotopic heterogeneity is maintained in microscale analyses of CV CAIs (Figs. 3b-c-d). The same basic pattern is observed in a coarse-grained type A CAI from the reduced CV chondrite Vigarano, which argues against isotopic exchange in melilite from Allende CAIs being the result of late-stage metasomatic alteration of the Allende chondrite. In contrast to this is the observation of a correlation of degree of aqueous alteration among whole CO chondrites with the oxygen isotopic composition of CAI melilite from those meteorites (Wasson et al., 2000).

The isotopic contrast in type B CAIs between near end-member $^{16}$O-enriched spinel and melilite near the TF line is maintained over extremely fine spatial scales, in some cases, < 10 µm. This is true whether the grains are located in the center of a large (2 cm diameter) inclusion (Fig. 5a) or are at the periphery where the CAI is rimmed by a Wark-Lovering mineral sequence (Fig. 5b). Significantly, no gradients are observed in melilite δ$^{18}$O and δ$^{17}$O as would be expected under any scenario in which gas-solid diffusion was the primary mechanism for isotopic exchange in melilite (Ryerson and
MCKEEGAN, 1994). Zoning is observed in anorthite (Fig 3b), but its geometry is generally inconsistent with diffusive exchange (MCKEEGAN et al., 1996). A sharp zoning profile within a single melilite crystal, and the first instance of $^{16}$O-enriched melilite in a CV CAI was discovered by Yurimoto and colleagues (YURIMOTO et al., 1998) who invoked a re-melting episode to explain the isotopic exchange pattern. Certainly many type B CAIs have experienced multiple partial melting events, as well as impulsive heating that produced the coarse-grained Wark-Lovering rims. The problem with generally appealing to partial melting to explain the isotopic patterns in CV CAIs, however, is that pyroxene, should melt prior to melilite upon reheating of the CAI (STOLPER and PAQUE, 1986), but in situ data found so far indicates that pyroxene nearly always preserves its $^{16}$O-rich composition (e.g., data in Fig 3).

A hint is provided by high-precision laser fluorination analyses of an Allende CAI which demonstrates a distinct difference in the oxygen isotopic composition of melilite which is inferred on chemical and petrographic evidence to have been partially altered by interaction with alkali-bearing aqueous fluids (YOUNG and RUSSELL, 1998). Melilite crystals lacking these indications of alteration lie on a mixing line (terminating at $^{16}$O-rich spinel) that has a slope exactly equal to unity, whereas the altered melilite in the CAI trends along the CCAM line with slope = 0.94. An extension of this pure $^{16}$O-mixing line passes through the data for the (anhydrous) components of ordinary chondrites suggesting the presence of a “primitive oxygen reservoir” in the solar nebula (YOUNG and RUSSELL, 1998). The oxygen compositions of chondritic components can then be modeled as the result of variable degrees of fluid-rock interaction at different temperatures affecting compositions corresponding to the primitive reservoir which is set by high temperature nebular processes (YOUNG et al., 1999).

The distribution of the O isotope anomaly in the inner solar system, and implications for the provenance of CAIs

The oxygen isotopic heterogeneity which is the single most pervasive feature characterizing unequilibrated chondritic materials on microscopic size scales is also reflected in the bulk compositions (Fig. 6) of chondrites, differentiated meteorites, and, even of entire planets (CLAYTON, 1993 and references therein). Although the
fundamental reason for this heterogeneous distribution of the oxygen isotopes on planetary size scales is not understood, it is presumably related in some sense to distinct accretion regions in the solar nebula and it provides a practical aid for classification purposes and deciphering possible genetic relationships among chondrites.

The ion microprobe allows measurement of samples that are too small and/or rare to be studied by fluorination techniques. We and our colleagues have used an ion microprobe to examine the oxygen isotopic records of previously unstudied types of refractory calcium-aluminum-rich inclusions (CAIs) from ordinary (MCKEEGAN et al., 1998b) and enstatite chondrites (FAGAN et al., 2001; GUAN et al., 2000), CH chondrites (MCKEEGAN et al., 2001), and micrometeorites (ENGRAND et al., 1999). With the notable exception of some CH CAIs (MCKEEGAN et al., 2001), the data show consistently large $^{16}\text{O}$-enrichments with $\delta^{18}\text{O} \approx \delta^{17}\text{O} \approx -40$ to -50‰ in all CAI minerals across all chondrite groups. Unlike the larger coarse-grained CAIs from CV chondrites (Fig. 3), isotopic heterogeneity within a CAI is relatively limited suggesting that these materials had simpler thermal histories and did not interact with oxygen isotopic reservoirs in the formation and accretion areas of chondritic components. The data are consistent with the hypothesis that all CAIs may have formed in a restricted nebular locale and were later distributed unequally throughout the various chondrite accretion regions (MCKEEGAN et al., 1998b; SHU et al., 1996).

**Stable isotope records in evolved materials**

The achondritic meteorites are igneous and metamorphic rocks and, thus, their stable isotope records can be utilized to investigate petrogenesis in the same manner as is done for analogous terrestrial samples (CLAYTON, 1986). These meteorites are derived from differentiated asteroids and planetary bodies. The oxygen isotope records of achondritic meteorites from the asteroid belt have been utilized to establish genetic relationships and to investigate thermal histories (e.g, isotopic equilibration temperatures). This extensive body of data has been summarized and reviewed from various contexts in the recent literature (CLAYTON, 1993; CLAYTON and MAYEDA, 1996; MITTLEFEHLDT et al., 1998), and the reader is directed to these sources. Here we discuss the H and O isotopic records from only those samples that are considered to represent planetary bodies.
Moon. Analysis of lunar samples returned via spacecraft and lunar meteorites and have a bearing on the origin of the largest satellite in the inner solar system. Oxygen isotopic compositions show a narrow range in $\delta^{18}O$ values from +4.2 to +6.4 ‰ and suggest a lunar bulk isotopic composition similar to Earth (e.g., Clayton and Mayeda, 1975; Clayton and Mayeda, 1996; Taylor and Epstein, 1970). Especially significant are the $\Delta^{17}O$ values that lie within analytical uncertainty (~0.1 ‰) of the terrestrial mass fraction line (Clayton and Mayeda, 1975; Clayton and Mayeda, 1996; Robert et al., 1992). Some "Giant Impact" models for lunar formation (e.g., Benz et al., 1986), in which an approximately Mars-sized body impacts the early Earth and forms the Moon from the residue of the event, predict that a large fraction of the Moon represents impactor material. The oxygen isotopic compositions of lunar materials suggest that if this hypothesis is correct, the impactor had $\Delta^{17}O$ value very similar to the Earth. An impactor with a Mars-like $\Delta^{17}O$ value (see below), for example, should have been detected with the available data. However, the most modern and precise laser fluorination techniques have not yet been applied to lunar materials, suggesting future work could put more stringent constraints on the similarity or difference of the $\Delta^{17}O$ of lunar and terrestrial materials.

The Moon is greatly depleted in volatile elements including C and H. Isotopic analyses of H in lunar materials typically reflect the isotopic composition of the solar wind (essentially D/H = 0) modified to varying degrees by terrestrial contamination (e.g., Epstein and Taylor, 1971). Very rare indigenous C components have $\delta^{13}C$ values of ~-19 to -26 ‰, and are also easily compromised by terrestrial contamination (e.g., DesMarais, 1978).

Mars. Martian (SNC) meteorites, remote sensing, and spacecraft exploration have provided insights into the origin, evolution and interaction of several light-element reservoirs on Mars including the lithosphere, hydrosphere and atmosphere. Beyond Earth, Mars is certainly the most exhaustively investigated body from a stable isotopic perspective.

Atmosphere: Owen et al. (1988) were the first to report detection of D on Mars. They derived a value of D/H of 6 ± 3 times the terrestrial value (SMOW) by observing
from Mauna Kea the intensity of a fundamental HDO absorption at 3.7 µm relative to H₂O lines in the martian atmospheric spectrum. The precision of this result was improved by Bjoraker et al. (1989), who made measurements from the Kuiper Airborne Observatory. They report a D/H of 5.2 ± 0.2 times terrestrial, corresponding to a δD value of +4200 ± 200, but this value has only been published in abstract form and its high precision is somewhat questionable. It is appropriate to note that the range of δD values commonly found on Earth is approximately -400 to +50 (Hoefs, 1997) although values as low as ~-500 have been reported for water vapor in the stratosphere. Thus, the value of D/H of water in the martian atmosphere is significantly higher than the D/H of any hydrogen found on the Earth. It is generally assumed that Mars originally contained water of similar D/H to the Earth and most meteorites (see chondrites section for a review) and that the present atmosphere D/H value is a result of preferential loss of H relative to heavier D from the martian atmosphere throughout the planet's history. The details of the timing of water loss and the evolution of the deuterium enrichment, however, remain highly unconstrained.

Carbon dioxide is the predominant constituent of the current martian atmosphere composing ~95 % of the ~7 mbar of gas present in the atmosphere today. Additionally, CO₂ is thought to have played an important role in martian climate in the past, possibly contributing to an early warmer climate due to the greenhouse effect (Fanale et al., 1992). The Viking entry mass spectrometer measured the values of 13C/12C and 18O/16O in martian atmospheric CO₂. Within the uncertainty of ± 5 %, the values of both of these ratios were found to be indistinguishable from terrestrial (Nier and McElroy, 1977), confirming the results of earlier, less precise measurements as summarized by Owen (1992). More recently, Krasnopolsky et al. (1996) measured C and O isotope ratios in CO₂ consistent with these observations using the 4 m telescope at Kitt Peak. The lack of enrichment of the oxygen isotopes is an interesting observation, since currently one oxygen atom could escape from Mars with each two hydrogen atoms. Considering the extremely fractionated hydrogen isotopes, the oxygen in the atmospheric water must be buffered by an additional reservoir of oxygen to explain the lack of heavy oxygen isotope enrichment.
Studies of martian meteorites can also provide insights into the composition of the atmospheric reservoir. These are discussed below.

**Stable isotopic composition of martian meteorites.** At this writing there are 17 members of the martian meteorite clan. All are igneous rocks that have been affected to differing degrees by secondary processing on Mars, including impact events and interactions with fluids in the martian crust. Evidence for the martian origin of these rocks is rooted in isotopic compositions and relative abundances of gases in impact-produced glasses in EETA 79001 and other martian meteorites (e.g., Becker and Pepin, 1984; Bogard and Johnson, 1983; Marti et al., 1995) which closely match the composition of the current martian atmosphere. McSween and Treiman (1998) provide the most recent overview of the mineralogy and petrology of these samples, and review in detail the evidence for martian origin.

Oxygen isotopes provide the most compelling evidence that the mineralogically diverse suite of martian meteorites represent samples from a single parent body. Clayton and Mayeda (1983; 1986; 1996), Romanek et al. (1998), and Franchi et al. (1999) report high-precision whole-rock 3-isotope oxygen analysis of martian meteorites. The most recent and precise data, laser fluorination analysis of powdered whole rocks from Franchi et al. (1999), show relatively restricted δ¹⁸O values from +4.2 to +5.2 ‰, consistent with the igneous origin of the samples and their variable primary mineralogy. The other above works report slightly offset (by up to ~0.3 ‰) but similar ranges in δ¹⁸O values, with interlaboratory differences probably attributable to slight sample heterogeneities and differences in reference gas calibration methods (Franchi et al., 1999). Δ¹⁷O values reported by Franchi et al. (1999) are very tightly clustered, with all 13 samples analyzed falling in a range of 0.30 to 0.34 ‰ (Fig. 7). Thus, all the martian meteorites fall on a common mass fractionation trend (the Mars silicate fractionation line or MSFL) with Δ¹⁷O = 0.32 ± 0.02 ‰, strongly supporting the hypothesis that these meteorites sample a common parent body. Again, these Δ¹⁷O values are consistent with previous whole-rock data (Clayton and Mayeda, 1983; Clayton and Mayeda, 1986; Clayton and Mayeda, 1996; Romanek et al., 1998), which are somewhat less precise. Given the ancient age of martian meteorite ALH84001 (4.5 Ga), and the large range in ages of the martian meteorites as a clan (from 180 Ma to 4.5 Ga; Jagoutz, 1991; Jagoutz et al., 1994; Nyquist
et al., 1995; Shih et al., 1982) the whole-rock oxygen isotopic data suggest that the lithosphere of Mars (here meaning the solid, rocky part of the outer planet) was isotopically homogenized very early in martian history.

Recent, more detailed investigations of oxygen isotopic compositions of martian meteorite components have focussed on secondary minerals and water contained in the samples. Studies that report analyses of all three oxygen isotopes consistently show that secondary minerals and water in the martian meteorites do not lie on the MSFL. Karlsson et al. (1992) observed elevated $\Delta^{17}O$ values, up to $+0.9 \%$e (or $\sim 0.6 \%$e above the MSFL) in water extracted by stepped heating from Nakhla, Lafayette and Chassigny, with the most pronounced effects observed in Nakhla. The water extracted from the shergottites generally records $\Delta^{17}O$ values between than the MSFL and the TF line. Farquhar and colleagues (2000; 1998) found $\Delta^{17}O$ values ranging from $+0.7 - 1.3 \%$e in carbonates and sulfates from ALH84001, Nakhla and Lafayette, also out of isotopic equilibrium with martian silicates. Secondary “iddingsite” in Nakhla, a mixture of secondary Fe-rich oxides, hydroxides and clays also show elevated $\Delta^{17}O$ of $\sim +1.4 \%$e (Romanek et al., 1998). Taken together, these analyses indicate that oxygen in the martian hydrosphere and lithosphere are not fully equilibrated. The most plausible hypothesis for the origin of the oxygen isotopic signature in secondary materials is that atmospheric mass independent isotopic effects, similar to those observed in a wide variety of terrestrial atmospheric species (see Thiemens, 1999 for a recent review), have been transferred to fluids in the martian hydrosphere that are sampled by the secondary minerals. This atmosphere-hydrosphere-lithosphere interaction is also indicated by hydrogen and carbon isotopic studies discussed below.

Oxygen isotopic compositions can also be used to gain insight into the environmental history of secondary materials in martian samples, similar to their use in terrestrial materials (although somewhat complicated by the observation that they are not strictly in isotopic equilibrium with their host rocks). In general the oxygen isotopic compositions of secondary carbonates and silicates have elevated $\delta^{18}O$ values relative to their host rocks, and the waters contained in the rocks (Carr et al., 1985; Clayton and Mayeda, 1988; Farquhar and Thiemens, 2000; Romanek et al., 1994; Romanek et al., 1998; Wright et al., 1988), suggestive of relatively low temperatures of formation. In the
one case where detailed in situ isotopic studies have been performed, however, the situation has proven to be quite complex. Carbonates in ALH 84001 show $\delta^{18}$O variation of ~20-25 ‰, from values of ~ 0 to +25 ‰ (Leshin et al., 1998; Saxton et al., 1998; Valley et al., 1997). These isotopic values correlate with mineral chemistry with the earliest-forming, Ca-rich carbonates having low the lowest $\delta^{18}$O values, and later-forming Mg-rich carbonates having the highest $\delta^{18}$O values. These very large isotopic effects are observed over distances of ~100 µm using ion microprobe techniques, and are explained as resulting from large temperature variations during carbonate formation, or fluid compositional variations either due to evaporation of a water-rich fluid or closed system evolution (Raleigh distillation) during carbonate formation from a CO$_2$-rich fluid. Comparable effects in secondary minerals from other martian meteorites have not been observed, although studies are much more limited.

Hydrogen isotopic systematics of bulk martian meteorites are reported by Leshin et al. (1996). Stepwise extraction of water from the samples generally shows terrestrial contamination at low temperatures (below 300-400 °C), and what is interpreted to be martian water, with elevated $\delta$D values, at higher temperatures. The high-temperature component ranges in $\delta$D from +50‰ for Chassigny to +2100 for Shergotty. All samples except Chassigny show a clear extraterrestrial signature in their bulk D/H values, and the Chassigny water arguably represents terrestrial contamination (Leshin et al., 1996). However, interpreting these values is complicated by the presence, probably to differing degrees, of addition of or isotopic exchange with terrestrial water, and by the varied geological history of these samples (e.g., differing degrees of interaction with groundwaters on Mars).

The D/H values of magmatic, hydrous minerals apatite, Ti-rich amphibole, and biotite have been analyzed in five martian meteorites by ion microprobe (Leshin, 2000; Rubin et al., 2000; Watson et al., 1994). The elevated and variable D/H values of water discovered in the minerals ($\delta$D~+800 to +4300) are interpreted qualitatively as representing a mixture of magmatic water in the minerals with a D-enriched component derived from the martian atmosphere (with a D/H value ~5 times terrestrial), through isotopic exchange with D-enriched groundwaters introduced after the phases crystallized. The presence of a "meteoric" (atmosphere-derived) D-rich component is also indicated by
ion microprobe analyses of carbonates in ALH84001, which have δD values up to 
~+2000 ‰ (Sugiura and Hoshino, 2000). The mixture between magmatic water and high
δD water is shown most quantitatively inapatite grains from shergottite QUE 94201
(Leshin, 2000). These data (shown in Fig. 8) show 2-component mixing, with the high-
δD component plausibly derived from the atmosphere (δD ~+4000 ‰), and the low-δD
component representing martian magmatic water. These data show that Martian
magmatic water has a D/H ratio of ~twice the terrestrial value, and is consistent with a
two-stage history of Martian volatiles where an initial D-enrichment of originally
"chondritic" water is achieved via early hydrodynamic escape, and the subsequent
enrichment to the current atmospheric value is achieved through Jeans (thermal) escape,
which continues today (Leshin, 2000).

There have been many reports of the abundances and $^{13}$C/$^{12}$C values of CO$_2$
extracted from SNC meteorites and their probable implications for the evolution of CO$_2$
on Mars (Carr et al., 1985; Clayton and Mayeda, 1988; Jull et al., 1997; Jull et al., 1995;
Leshin et al., 1996; Romanek et al., 1994; Wright et al., 1986; Wright et al., 1988; Wright
et al., 1990; Wright et al., 1992). These studies suggest the presence of three main
carbon-bearing components in SNC meteorites, distinguished by their temperature of
release (or release by reaction with orthophosphoric acid) and their δ$^{13}$C\textsubscript{PDB}. The first
component, released at temperatures below ~500°C, is interpreted as low-temperature
carbonaceous material mostly from contamination by terrestrial organic matter but
possibly mixed with extraterrestrial organics. This component has a δ$^{13}$C of -20 to -30
‰ (Carr et al., 1985; Grady et al., 1994; Jull et al., 2000; Jull et al., 1998; Leshin et al.,
1996; Wright et al., 1986; Wright et al., 1992). The second carbon-bearing component,
released between 400 and 700°C in heating experiments, or by reaction of samples with
orthophosphoric acid, originates from breakdown of carbonate. This component is
associated with $^{13}$C–enriched CO$_2$ in several of the Martian meteorites: in Nakhla it has
δ$^{13}$C up to ~+35 ‰ (Carr et al., 1985; Jull et al., 1995; Leshin et al., 1996; Wright et al.,
1992); in orthopyroxenite ALH84001 it has δ$^{13}$C up to +42 ‰ (Grady et al., 1994; Jull et
al., 1997; Jull et al., 1995; Leshin et al., 1996; Romanek et al., 1994). The $^{13}$C –enriched
nature of this component provides strong evidence of a preterrestrial origin (since
terrestrial carbonates generally have δ$^{13}$C near or slightly below zero). The third
component consists of carbon released at temperatures above 700°C, generally with $\delta^{13}\text{C}$ values of -20 to -30‰, and has been interpreted as a "magmatic" carbon component representative of the isotopic composition of CO$_2$ in the martian interior (Carr et al., 1985; Wright et al., 1986; Wright et al., 1990; Wright et al., 1992). If the high-temperature fraction discussed above really does represent magmatic carbon, the $\delta^{13}\text{C}$ value of -20 – -30‰, which could represent the martian "primitive" value given the probably lack of plate tectonics on Mars, is distinct from the proposed value for terrestrial carbon bulk $\delta^{13}\text{C}$ (-5‰). However, it remains difficult to rule out the concern that this value represents terrestrial organic contamination that lingers even to high temperature in the bulk heating experiments.

Taken together the stable isotopic data on all martian meteorite components produce a relatively coherent picture of martian volatile cycles. The solid planet was isotopically homogenized very early in martian history, as evidenced by the homogeneity of the $\Delta^{17}\text{O}$ values of the igneous silicates in samples which range in age from 4.5 to 0.18 Ga. Atmospheric C, H and O isotopic signatures are preserved in many phases in martian meteorites, thus the crustal and atmospheric volatile reservoirs are clearly in isotopic communication. Martian atmospheric plus crustal volatile reservoir is clearly not in isotopic equilibrium with the planetary interior based on the $\delta\text{D}$, $\delta^{13}\text{C}$, and $\Delta^{17}\text{O}$ measurements discussed above, which preserve a degree of isotopic heterogeneity unmatched in any suite of terrestrial igneous rocks. The lack of equilibration of the crustal and interior volatile reservoirs argues against a large degree of crustal recycling on Mars.

**Unresolved issues and future directions**

We have attempted a review of a small portion of a rapidly developing field, one which is poised to achieve breakthroughs on several problems of fundamental importance for understanding the formation and evolution of our planetary system. We fully expect that this review will quickly become obsolete as an overview of current ideas because of the new discoveries that are clearly on the horizon. After a decade of rapid progress, laboratory techniques for the precise measurement of stable isotope abundances at an appropriate scale of spatial resolution or sensitivity for specific compounds in many
extraterrestrial materials are operational in a couple of dozen laboratories worldwide, and new developments are underway in anticipation of the first returned samples from known extraterrestrial bodies in more than a generation. First order discoveries await with respect to solar isotopic abundances (Genesis mission), the correlated isotopic and mineralogic compositions of known cometary dust particles (Stardust mission), and, hopefully, sample returns from asteroid(s) and from Mars. Other important advances can be anticipated in the near term through application of the maturing techniques of laser and ion microprobe stable isotope analysis, among others, to samples already in hand. We close by noting some of the more significant outstanding problems which we expect will occupy the creative energies of that cadre of isotope geochemists who turn their instruments on the strange and wonderful materials which come to us from the heavens.

- Origin and distribution of the oxygen isotopic anomaly: It is presently unclear whether the premier isotopic anomaly in meteorites is ultimately due to early solar system chemistry or to stellar nucleosynthesis. The resolution of this issue has first-order astrophysical implications for the origin of the solar system. Because oxygen is the dominant rock-forming element, and the oxygen isotopic anomaly is even manifest on a planetary scale within at least the inner solar system, if it turns out that this effect is ultimately due to symmetry dependent non-equilibrium chemistry, this would represent a major process during solar system formation about which we know precious little.

- Origin of Solar System water: Assessment of the degree the isotopic variability of water on various solar system bodies is essential to understanding the origin of water in our Solar System. Remote isotopic analysis of water (and other species) from more comets, as well as the analysis of returned, pristine cometary samples is required. Further analysis of meteorite samples with modern analytical techniques is also crucial. Specifically, H isotopic variability of water over µm-scales in primitive meteorites must be confirmed by further analysis, because it is this observation that is driving the direction of models of water evolution in the Solar System.
• The Origin of the Moon and planets: High precision laser fluorination 3-oxygen isotopic analyses of lunar materials could put stringent constraints on the composition of the hypothesized Giant Impactor. Similar isotopic analyses of samples returned from Mars would quickly confirm (or not) the hypothesis that the Martian Meteorites are indeed samples of our planetary neighbor. Returned samples from Venus and Mercury would permit complete examination of O isotopic heterogeneity in the inner solar system, and would allow hypotheses about the mixing of materials in the inner solar system during planetary formation to be tested. In addition such data could hold important clues to the origin of the O isotope anomaly.

• Mars Astrobiology: Understanding the distribution of water on Mars is key to assessing Mars' biological potential. Further H isotopic studies are needed to address the origin of isotopic variations observed in several martian meteorites. Carbon reservoirs on Mars also need to be explored, as C isotope data are currently limited predominantly to stepped heating analyses of bulk samples. Isolation and isotopic analysis of C carriers in Martian Meteorites is an important step towards understanding the origin of the isotopic variation observed in bulk samples. Stable isotopic analysis will obviously play a key role in study of any Mars samples returned by spacecraft. Such analyses will ultimately be needed to unravel decisively the origin, distribution, and history of Martian volatiles.
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Figure Captions:

Fig 1. (a). Schematic representation of the traditional 3-isotope plot for oxygen with $\delta^{18}O$ on the abscissa and $\delta^{17}O$ on the ordinate. On such a plot, mixtures of 2 isotopic reservoirs (e.g., A and B) lie on a straight line connecting the end-member compositions. Most chemical reactions partition isotopes in a mass-dependent manner which, for small degrees of fractionation, results in a dispersion along a line of slope $= 0.52$. All terrestrial rocks and fluids lie on such a fractionation line (TF), passing through the origin defined by standard mean ocean water (SMOW). The deviation of a point above or below the TF line is expressed by $\Delta^{17}O$ which indicates the difference between its $\delta^{17}O$ value and the $\delta^{17}O$ of a point on the TF line at the same value of $\delta^{18}O$. Components which are fractionated from a homogeneous reservoir only by normal, mass-dependent processes lie on a line of slope $= 0.52$ that is parallel to the TF line, and hence such compositions are characterized by a constant $\Delta^{17}O$ value. (b). Alternate representation of the same oxygen 3-isotope data with $\delta^{18}O$ remaining on the abscissa and $\Delta^{17}O$ now plotted on the ordinate. Compositions which are related by mass-dependent fractionation to a common reservoir plot on horizontal lines with the degree of mass fractionation indicated by the difference in their $\delta^{18}O$ values. Mixing lines between unequilibrated compositions can still exhibit any possible slope in this representation.

Fig. 2. Oxygen isotopic compositions of the nebular components of chondrites plotted on the traditional 3-isotope diagram. Shown are high precision ‘bulk’ and mineral separate analyses [data sources: Bridges et al., 1998, Clayton and Mayeda, 1977, Clayton et al., 1977, 1983, 1984, 1991; Davis et al., 1991; Gooding et al., 1983; Lee et al., 1980; Li et al., 2000; Mayeda et al, 1986; Rubin et al., 1990; Weisberg et al., 1991] of individual CAIs and chondrules from the three main chondrite classes: ordinary (OC), enstatite (EC), and carbonaceous (CC). The $^{16}$O-mixing line discovered by R. Clayton and colleagues (CLAYTON et al., 1973) from analyses of anhydrous minerals from carbonaceous chondrites is indicated as ‘CCAM’. The majority of CAIs analyzed from the Allende (CV3) meteorite plot on this line, but data from 6 so-called FUN CAIs fall significantly to the right of CCAM.
Fig. 3. Oxygen isotopic compositions of minerals in CAIs. (a). Data obtained by the BrF₅ method on ~mg quantities of mineral separates from coarse-grained type B inclusions from Allende (data sources: CLAYTON et al., 1977; MAYEDA et al., 1986). To facilitate comparison with the ion microprobe, only data for relatively pure mineral separates are plotted; error bars are smaller than the symbol sizes. (b). Ion microprobe in situ data for minerals of Allende 3529-Z, a coarse-grained type B CAI; error bars are 1σ (McKEEGAN et al., 1996 and unpublished data). (c). Ion microprobe measurements of mineral phases in the interior and rim phases of inclusion 1623-3, a coarse-grained type A CAI from the reduced CV3 chondrite Vigarano (McKEEGAN et al., 1998a). (d). Ion microprobe measurements of individual mineral phases in Allende 7R-19-1 (YURIMOTO et al., 1998).

Fig 4. (a). Oxygen isotopic compositions of FUN inclusions from the CV3 chondrites Allende and Vigarano obtained by gas-source mass spectrometry [data sources: Clayton, 1984 #273; Clayton, 1977 #128; Lee, 1980 #275]. Isotopic mixing arrays are seen for 4 FUN CAIs for which mineral separates or different aliquots were analyzed (for CG-14 and Vigarano 1623-5 only bulk data exist). The dashed line indicates a hypothetical mass fractionation line from through an estimate of the 16O-rich terminus of each individual mixing line. (b). Oxygen isotope compositions of individual minerals in FUN CAI Vigarano 1623-5, obtained by ion microprobe (DAVIS et al., 2000). Olivine – pyroxene – spinel define a mass fractionation trend close to the postulated initial FUN line, whereas melilite exchanged oxygen isotopes to a more 16O-poor composition compatible with melilite in other FUN CAIs and ‘normal’ CAIs.

Fig 5. (a). Secondary electron micrograph (SEM) of a central region of Allende 3529-Z showing ion microprobe sputtered holes in a large melilite crystal that encompasses a cluster of spinel grains which, in turn, surround a pocket of late-crystallizing fassaite. Analysis spots are labeled by their Δ¹⁷O values; typical 1σ uncertainties are ~1‰ (unpublished data from the UCLA laboratory). (b). Backscattered electron image of a portion of the rim sequence surrounding Vigarano 1623-2, a Type A CAI, showing the
locations of 3 ion probe craters where oxygen isotope compositions were determined (McKeegan et al., 1998a). Shown are $\delta^{18}O$ values (typical errors are ~1‰) indicating large isotopic heterogeneity (along a slope ~1 mixing line) between different mineral phases in the Wark-Lovering rim sequence. The inclusion interior is toward the top of the image; the light-gray material at the top is melilite.

Fig. 6. Oxygen isotopic composition of whole-rock chondrites according to group. Plotted are $\Delta^{17}O$ vs. $\delta^{18}O$ obtained by the BrF$_5$ method; most data are obtained in the laboratory of R. Clayton [data sources: Bischoff et al., 1993; Clayton and Mayeda, 1984, 1999; Clayton et al., 1976, 1977, 1984, 1991, 1995; Rowe et al., 1994; Rubin et al., 1983; Weisberg et al., 1993] with error bars generally similar to the symbol sizes. Each meteorite group occupies a distinctive field on this diagram enabling oxygen isotope compositions to be used as a classification tool, although there is a significant degree of overlap between certain groups (e.g., CV-CO-CK, and CR-CH) possibly indicating genetic affinities. On this plot, mass-dependent fractionation lines are horizontal. The carbonaceous chondrite anhydrous minerals [CCAM; \Clayton, 1977 #120] and Young & Russell [YR; \Young, 1998 #446] mixing lines are indicated.

Fig. 7. Laser fluorination analyses of whole-rock Martian (SNC) Meteorites after Franchi et al. (1999). The data demonstrate that the meteorites sample a common parent body with a $\Delta^{17}O$ value of +0.32 ‰.

Fig. 8. D/H and water contents of apatite grains from Martian Meteorite QUE94201 after Leshin (2000). The data are interpreted to represent a mixture of two end members, and most plausibly represent addition (or exchange) of water with an atmospheric D/H signature ($\delta D$~+4000‰) to minerals which initially uniformly contained water with $\delta D$ of ~+900±250‰, or ~twice the D/H value commonly assumed for magmatic water on Mars. The curve shows the mixing model from which the initial D/H of the minerals was calculated.
Fig. 1
Fig. 2
Fig. 4
Fig. 5a  (to be redone)

Fig. 5b
Oxygen isotope compositions of whole-rock chondrites

Fig. 6
Fig. 7

\[ \Delta^{17}O_{\text{Mars}} = 0.321 \pm 0.013 \, \text{‰} \]
Fig. 8