

EXTRATERRESTRIAL MATERIALS

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Chapter 13

EXTRATERRESTRIAL MATERIALS

13.1 Introduction

Some of the earliest problems addressed with stable isotope chemistry involved the origin and heterogeneities of the solar system. Hyperbolic orbits identified (erroneously) for certain meteorites suggested that there might be matter from outside the solar system that ultimately reached the Earth. Early attempts to find exotic carbon, oxygen and chlorine isotope ratios in meteorites failed (Harkins and Stone, 1926; Manian et al., 1934; Jenkins and King, 1936), in part because precision of the measurements was not sufficiently high at the time, and also because the anomalous material that does exist was simply not analyzed. Hydrogen isotope analyses followed in the 1950's, when δD values approaching 300‰ from the carbonaceous chondrites Ivuna and Orgueil were measured (Boato, 1954). Additional isotopic systems were studied in the coming decades, including sulfur (Trofimov, 1949), nitrogen (Injerd and Kaplan, 1974) and carbon (Krouse and Modzeleski, 1970). There was a flurry of interest in lunar materials when Apollo samples were returned to Earth. Most lunar samples had $\delta^{18}O$ values very similar to equivalent terrestrial rock types, indicating a close genetic relationship between Earth and Moon. Then in 1973, Clayton *et al.* (1973) published a paper that completely changed the meteorite community. For the first time, an 'exotic' stable isotope component in meteorites had clearly been identified. From then on, stable isotope geochemistry has become one of the most important tools for constraining mechanisms of formation and history of the early solar system.

There are no distinct boundaries between traditional earth sciences, cosmochemistry, space sciences and astrophysics, and so it is difficult to limit the scope of this chapter. For example, the isotope chemistry of interstellar grains (Anders and Zinner, 1993; Nittler, 2003) is important in the study of nucleosynthesis and stellar evolution. And, at the other end of the spectrum, the chemistry of certain meteorite types is used to estimate the bulk chemical composition of the Earth. This data are then applied to terrestrial studies completely unrelated to meteorite research. All of these fields overlap one other to a certain extent. In this chapter we will limit our examinations to more traditional meteorite research. Readers interested in processes of star formation and nucleosynthesis of elements and their isotopes are referred to Anders and Zinner (1993, in appendix) and Nittler (2003) for a review and additional references. It must be stressed that the 'normal' stable isotopes (H,C,N,O,S) are not used independently of other isotopic systems, such as noble gas, non-traditional isotopes (*e.g.*, Mg, Si), and short-lived radiogenic isotopes. But again, discussion of these systems is beyond the scope of this chapter. Further information beyond the short review here can be found in Clayton (1993) for oxygen isotopes and McKeegan and Leshin (2001) for H, C, N, O stable isotope systems.

13.2 Classification of meteorites

The alphabet soup of meteorite names can be very confusing to the uninitiated, but is really not complex after a simple review. Table 13.1 and Fig. 13.1 illustrate the basic classification of meteorites.

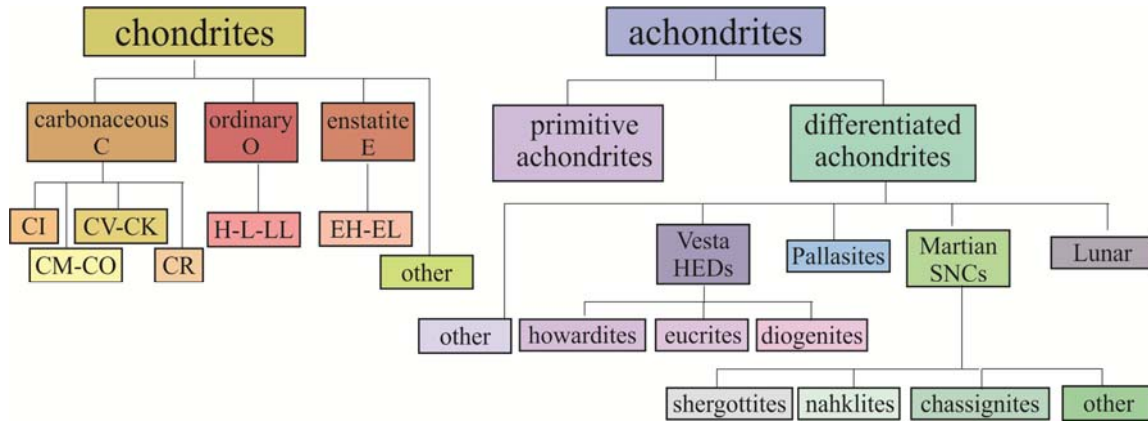


Fig. 13.1. Simplified meteorite classification. Meteorites are divided into chondrule-bearing chondrites and chondrule-free achondrites. The chondrites are further divided into carbonaceous, ordinary and enstatite chondrites. Achondrites include differentiated bodies including samples from the bodies 4-Vesta, Mars, and Moon.

The primary division of meteorites is between chondrites and achondrites. Chondrites contain chondrules¹ embedded in a fine-grained matrix. Chondrules are spherules of olivine and/or pyroxene with or without glass and metal inclusions thought to have formed by melting of nebular dust during flash heating. The fine-grained interstitial matrix consists of silicates, oxides, metal, sulfides and organic matter. The chondrites are considered to be agglomeration of rocky and icy material from unprocessed remnants of planetesimals from the asteroid belt. Chondrites also contain interstellar grains, calcium-aluminum inclusions (CAIs), and other refractory primitive objects. Achondrites are more processed material, often representing crustal magmatic or metamorphic rocks from dismembered planetesimals. Achondrites have undergone planetary differentiation, where early heating by radioactive decay of short lived isotopes caused segregation between an iron-rich core and silicate mantle. **Iron meteorites** are the fragments of the cores of asteroids/planetesimals. **Stony iron meteorites**, such as pallasites, may be core-mantle boundary material, and **stony meteorites** are considered to be silicate mantle material of a segregated body. The origin of many achondrites can be attached to one of several large bodies, including Mars (the SNC meteorities), the Moon, and the asteroid 4 Vesta (HED² meteorites).

¹ CI chondrites have been so heavily aqueously altered on their parent body that no chondrules survive. Nevertheless, they come from a parent body that contained chondrules and did not go through differentiation.

² Howardites, Eucrites and Diogenites

Table 13.1. Classification of different meteorite types (Brearley and Jones, 1998; Shearer et al., 1998).

Name	Mineralogy	Source	
Iron meteorites	Iron-nickel metal; iron sulfide	Cores of disrupted asteroids	Groups distinguished by trace element abundances and textures
Stony-iron meteorites-pallasites mesosiderites	Roughly equal proportions of Fe,Ni-metal and silicate	Core-mantle boundary of disrupted asteroids?; impacts on asteroids	
Stony meteorites - achondrites			
Basaltic achondrites-howardites eucrites diogenites	Pigeonite-plagioclase-bearing basalts, orthopyroxenites, or mélange of each	Thought to be a basaltic magma system from asteroid 4 Vesta	Distinguished from other achondrite groups on the basis of oxygen isotopes
Other achondrites-aubrites, ureilites, angrites, etc.	Exotic basalts and related igneous rocks	Main belt differentiated asteroids	Each group distinguished on the basis of oxygen isotopes
Martian meteorites (SNC meteorites) – Shergottites, nakhlites chassignites, other	Magmatic basalts, lherzolites, clinopyroxenites, orthopyroxenite, dunite	Mars	Young (most <1.3Ga) (<i>ALH84001 is 4.5 Ga</i>). Characteristic stable and rare gas isotope ratios
Lunar	Basalts, anorthosites, and lunar breccias	Moon	Compare closely with returned samples from the Apollo and Luna missions.
Stony meteorites – chondrites			
Agglomeratic rocks containing rocky and metallic materials. Unprocessed remnants of planetesimals from the asteroid belt. Some of the least processed material in the solar system. Consist of high-temperature chondrules hosted in a fine-grained matrix which represents low-T fraction of nebular material. Also contain interstellar grains, calcium-aluminum inclusions (CAIs), and other refractory objects. Groups are distinguished by chemistry and oxygen isotope ratios. Divided into types 1-6, where 3 is least altered, 2 and 1 are higher levels of low-T aqueous alteration and 4-6 are increasing levels of thermal metamorphism.			
Carbonaceous or C chondrites	8 groups – CI, CM, CR, CV, CO, CK, CH, CB; named after type fall-locality.		
Ordinary or O chondrites	3 groups – H, L and LL: H – high total Fe content; L – low total Fe content; LL – low metallic Fe		
Enstatite or E chondrites	2 groups – EH, EL: EH – high total iron; EL – low total iron		
Other classes	Rumuruti-like (R), Kakangari-like (K), Tagish Lake		
Other extraterrestrial material			
Interplanetary dust particles (IDPs)	Divided into chondritic and non-chondritic types	Active periodic comets from Oort cloud and Kuiper belt.	Primordial ‘icy dust balls’ (Rietmeijer, 1998). Average size is 10µm

13.3 Oxygen isotopes in the solar system

13.3.1 Introduction

The pioneers of fluorination included meteorites (or tektites) in their rock suites to fill out the general overview of natural oxygen isotope variations (Baertschi, 1950;

Silverman, 1951). Vinogradov *et al.* (1960) measured a suite of meteorites using the method of carbon reduction and found noticeable, but small $\delta^{18}\text{O}$ variations between different types. Similar conclusions were reached in a later thorough examination of different meteorite types (Reuter *et al.*, 1965). Silicate separates from 27 chondrites varied by only 1.2‰. Chondrules had the same values as the whole rock. Pallasites were several per mil lower than the chondrites, but overall, it appeared that meteorites were not particularly interesting from a stable isotope viewpoint. In the same year, the same group (Taylor *et al.*, 1965) found much larger variations in chondrites when they measured only pyroxene and not olivine³. Now the variations were larger; 9‰ for pyroxenes and 13‰ between different bulk rock samples. They developed a meteorite classification scheme of three groups with distinct $\delta^{18}\text{O}$ values.

The return of the Apollo lunar samples led to a flurry of activity by a number of stable isotope laboratories in the United States (e.g., Epstein and Taylor, 1970; Friedman *et al.*, 1970; Onuma *et al.*, 1970; Kaplan and Petrowski, 1971). It was quickly recognized that the $\delta^{18}\text{O}$ values of lunar basalts and anorthosites were the same as terrestrial equivalents⁴. These data demonstrated that the Earth and Moon were closely related, but said little about the genesis of the solar system.

13.3.2 Discovery of an ^{17}O anomaly

The importance of oxygen isotope geochemistry as it pertained to meteorites was recognized when Clayton *et al.* (1973) made one of the most striking discoveries in the field of planetary science. They analyzed anhydrous high temperature phases (calcium aluminum inclusions, or CAIs) from carbonaceous chondrites, mostly Allende (which had only fallen to Earth on Feb. 8, 1969, in Chihuahua, Mexico⁵). The range of $\delta^{18}\text{O}$ values was extraordinary, covering over 30‰. This in itself was far more than anyone had measured previously. But as a result of their extremely careful analytical procedure, Clayton's group found something else that was far more surprising – namely that the $\delta^{17}\text{O}$ values of these primitive samples varied in a non-mass dependent way. This discovery was made not by measuring the $\delta^{17}\text{O}$ values directly, but rather by noting that the 'apparent' $\delta^{13}\text{C}$ values of the CO_2 gas that they were analyzing was not constant. The reason and significance is worth the short explanation in the following paragraphs.

The Chicago group analyzed silicates by reacting them with BrF_5 at high temperatures⁶. The evolved oxygen was converted to CO_2 by reaction with spectroscopic graphite at high temperatures and the CO_2 was analyzed for its $\delta^{18}\text{O}$ value. This was standard procedure in most laboratories at the time. What was unusual in the Allende samples was that there was a systematic variation in the apparent $\delta^{13}\text{C}$ value of the CO_2 gas that correlated with the measured $\delta^{18}\text{O}$ value. This was puzzling because the two isotopic systems carbon and oxygen are independent of each other. The carbon comes from the graphite rod and should have a constant value, whereas the oxygen is derived

³ Olivine is a notoriously difficult mineral to fluorinate using conventional methods. See 11.2.1 for more details.

⁴ Later analyses confirmed that $\delta^{17}\text{O}$ values were also identical to terrestrial ones (Clayton and Mayeda, 1975).

⁵ The other important CC meteorite that was analyzed was Murchison, which fell in Australia only a few months later.

⁶ A typical reaction would be $2 \text{MgSiO}_3 + 12/5 \text{BrF}_5 \rightarrow 2 \text{MgF}_2 + 2 \text{SiF}_4 + 6/5 \text{Br}_2 + 3\text{O}_2$.

from the fluorinated silicate. The three isotopologues of CO₂ have masses of 44 (¹²C¹⁶O₂), 45 (¹³C¹⁶O₂ and ¹²C¹⁶O¹⁷O) and 46 (¹²C¹⁶O¹⁸O) ⁷. In almost all known chemical fractionation mechanisms, the following relationship is valid

$$\left(\frac{^{17}\text{O}}{^{16}\text{O}}\right) \approx \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)^{0.52} \quad 13.1,$$

which translates to $\delta^{17}\text{O} \approx 0.52(\delta^{18}\text{O})$. (See section 3.7 for details about the three isotope system). Normally, there is no reason to measure the $\delta^{17}\text{O}$ value of a sample, because it varies with $\delta^{18}\text{O}$ according to equation 13.1. By subtracting out the ¹⁷O contribution to the mass 45 isotopologue of CO₂ – the so-called ¹⁷O correction – we can calculate the $\delta^{13}\text{C}$ value of CO₂ gas from the 45/44 ratio. Clayton *et al.* noticed that the calculated $\delta^{13}\text{C}$ values were changing in concert with the $\delta^{18}\text{O}$ values. What they were actually measuring, and quickly realized, was that the variations in the 45/44 ratio were ¹⁷O/¹⁶O ratios that did not conform to equation 13.1. When plotting $\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ (assuming that the ¹³C/¹²C ratio was constant), the chondrite data did not plot on the normal *Terrestrial Fractionation Line* (TFL) with slope of ~0.52 as is seen for almost all materials in the

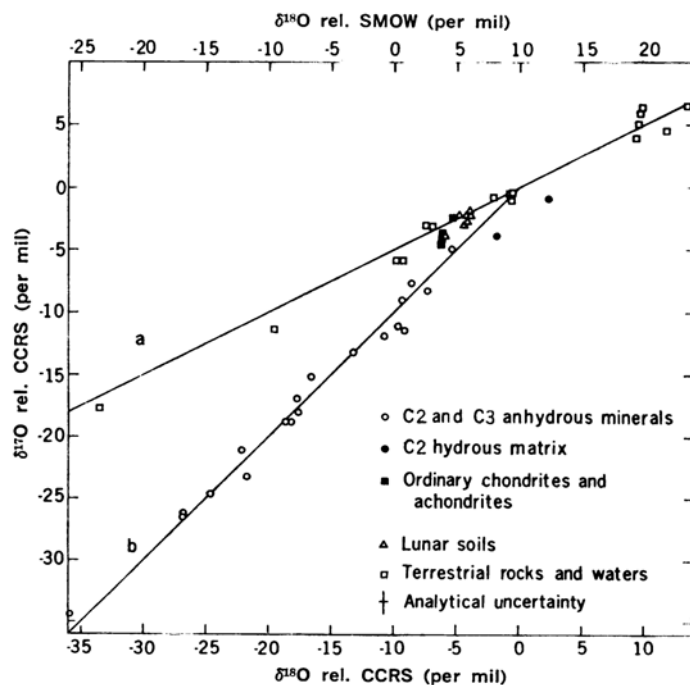


Fig 13.2. Plot of $\delta^{17}\text{O}$ vs $\delta^{18}\text{O}$ values for anhydrous (high T) chondritic samples (open circles), aqueously altered chondritic samples (filled circles) and terrestrial material. The chondrite data plot with a slope 1, whereas the terrestrial samples plot on the terrestrial fractionation line (TFL) (slope ~1/2). All data are plotted relative to a carbonaceous chondrite reference standard (CCRS) defined as the intersection of the slope 1 line from chondrite data with the TFL. Plotted in this way, the chondrite data are explained in terms of mixing between two components; a nebular gas near CCRS and a very ¹⁶O enriched source, possibly from outside the solar system. Reprinted from Clayton *et al.* (1973) with permission. Note that by defining their data in terms of the carbonaceous chondrite reference standard (CCRS), the mixing line b in figure 13.1 meets the criterion $\delta^{17}\text{O} = \delta^{18}\text{O}$.

Box 13.1 The three isotope plot for oxygen.

All chemical fractionation processes (except for certain photochemical effects) fractionate the three isotopes of oxygen according to equation 13.1. On the three isotope plot $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$, this leads to all data defining a $\delta^{17}\text{O}/\delta^{18}\text{O}$ slope of ~ 0.525 (mass fractionation line – *mfl*). All terrestrial samples plot on a *mfl* which approximately intersects $\delta^{17}\text{O} = \delta^{18}\text{O} = 0\text{‰}$ (vs. SMOW) and is called the *Terrestrial Fractionation Line (TFL)*. Any object that undergoes mass dependent fractionation will spread out on a *mfl* line, illustrated by the dashed line with slope 0.52 emanating from point *a*. Mixing between two reservoirs with distinct $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values will result in samples plotting on a straight line, whose slope is defined by the compositions of the two endmembers. The mixing line of slope 1 could be explained by mixing between an average nebular composition given by CCRS in Fig. 13.1 and a second component rich in ^{16}O . How far a sample plots off the *TFL* line is defined in terms of $\Delta^{17}\text{O}$ by the equation $\Delta^{17}\text{O} = \delta^{17}\text{O} - (0.52x)\delta^{18}\text{O}$. The inset box shows the $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values of samples from Mars. They plot on a *mfl* with a $\Delta^{17}\text{O}$ value of $+0.3\text{‰}$.

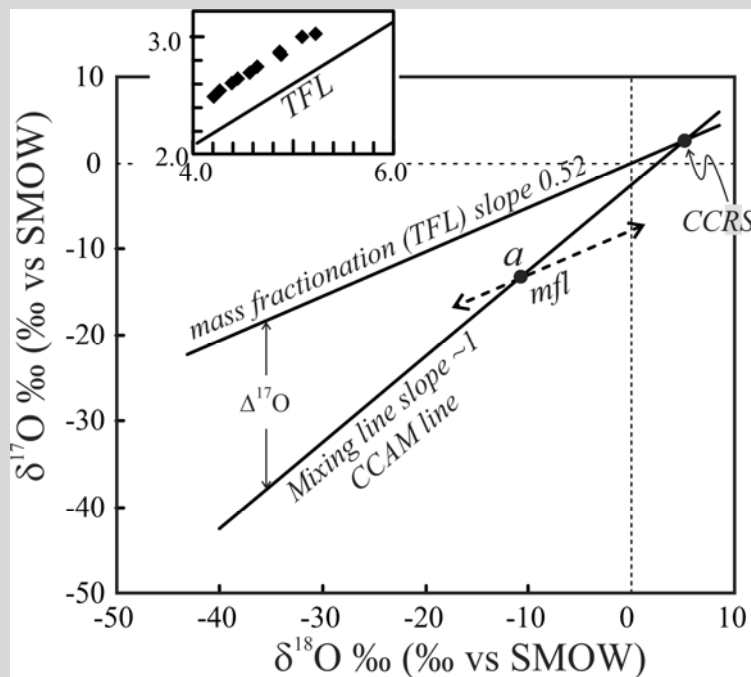


Fig. B.13.1.

Earth and Moon, but rather on a slope 1 line, below the TFL line (Fig. 13.2). (See Box 13.1 for discussion of $\delta^{18}\text{O}$ vs $\delta^{17}\text{O}$ plots).

13.3.3 Possible explanations: mixing of two distinct reservoirs

Clayton *et al.* interpreted their data as evidence for mixing between two distinct reservoirs: the first was the heavy nebular (solar) reservoir and the second was a primitive, pre-solar ^{16}O -rich dust source that originated outside of the solar system.

Clayton *et al.* postulated that the ^{16}O -rich component was probably extremely impoverished in ^{17}O and ^{18}O , as might be expected from oxygen formed from a young helium burning star, where only ^{16}O is produced. Clayton (1993) assigned $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values to the solar nebula of 24.2 and 30‰, respectively while the light exotic dust component had $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of a composition with $\delta^{18}\text{O} = \sim -42\%$, and $\sim -40\%$. A linear trend is seen in the triple oxygen isotope data of CAIs with a slope of 0.96, resulting from simple mixing between the ^{16}O -rich and nebular components.

The original ‘mixing of two reservoirs’ explanation for the oxygen isotope trends in early-formed material has some inconsistencies, which alternative models have sought to explain. Some of the concerns are the following:

- If the ^{16}O -rich component formed by stellar nucleosynthesis of helium burning, then the $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values should correlate with other isotope systems, such as Mg and Si. However, no such correlations are found.
- The presolar component should be nearly pure ^{16}O . However all measurements of CAI inclusions have $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values that ‘bottom-out’ around -50 to -40‰ (McKeegan and Leshin, 2001). Only presolar grains have lower values (Nittler *et al.*, 1997; Amari, 2014), but the estimated abundance of such grains is less than 0.25 parts per billion. If the exotic ^{16}O rich source was not pure ^{16}O , then why is the $^{18}\text{O}/^{17}\text{O}$ ratio the same as the solar nebular value (thereby giving the slope 1 line)?
- If an ^{16}O -rich melt exchanged with the solar nebular gas during crystallization, the degree of ^{17}O and ^{18}O enrichment should correlate with the order of crystallization, which is not the case. Melilite has the highest $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values, but should crystallize before pyroxene (Stolper, 1982). Alternatively, exchange with the heavy nebular gas occurred by diffusion. Appropriate diffusion data are not sufficient to properly evaluate this possibility.

13.3.4 Mass-independent fractionation

An alternative to the two reservoir mixing hypothesis was born when Thiemens and Heidenreich (1983) discovered that ozone (O_3) produced by dissociation of molecular oxygen (O_2) in a high frequency discharge occurred with a mass-independent fractionation. The $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values of the residual oxygen and newly-formed ozone plot on a slope 1 line (Fig. 13.3), nearly identical to the slope for carbonaceous chondrite mineral inclusions found by Clayton *et al.* (1973).

Thiemens and Heidenreich initially suggested a mechanism of optical self-shielding to explain the mass-independent fractionation. O_2 gas undergoes strong absorption of ultraviolet light by the Schumann-Runge absorption bands between $1.76 \times 10^{-7}\text{m}$ and $1.926 \times 10^{-7}\text{m}$, causing photodissociation of O_2 . The absorption bands are slightly different for ^{16}O - ^{16}O and the other isotopologues ^{17}O - ^{16}O and ^{18}O - ^{16}O . Because $>99.5\%$ of O_2 consists of $^{16}\text{O}_2$, radiation corresponding to $^{16}\text{O}_2$ will strongly be absorbed (or self-shielded), so that only the wavelengths absorbed by ^{17}O - ^{16}O and ^{18}O - ^{16}O will filter through to the center of the reaction chamber. These UV rays will then cause mass-independent dissociation of the rare isotopologues ^{17}O - ^{16}O and ^{18}O - ^{16}O . The dissociated ^{17}O and ^{18}O ultimately react with $^{16}\text{O}_2$ to form ozone. Figure 13.3 shows the ozone

enriched in the heavy isotopes and the residual O_2 with preferential removal of ^{18}O and ^{17}O .

More recently, it has been shown that it is the role of symmetry that is the primary cause of the non-mass dependent fractionation (e.g., Michalski and Bhattacharya, 2009). The O_2 starting material is photodissociated by UV radiation. The O radicals react with surrounding O_2 to O_3 via a metastable transition state. The stability of the transition state is function of the symmetry. Highly symmetric transition state $^{16}O_3$ is less stable than $^{16}O-^{16}O-^{17}O$ and $^{16}O-^{16}O-^{18}O$, both of which have a lower symmetry. As a consequence, stable O_3 is enriched in both of the rare isotopes without distinction between ^{17}O and ^{18}O .

The data therefore define a MIF line with a slope of 1. Such ^{17}O and ^{18}O enriched O_3 is observed in the stratosphere (Thiemens, 2006). The positive anomaly of stratospheric O_3 is counterbalanced by a marked negative anomaly of tropospheric O_2 (Luz et al., 1999).

Mass independent isotope fractionation has been predicted to occur in interstellar clouds by the process of self-shielding. Some interstellar clouds appear to be enriched in ^{13}CO by a factor of 2.3 compared to the Sun. Langer (1977) suggested that the enrichment is the result of self-shielding in the interstellar clouds. Bally and Langer (1982) showed that the CO gas of interstellar clouds is enriched in ^{16}O as well.

The idea behind the self-shielding hypothesis is the following: CO is dissociated by distinct frequencies of UV radiation. The molecular cloud would be more opaque to the frequencies absorbed by $C^{16}O$ rather than $C^{17}O$ and $C^{18}O$ due to the former's much higher concentration. Radiation that is only absorbed by the rare isotopologues is able to penetrate far more deeply into the molecular cloud. As a result, only the rare isotopes $C^{17}O$ and $C^{18}O$ are dissociated in the cloud's interior. The oxygen produced by this dissociation then combines with hydrogen to produce ^{17}O - and ^{18}O -enriched water ice, which ultimately becomes incorporated in solid phases (Yurimoto and Kuramoto, 2004). Chakraborty *et al.* (2008) suggested that self-shielding was not necessary, arguing that the ^{17}O and ^{18}O enrichment in CO could be due to a stronger coupling coefficient, in which $C^{17}O$ and $C^{18}O$ are more efficiently dissociated than $C^{16}O$. This idea has been questioned (Lyons et al., 2009), but regardless of the actual mechanism, preferential photodissociation of $C^{17}O$ and $C^{18}O$ in the molecular cloud can lead to ^{17}O - and ^{18}O -

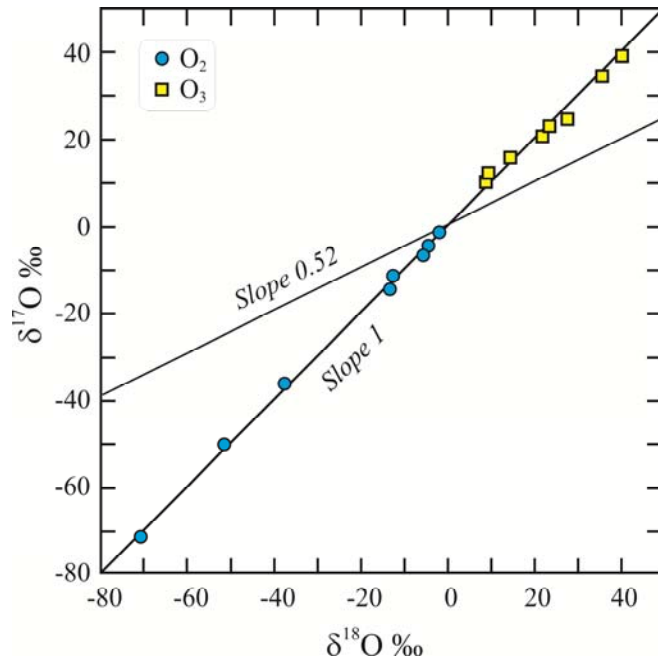


Fig. 13.3. $\delta^{18}O$ - $\delta^{17}O$ values of O_2 and O_3 during ozone formation by high-frequency discharge. The product ozone is enriched in both ^{17}O and ^{18}O by a mass-independent mechanism, which was believed to be due to self-shielding (Thiemens and Heidenreich, 1983).

enriched H₂O. The H₂O is ultimately incorporated in chondrites which will lead to a heavy oxygen component relative to the overall nebular value.

With the new model, we would expect the solar nebula and Sun to have $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ values of $\sim -50\%$, in contrast to the Clayton mixing model where the solar component is the heaviest ($> +20\%$). Evidence for a low $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ solar wind was found by Hashizume and Chaussidon (2005), who measured the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of solar energetic particles that had been implanted in metal grains on the lunar regolith. The measured $\Delta^{17}\text{O}$ value of the solar particles was $-33\pm 16\%$, corresponding to a protosolar nebula of $\sim -67\%$ for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ (when appropriate fractionations are considered). More recently, direct analysis of solar wind implanted on SiC targets during the NASA Genesis mission were made (McKeegan et al., 2011). The calculated value for the Sun is $\delta^{17}\text{O} = -59.1\%$ and $\delta^{18}\text{O} = -58.5\%$ (vs SMOW). The $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ slope 1 data for the CCAM samples is then explained by simple mixing with the light nebular reservoir (Sun) and a molecular cloud enriched in ^{18}O and ^{17}O due to photochemical reactions. Young and Russell (1998) suggested that the mixing between these two reservoirs has a slope of exactly 1.0, and that the shallower slope of 0.996 suggested by Clayton's early work is explained by aqueous alteration of some meteoric material.

13.3.5 Oxygen isotopes in meteorites – undifferentiated bodies

The bulk isotopic compositions of meteorite parent bodies generally fall on a mixing line between the isotopically light solar component and heavy 'ice-derived' component. Further modification due to volatile loss to space and low temperature reequilibration/alteration expands the isotopic range to higher $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values with a slope less than 1. Each meteorite group occupies a distinct isotopic range (Fig. 13.4), although there is some overlap between groups. Indeed, one of the most diagnostic tools used for categorizing meteorites is the triple oxygen isotope composition.

The overall oxygen isotope compositions of different extraterrestrial materials are explained in the following way. The earliest-formed anhydrous phases plot with low $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values that are equilibrated with the unmodified nebula (Krot et al., 2002). Later-formed silicate minerals follow a mixing line with a slope close to or equal to 1 (the CCAM line) to higher delta values due to mixing with the isotopically heavy H₂O-derived component. Alteration occurring on a parent body with an aqueous fluid causes the isotope composition of that body to spread out along a mass dependent fractionation line, and loss of light water from a small body will draw the combined $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values upward (Young et al., 1999). Under equilibrium conditions, the slope defined by a set of samples from a single body will be ~ 0.52 , characteristic of mass-dependent fractionation. The highest $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values are found in highly altered CM and CI chondrites. These hydrous, highly oxidized samples have experienced high fluid/rock ratios and their oxygen isotope compositions reflect the heavy aqueous component. Chondrite classes that plot with distinct slopes between 0.52 and 1, such as the CR chondrites, are thought to represent partial mixing between material plotting along the CCAM line and unrelated altered material. Alteration with an aqueous fluid will tend to cause the isotope data to spread out on a mass dependent fractionation line, and loss of light water to space will draw the combined $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ values towards higher values (Young et al., 1999).

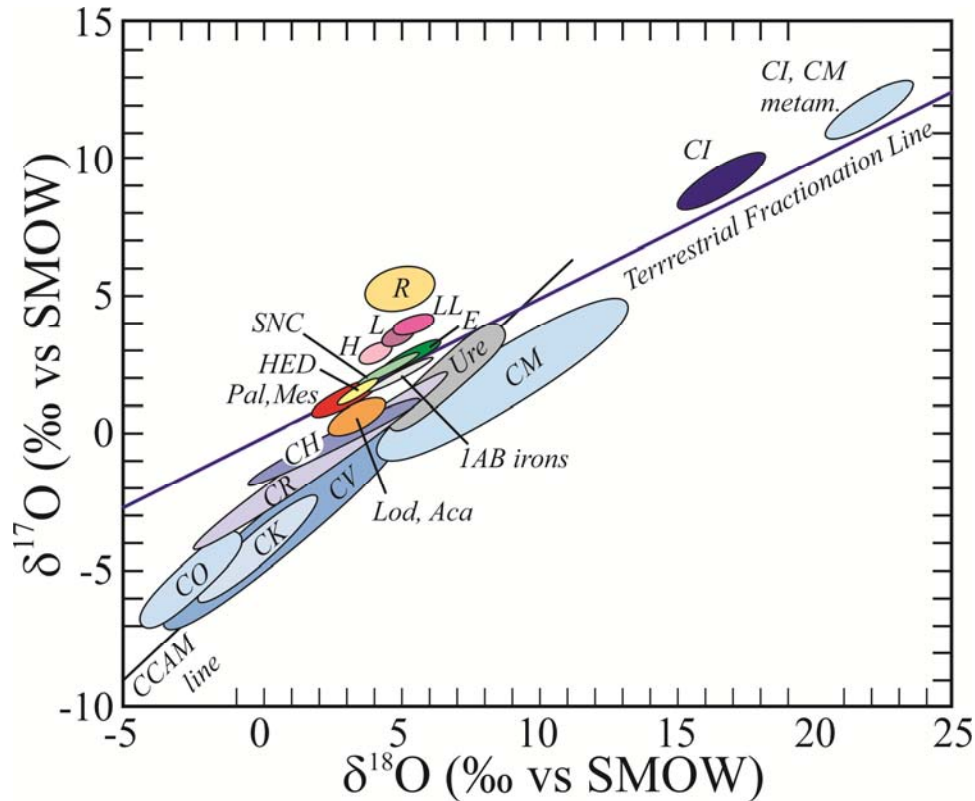


Fig. 13.4. Oxygen isotope fields for different meteorite types. Apollo (lunar) samples plot essentially on the Terrestrial Fractionation Line. Most Martian meteorites have $\delta^{18}\text{O}$ values between 3.5 and 5.5 with a $\Delta^{17}\text{O} = 0.32$ (Franchi et al., 1999). A Martian basaltic breccia has higher $\delta^{18}\text{O}$ values (5.6-7.5) and a distinctly high $\Delta^{17}\text{O}$ value of 0.58 ± 0.01 (Agee et al., 2013). The Moon is virtually indistinguishable from Earth. Abbreviations: Ure – urelites; Pal, Mes – pallasites, mesosiderites; HED – howardites, eucrites, diogenites; SNC – shergottites, nakhlites, chassignites (most Martian meteorites), Lod, Aca – lodranites, acapulcoites; E – enstatite chondrites; C – carbonaceous chondrites; H, L, LL – ordinary chondrites; R – R chondrites. Compiled from various sources.

13.3.6. Oxygen isotopes in meteorites – differentiated bodies

Samples from a well-mixed, differentiated body should plot on a mass dependent fractionation line passing through the bulk $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ value of that body, and indeed this is the case. Most samples from differentiated bodies, including the Moon, Mars, HEDs (4 Vesta), angrites, aubrites, mesosiderites, and pallasites, all fall on $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ arrays with a slope of ~ 0.525 , parallel to that of the Earth (Fig. 13.5). The $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$ array for the Earth and Moon are virtually indistinguishable. It is generally accepted that the Earth-Moon system formed during the collision of a Mars-sized body (informally called Theia) with the proto Earth approximately 60-100 Ma after the formation of our solar system (the collapse of the proto solar nebula). The remarkably similar $\Delta^{17}\text{O}$ values for lunar and terrestrial samples suggests that the two bodies either had identical initial $\Delta^{17}\text{O}$ values or that the two bodies were well mixed during the Giant Impact responsible for the Earth-Moon system.

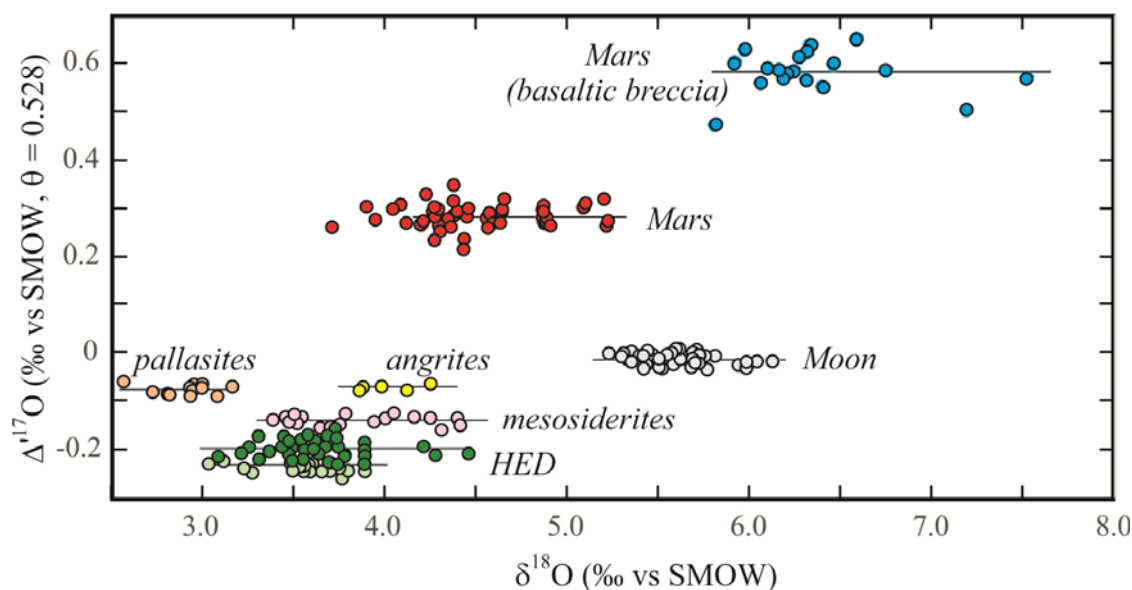


Fig. 13.5 Triple oxygen isotope composition of differentiated meteorites. The $\Delta^{17}\text{O}$ values are defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.528 \times \delta^{18}\text{O}$, where the ' refers to the linearized delta value (see Text box 3.1). The data for each group of differentiated meteorites defines a linear array consistent with isotopic equilibrium for the three isotope system. Two HED data sets are plotted: (Wiechert et al., 2004, dark green) and (Greenwood et al., 2005, pale green). Both show flat trends. The difference in the two data sets is probably due to slightly different calibration standards. Data from the following sources: (Franchi et al., 1999; Wiechert et al., 2001; Wiechert et al., 2004; Greenwood et al., 2005; Greenwood et al., 2006; Spicuzza et al., 2007; Rumble III and Irving, 2009; Greenwood et al., 2012; Agee et al., 2013; Herwartz et al., 2014; Young et al., 2016).

13.4 Hydrogen

13.4.1 Introduction

The D/H ratios of materials in our Galaxy span such an enormous range as to strain the utility of the delta notation. Solar wind is virtually deuterium-free, with δD values approaching -1000‰ . At the other end of the spectrum, cold molecular clouds have spectroscopically-measured D/H ratios as high as 10^{-1} , corresponding to $>600,000\text{‰}$ (see Robert et al., 2000 for a review of galactic values). Hydrogen isotope systematics differ significantly from those of oxygen, and the information available from D/H ratios is quite different as well. Hydrogen has only two stable isotopes, in place of oxygen's three, so that mixing of distinct sources can only be tracked in 'one dimension' instead of two. Hydrogen, while far and away the most abundant phase in molecular clouds and our solar system, is rare in solids preserved in meteorites. And finally, the isotopes of hydrogen have a very different formation history than oxygen. Oxygen is produced during star-forming events, with each isotope identified with specific nucleosynthetic processes. Deuterium, in contrast, was formed in the Big Bang (Burbidge et al., 1957). There is no additional stellar input to the primordial mix. For oxygen, the solar isotope abundances define the starting point for the composition and evolution of the solar system. For the hydrogen-deuterium system, the Sun is of no help in giving us average

solar system values, as all deuterium was ‘burned’ during contraction of our proto-Sun⁸.

The D/H ratios of various materials are shown in Fig. 13.6. The D/H ratio following the Big Bang is estimated as $67\text{-}90 \times 10^{-6}$ or -520 to -420‰ (Copi et al., 1995). Deuterium is destroyed during star burning, so that the average D/H ratio of the Universe has decreased with time. Spectroscopic analysis of local interstellar medium gives a D/H ratio of $(14\text{-}17) \times 10^{-6}$. The presolar D/H ratio is estimated at $\sim (20 \pm 3.5) \times 10^{-6}$ using the ${}^3\text{He}/\text{H}$ ratio of the solar wind. Jupiter can also be used as a proxy for the presolar D/H

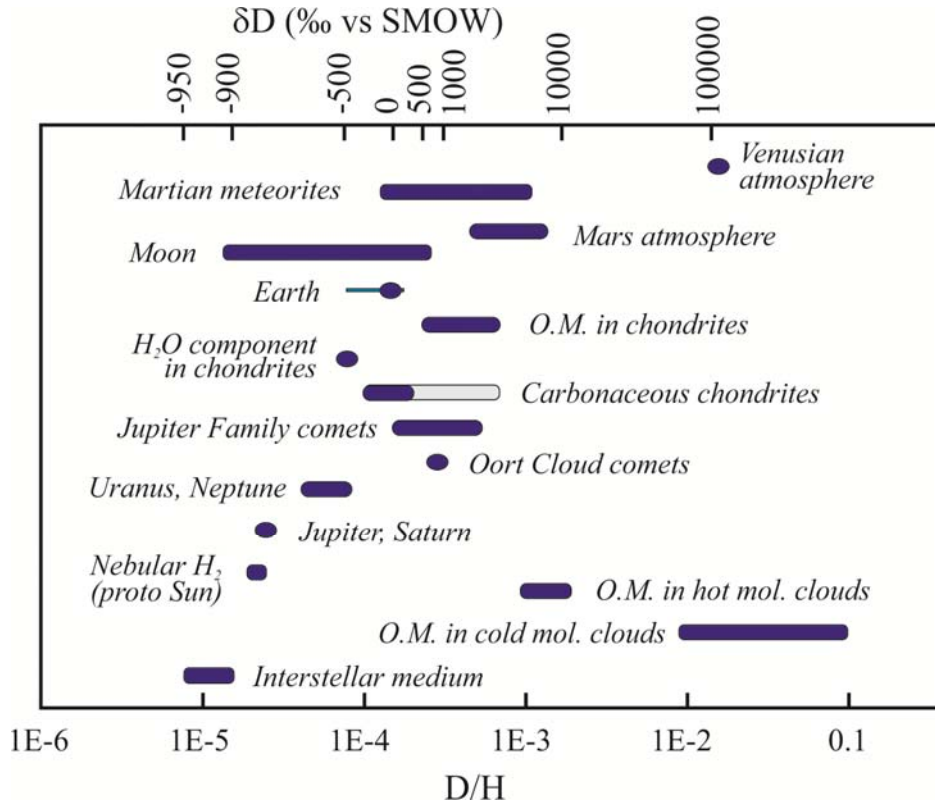


Fig. 13.6 D/H ratios for galactic and solar system bodies. The solar nebula (measured for Jupiter and Saturn and inferred for the proto Sun) are nearly pure H_2 . High δD values of organic matter in molecular clouds is explained by extreme fractionation during ion exchange reactions. The high D/H ratios of Venus are thought to be due to hydrodynamic escape of protium to space. Comets are generally light although several Jupiter family comets have measured D/H ratios that overlap the bulk Earth value. The bulk Earth is $\sim -40\text{‰}$. The full range of Earth values is given by the thin dark line. Most carbonaceous chondrites fall in the dark blue range, although anomalous heavy chondrites (Ornans, Semarkona) have δD values as high as $>2000\text{‰}$ (grey band). Data from compilations of Robert *et al.* (2000) and Sharp (2017).

ratio. Jupiter formed very shortly after the birth of our solar system, and because of its enormous size, Jupiter would have incorporated all hydrogen in its orbit without fractionation. Spectroscopic analysis of Jupiter gives a D/H ratio of Jupiter $(26 \pm 7) \times 10^{-6}$, which is in excellent agreement with the solar estimate. Knowing the baseline for the D/H ratio of the solar system, allows us to explain higher D/H ratios of terrestrial and

⁸ Of all the isotopes of all elements, deuterium is the most easily destroyed in thermonuclear reactions.

extraterrestrial materials in terms of preferential incorporation of deuterium during various discrimination processes in the solar nebula.

There are enormous deuterium enrichments in dense molecular clouds. D/H ratios as high as 10^{-1} and 10^{-3} are detected in organic matter from cold (10 K) and hot (>80 K) molecular clouds, respectively. Such high δD values (>600,000‰) can only be achieved by isotopic enrichments occurring at extremely low temperatures. Normal gaseous exchange reactions do not occur at such low temperatures. Instead, ion exchange reactions, in which gaseous molecules are ionized by ultraviolet radiation and then undergo isotopic exchange, are called upon to explain the extreme deuterium enrichments. Two such reactions are (Robert et al., 2000)



and



With this process in mind, organic matter formed under low temperature conditions in the nebula should be extremely heavy, and indeed, δD values well above 1,000‰ and approaching 12,000‰ have been measured (Alexander et al., 2010). These extreme values are explained as a result of low temperature reactions similar to equation 13.3 and/or oxidation of H_2O at low temperatures producing very light H_2 which was removed from the system.

At low temperatures, the fractionation between H_2O and H_2 are extremely large. $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ values range from 9.5 at 180 K to 5.5 at 230 K (Reeves and Bottinga, 1972). Oxidation of H_2 to H_2O at such low temperatures could therefore lead to extreme D enrichments resulting in δD values easily approaching +500‰. *In situ* D/H analyses of phyllosilicates in the matrix of the ordinary chondrite Semarkona are remarkably high, reaching values of 3300 to 4600‰ (Deloule and Robert, 1995). Such extreme values can be explained by the ion exchange reaction given by equation 13.2 above at temperatures on the order of 110-140 K.

13.4.2 Hydrogen in chondrites

The first hydrogen isotope measurements of meteorites gave ‘unearthly’ high δD values up to +300‰ (Boato, 1954). The range was greatly expanded in the 70’s and 80’s. For example, Kolodny *et al.* (1980) measured δD values between -70 and +771‰ from seven carbonaceous chondrites. McNaughton *et al.* (1981) measured values as high as 3,000‰ in several ordinary chondrites. δD values of bulk chondrites typically range from ~-200 to in excess of +600‰ and vary with chondrite type (Fig. 13.7). The bulk values are a mixture of phyllosilicate hydrogen (*e.g.*, water) and organic matter. Alexander *et al.* (2012) measured the hydrogen isotope composition and C/H ratios of a large number of chondrites. They plotted the δD values against the C/H ratios and extrapolated the best-fit line to a C/H ratio of 0, following the approach of Kolodny *et al.* (1980). They interpreted the y-intercept (C/H = 0) as the phyllosilicate portion of the mixture, which is essentially the hydrous component of the phyllosilicate. The H_2O contents have δD values of -500‰ (CM, CI and CO chondrites) and +100‰ (CR chondrites). The result is in excellent agreement with the earlier work of Kolodny *et al.* (1980), and can be explained by low

temperature equilibrium fractionation between solar H₂ and small amounts of oxidized H₂O.

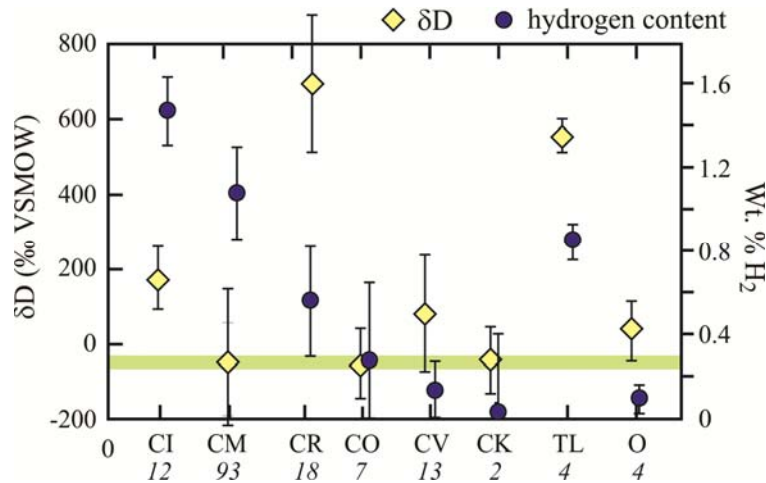


Fig. 13.7. H₂O content and δD values of chondritic meteorites. The green band is the bulk Earth δD value. O- ordinary chondrites; TL – Tagish Lake. From Sharp (2017). Italicized numbers refer to number of analyses made.

13.4.3 Hydrogen in differentiated meteorites.

The source of hydrogen in differentiated bodies is an unsettled question. The Earth, Moon and Mars all have some ‘water component’, where ‘water’ is loosely defined as the hydrogen-bearing phase. On Earth, a significant portion of H does occur as water in the ocean today, with equal or likely greater amounts in the mantle and perhaps core. Mars has evidence for large quantities of water in the past (Villanueva et al., 2015), and even the Moon, which was long thought to be devoid of hydrogen, has now been shown to contain hydrogen in trace quantities in minor phases, such as melt inclusions and apatite grains⁹ (Saal et al., 2008; McCubbin et al., 2010). Other differentiated bodies, such as the HEDs, also have H-bearing phases.

The surprising thing is that the terrestrial planets are thought to have formed inside the ‘snow line’ or ‘frost line’ and therefore should not contain any indigenous water. During collapse of the proto-nebular cloud, adiabatic heating during infall of the nebular cloud to a disk would have raised the temperature of the disk to 1250-1450°C. Subsequent cooling would lead to condensation of the elements in relation to their volatility. Hydrogen condenses as water ice at temperatures of ~150 K and the solid ice is then incorporated into the growing planetesimals. The snow line is the inferred region inside of which temperature were too high for H₂O to condense *prior* to dissipation of the nebular cloud. The snow line is thought to have been at the radial position of the asteroid belt. As a result, the growing terrestrial planets sunward of this radial distance should not have incorporated any water. And yet we see that all of the terrestrial planets (perhaps with the exception of Mercury) have or had significant amounts of water. The question then becomes ‘how did these bodies, inside of the snow line, acquire their water?’

⁹ Water ice has been detected in the permanently shadowed regions of the south pole. The origin for this water is likely due to delivery from comets.

A number of hypotheses have been proposed to explain the incorporation of water by the terrestrial planets (see Sharp, 2017 for a detailed review). These include direct incorporation of nebular H₂ gas, addition of hydrous bodies from beyond the snow line and late addition to the planets by bombardment from carbonaceous chondrites – the so called ‘late veneer’ or ‘late accretion’ hypothesis.

The late veneer hypothesis has received considerable attention because it explains the high concentration of highly siderophile (HSE) elements in the mantle. The HSEs (Os, Ir, Ru, Rh, Pt, Pd, Re, Au) are strongly partitioned into iron metal. As a result, they should have been completely sequestered into the core during early planetary formation. The higher-than-expected concentration of the HSEs in the mantle was first explained by late addition of chondritic material following core formation. Addition of 0.7% chondritic material after the Giant Impact event responsible for the Moon formation is sufficient to explain the elevated HSE abundance of Earth’s mantle. If the impactors were hydrous chondrites, represented by CM chondrites, then the δD value of late accreted material would match that of Earth with $\sim 2\%$ delivery needed to account for the minimum estimate of the Earth’s water content.

If a significant fraction of chondrite types *other* than CM were delivered during late accretion, then the integrated δD value of the delivered material would be too high to match Earth. This deuterium excess could be counterbalanced by light hydrogen if direct

ingassing of nebular H₂ occurred as the planetesimals were nearing their final size (Sharp, 2017). Ingassing of light nebular H₂ also allows for the possibility of some heavy cometary volatiles to be added to the Earth system. Marty *et al.* (2012) conclude that the H and N isotope composition of Earth is explained by a combination of chondritic and solar compositions without isotopic fractionation during hydrodynamic escape. Sharp (2017) proposed that a combination of nebular ingassing followed by hydrodynamic escape and late addition of chondritic and cometary material explains the isotopic composition of Earth as well as the high $f(O_2)$ of the mantle. Primordial ³He, found in many mantle hot spots may also be sourced directly from nebular ingassing. The remarkably high δD value 125,000‰ for the atmosphere of Venus is explained by near complete loss of H by heating of the upper atmosphere by extreme ultraviolet radiation from the early Sun and hydrodynamic escape of H or H₂ through a CO₂-rich atmosphere (Donahue et al., 1982). Whether the Earth has had its D/H ratio modified by hydrodynamic escape remains unresolved.

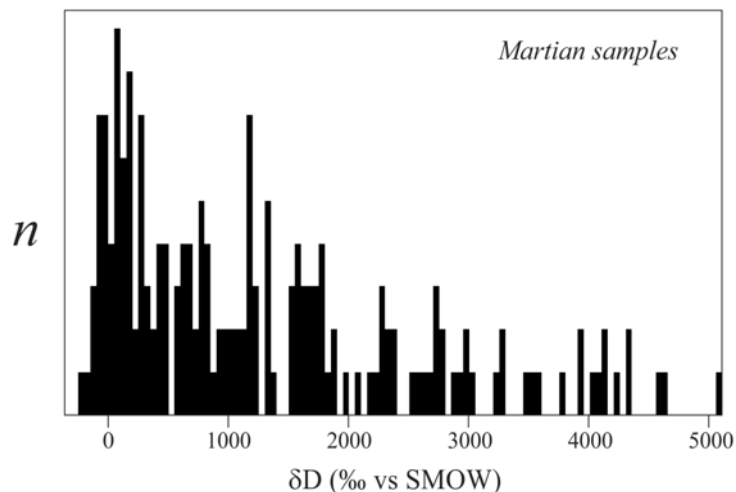


Fig. 13.8. Compilation of δD values of Martian meteorites. Most analyses are from ion microprobe measurements of apatite grains. Compilation from Sharp, (2017).

Like Venus, although to a much lesser extent, the Martian atmosphere also has a high δD value ($\delta D = 4000\text{‰}$), again explained by preferential loss of H_2 to space. Martian meteorites have a wide range of δD values ranging from near zero up to $5,000\text{‰}$ (Fig. 13.8).

Until recently, most hydrogen in lunar samples was thought to be due to solar wind implantation (Epstein and Taylor, 1970). The δD value of hydrogen extracted from lunar soils is between -890‰ and -1000‰ , explained as being entirely sourced by deuterium-free solar wind. Hydrogen was recognized as a primary phase in lunar glass (Saal et al., 2008; 2013) and the volatile-rich phase apatite ($Ca_5(PO_4)_3(OH,F,Cl)$) (McCubbin et al., 2010). The δD values of lunar apatites cover an extremely wide range (Fig. 13.9). The unmodified bulk Moon is thought to have a δD value equal to or higher than Earth (Hauri et al., 2017). The lowest values (not shown in Fig. 13.9) are measured on bulk lunar soil samples. The δD values approach $-1,000\text{‰}$ and are explained as direct implantation of protium-rich solar wind. The highest δD values are either due to heavy cometary input (Greenwood et al., 2011) or loss of H_2 to space during degassing (Sharp et al., 2013). Low δD values (~ -600 to -300) may represent a distinct volatile source (Robinson et al., 2016) that may be tapping a nebular ingassing component (Sharp, 2017).

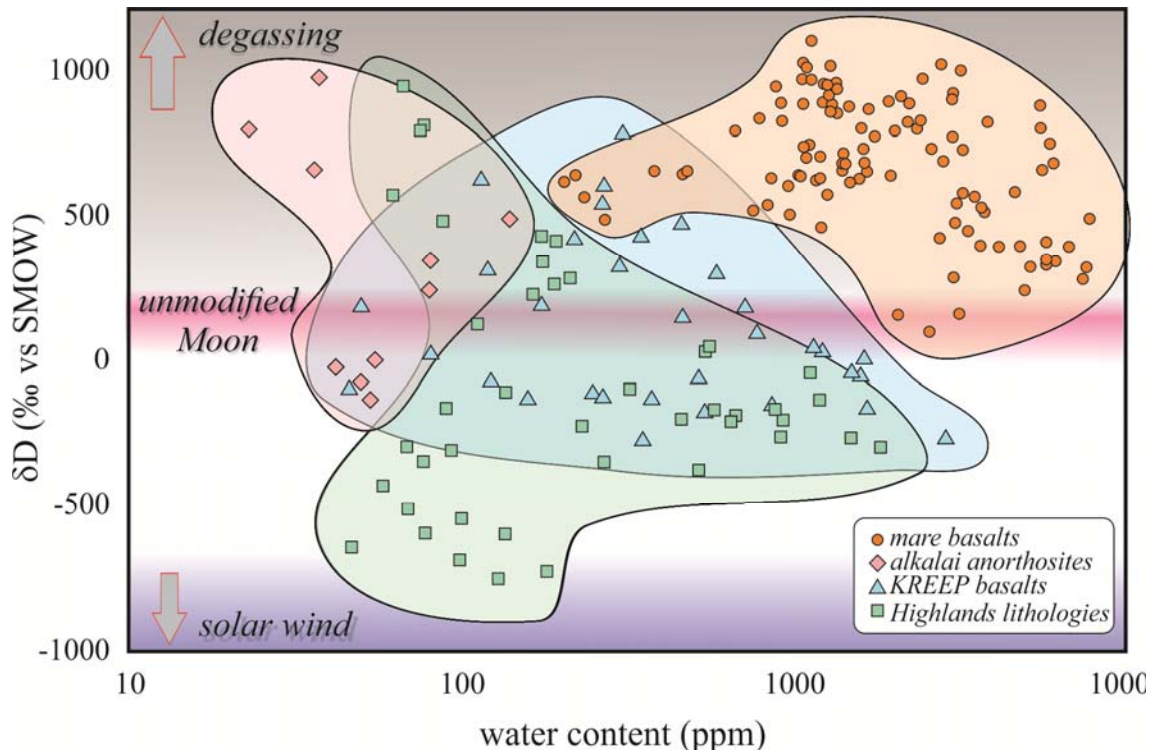


Fig. 13.9. Hydrogen isotope values vs. water content $[H_2O]$ of lunar apatite grains. Different lithologies have distinct $[H_2O]$ - δD fields. Mare basalts have the highest $[H_2O]$ and δD values. Modified from Robinson *et al.* (2016).

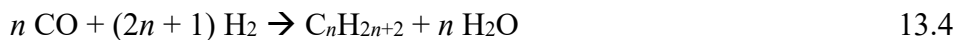
13.5 Carbon

Carbon isotope analyses of meteorites began extremely early-on in the stable isotope game, motivated by the identification of a distinct spectroscopic bands found in N-type stars attributable to high concentrations of $^{12}\text{C}^{13}\text{C}$. In 1936, several attempts were made to measure the $^{13}\text{C}/^{12}\text{C}$ ratio of graphite from Canyon Diablo iron meteorite using spectrographic measurements of graphite discharge. Unfortunately, the spectrographic image was identical to that obtained from terrestrial graphite (e.g., Jenkins and King, 1936), suggesting that no ^{13}C anomaly existed in meteorites. Murphey and Nier (1941) determined the carbon isotope composition of ‘meteorite carbon’ from seven samples, which ranged from -33 to -11 ‰ (approximate PDB scale). Additional analyses in the coming decades also found that meteoritic carbon had $\delta^{13}\text{C}$ values that overlapped with terrestrial values. The first anomalous values were found in the carbonate fraction of two carbonaceous chondrites (Orgueil and Ivuna), where $\delta^{13}\text{C}$ values of $\sim +60\%$ (PDB) were measured on the dolomite fraction (Clayton, 1963). Along with Boato’s early high δD values in meteorites, this was one of the first findings of anomalous stable isotope ratios in extraterrestrial material.

In the same year, Briggs (1963) reported $\delta^{13}\text{C}$ values of solvent-extractable organic material from carbonaceous chondrites that were only slightly less than 0‰, higher than terrestrial equivalent organic matter. The anomalous $\delta^{13}\text{C}$ values provided some of the strongest evidence to date that organic material in meteorites was indeed of extraterrestrial origin.

Two papers appearing in 1970 expanded the data base for carbonaceous chondrites (Krouse and Modzeleski, 1970; Smith and Kaplan, 1970). Both showed very high $\delta^{13}\text{C}$ values of carbonates and less convincing, but still high, $\delta^{13}\text{C}$ values of organic extracts (Fig. 13.10). The data were clearly incompatible with a terrestrial carbon origin. Instead, the ‘endogenous’ carbon (Smith and Kaplan, 1970) in carbonaceous meteorites was firmly established.

The emerging picture was that the $\delta^{13}\text{C}$ values of organic carbon averaged around -16‰, while the much less abundant carbonate had $\delta^{13}\text{C}$ values as high as +60 or +70‰. The fractionation of $>80\%$ between the oxidized and reduced form was far larger than what was observed on Earth, where the differences were only on the order of 25 to 30‰. Urey (1967) considered two distinct carbon synthesis events in the solar system as a possible explanation. Several year later, Lancet and Anders (1970) proposed an alternative explanation that did not require an exotic carbon source. They showed experimentally that oxidation-reduction reactions of CO (Fischer-Tropsch synthesis) given by



and



could produce large carbon isotope fractionations. In this reaction, both oxidized and reduced carbon are formed abiogenically. Another possible low-temperature exchange reaction is



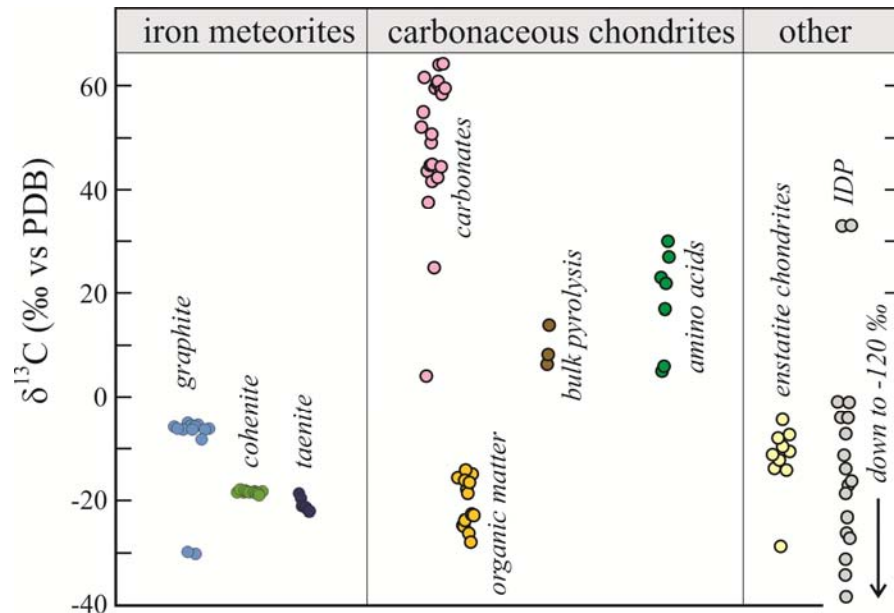


Fig. 13.10. Carbon isotope composition of different extraterrestrial materials. The Sun has a $\delta^{13}\text{C}$ value of $-105\pm 20\%$. All other materials have higher $^{13}\text{C}/^{12}\text{C}$ ratios (except one IDP), consistent with low temperature reactions that enrich solid phases in ^{13}C . Data from the following sources: (Craig, 1953; Clayton, 1963; Krouse and Modzeleski, 1970; Smith and Kaplan, 1970; Deines and Wickman, 1975; Grady et al., 1986; Epstein et al., 1987; Engel et al., 1990; Messenger, 2000; Hashizume et al., 2004).

The low temperature oxidation-reduction reactions can explain the high $\delta^{13}\text{C}$ value of most solar system materials relative to the Sun. The Sun is thought to have a $\delta^{13}\text{C}$ value of $-105\pm 20\%$ (Hashizume et al., 2004). Interplanetary dust particles (IDPs) have a very wide range of $\delta^{13}\text{C}$ values from -120 to $+33\%$ (Messenger, 2000), consistent with a low protosolar nebula value and heavier samples resulting from low temperature reactions such as 13.4-13.6.

The isotopic composition of individual amino acids from CM chondrites have been measured (Engel et al., 1990). The $\delta^{13}\text{C}$ values are as high as $+30\%$, clearly of extraterrestrial origin. Interestingly, the measured samples are not racemic¹⁰, which had been used as previous evidence for terrestrial contamination. The high $\delta^{13}\text{C}$ values eliminate contamination as a possibility of their origin. The isotopic ratios of nitrogen, and hydrogen from the hydroxy acids from Murchison are also extraterrestrial, with $\delta^{15}\text{N}$ values of 37 - 184% (Engel and Macko, 1997) and δD topping out at $>500\%$ (Cronin et al., 1993).

In a number of stepwise combustion analyses of carbonaceous chondrites, an extremely high $\delta^{13}\text{C}$ value of 1100% was measured (Swart et al., 1983). Later work

¹⁰ A racemic amino acid is one that has equal abundance of left- and right-handed optical isomers (enantiomers). The Murchison sample has a D/L value of 0.85, significantly different from the racemic value of 0.5. It is normally assumed that non-racemic amino acids are due to biological synthesis.

using high spatial resolution ion microprobe analyses revealed $\delta^{13}\text{C}$ values in interstellar residual grains in excess of 7000‰ (Zinner and Epstein, 1987). These are primitive and rare grains of ‘stardust’.

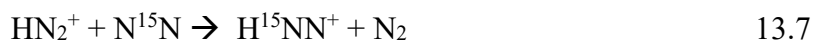
13.6 Nitrogen

The wide range of nitrogen isotope variations in the solar system is exceeded only by hydrogen. Studies of the nitrogen isotope geochemistry of meteorites lagged behind the other ‘traditional’ light stable isotope elements mostly because nitrogen concentrations in meteorites are low and the analyses are difficult. Some of the first measurements of carbonaceous chondrites found a range considerably broader than what existed on Earth. Injerd and Kaplan (1974) measured $\delta^{15}\text{N}$ ratios between -20 and +46‰ from four chondrites. Kung and Clayton (1978) expanded the number of analyses and extended the total range observed for carbonaceous chondrites from lows of -40 to -30‰ for enstatite chondrites to highs of +30 and +50‰ (Renazzo with an anomalous 170‰). They felt that the variations were too large to be explained by mass dependent fractionation, and instead suggested that the meteorites were recording nitrogen isotope heterogeneities in the solar nebula.

As we have seen for hydrogen and carbon, the nitrogen isotope composition of the Sun represents the overall $\delta^{15}\text{N}$ value of the solar system. The Sun has the lowest $^{15}\text{N}/^{14}\text{N}$ ratio of any materials in our solar system. All processes that have occurred in the protoplanetary disk and after its dissipation, lead to an enrichment in ^{15}N which is then incorporated into growing planetary bodies. The solar system can be broadly characterized of consisting of three distinct ‘regions’ in terms of $\delta^{15}\text{N}$ values (Mandt et al., 2014). The Sun, Jupiter and Saturn, with their very low $^{15}\text{N}/^{14}\text{N}$ ratio, the inner solar system, with $\delta^{15}\text{N}$ values of 0-50‰ and cometary ices, with $\delta^{15}\text{N}$ values of $850\pm 150\%$ (Fig. 13.11).

Hashizume *et al.* measured the $\delta^{15}\text{N}$ value of metal grain from the lunar soil in order to obtain the value of the solar wind. Their estimate was very light, at $\leq -240\%$. A more recent measurement of solar wind implanted on the SiC plates of the Genesis mission corresponds to a $\delta^{15}\text{N}$ value of the solar wind of $-407\pm 7\%$ and a $\delta^{15}\text{N}$ value for the Sun (and protosolar nebula) of $-383\pm 8\%$ (Marty et al., 2011). For comparison, the $\delta^{15}\text{N}$ value of Jupiter was measured to be $-374\pm 80\%$ from the *Galileo* Probe Mass Spectrometer (Owen et al., 2001).

The heavy nitrogen isotope composition of some solar system materials, such as organic matter, ‘organic globules’ in the Tagish Lake chondrite (Nakamura-Messenger et al., 2006) and comets (Fig. 13.11) has been attributed to low temperature ion molecule exchange reactions that could occur in a cold molecular cloud or in the protostellar nebula far from the Sun. One such reaction is



where the HN_2^+ ion (isodiazene) becomes enriched in ^{15}N and then becomes incorporated into ices and organic matter (Furi and Marty, 2015).

Nitrogen enrichment can also occur by escape from a planetary surface, such as Mars (as evidenced by the high $\delta^{15}\text{N}$ of the Martian atmosphere) and Titan. The moderately elevated $\delta^{15}\text{N}$ values of many asteroidal materials is probably related to kinetic and equilibrium isotope fractionations between nitrogen. The large fractionations relative to what is seen on Earth are difficult to account for and almost certainly require, at minimum, fractionation associated with an oxidation state change (*e.g.*, N_2 to NH_2^+) and low temperature dynamic interactions. Alternatively, the large range of $\delta^{15}\text{N}$ values has been suggested to reflect primordial nebular inhomogeneities (Thiemens and Clayton, 1981; Prombo and Clayton, 1993).

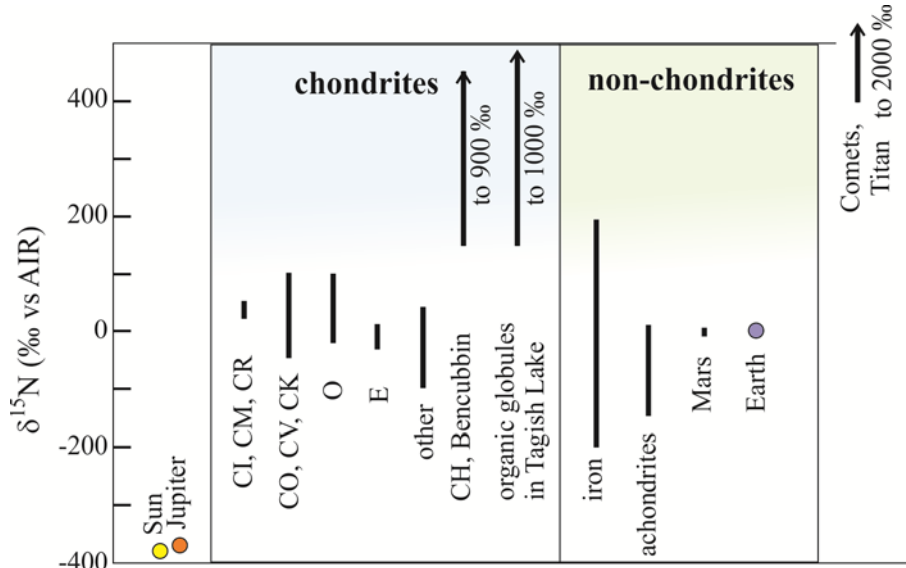


Fig. 13.11. Nitrogen isotope composition of different extraterrestrial materials. The Sun has the lowest $\delta^{15}\text{N}$ value of -383‰ . All other solar system materials have higher $\delta^{15}\text{N}$ values. Samples formed at low temperatures far from the Sun, such as comets and Titan ($\delta^{15}\text{N} = 620\text{‰}$) have the highest $\delta^{15}\text{N}$ values consistent with molecular ion reactions at low temperatures. The intermediate values found in meteorites may be related to kinetic or equilibrium molecular exchange reactions. Data from the following sources: (Owen et al., 2001; Grady and Wright, 2003; Nakamura-Messenger et al., 2006; Marty et al., 2011; Mandt et al., 2014; Furi and Marty, 2015).

13.7 Sulfur

In the meteorite world, the most remarkable thing about sulfur is how unremarkable it is. Hulston and Thode (1965) noted in a comprehensive study of meteoritic $\delta^{34}\text{S}$ values “that the isotopic composition of the total sulfur is remarkably constant from meteorite to meteorite.” Most meteorites have a $\delta^{34}\text{S}$ value that falls in the range of -2 to $+3\text{‰}$. Hulston and Thode did not find any $\delta^{33}\text{S}$ or $\delta^{36}\text{S}$ anomalies that might be evidence of an exotic nucleosynthetic source. The data suggest that sulfur underwent some fractionation on the parent bodies, but that the source within the solar system was more-or-less constant (Kaplan and Hulston, 1966). This conclusion is consistent with the idea that sulfur condensed out of the solar nebula as FeS without fractionation and that no oxidation state changes occurred prior to incorporation into the parent bodies. The one interesting theme that has been observed in sulfur isotopes is the non-mass dependent fractionation (see section 10.5.5 for more information) seen in some differentiated bodies. Farquhar *et al.* (2000a) measured urelite samples with a small ^{33}S

anomaly which they attributed to gas phase reactions in the solar nebula that resulted in small anomalies in the protoplanetary disk. Both positive and negative ^{33}S anomalies have also been seen in Martian meteorites, which are explained by deposition of oxidized sulfur produced by atmospheric chemical reactions (Farquhar et al., 2000b). The common sulfur anomaly on Mars indicates widespread incorporation of surficial sulfur into Martian materials that have been delivered to Earth (Franz et al., 2014). A sulfur-36 anomaly has also been seen in some primitive differentiated bodies, presumably due to decay of ^{36}Cl early in solar system history (Defouilloy et al., 2016).

13.8 Chlorine

Chlorine isotopes are considered in this chapter because of the large isotope variations that have been seen in extraterrestrial materials. There are two stable isotopes of chlorine, ^{35}Cl and ^{37}Cl . The isotope ratios are reported in the standard delta notation with seawater – Standard Mean Ocean Chloride or SMOC – assigned a $\delta^{37}\text{Cl}$ value of 0‰. The bulk Earth $\delta^{37}\text{Cl}$ value is also close to 0‰. There are large variations in terrestrial materials due to near-surface processes (Barnes and Sharp, 2017), but most of these fractionation mechanisms are not relevant to extraterrestrial materials.

The $\delta^{37}\text{Cl}$ value of chondrites range from -4.5 to 2.5‰ (Fig. 13.12). The majority fall between -2 and +1‰, roughly consistent with the bulk Earth. What is perhaps most interesting is that three of the chondrite samples have $\delta^{37}\text{Cl}$ values less than -4‰. Mars has a wide range of $\delta^{37}\text{Cl}$ values, covering over 10‰ total variation. This is far larger range than for equivalent lithologies on Earth. The high $\delta^{37}\text{Cl}$ values are thought to be due to preferential loss of the light isotope (^{35}Cl) to space, leaving a heavy residue. The low $\delta^{37}\text{Cl}$ values (deep red color in Fig. 13.12) are the olivine phyric shergottites, which are thought to be the samples least contaminated by crustal material. Finally, the iron meteorites are negative, and reach the lowest $\delta^{37}\text{Cl}$ values of any extraterrestrial material measured to date (Gargano et al., 2017). It is suggested that the negative $\delta^{37}\text{Cl}$ values reflect direct incorporation of Cl from the solar nebula, and that the Sun presumably also has a negative $\delta^{37}\text{Cl}$ value (Sharp et al., 2016). The higher $\delta^{37}\text{Cl}$ values of most chondrites are explained by addition of an HCl-bearing ice ($\text{HCl}\cdot 3\text{H}_2\text{O}$) formed beyond the snowline prior to dissipation of the solar nebula. The ice would preferentially incorporate ^{37}Cl ultimately leading to the heavy Cl isotope compositions of most chondrites.

The most remarkable Cl isotope variations are seen on the Moon, with a spread in excess of 40‰ (Fig. 13.12). The lowest values are close to 0‰ with one negative sample. Other than hydrogen, no other isotopic system shows such a large lunar range in its isotopic composition. The high $\delta^{37}\text{Cl}$ values are most likely due to degassing. In detail, a number of ideas have been proposed, including the following:

1. Local degassing of a solidifying magma, with the light isotopes preferentially lost to the vapor phase (Sharp et al., 2010);
2. Some samples may be related to vapor phase deposition related to meteorite impacts (Treiman et al., 2014);
3. Degassing into a vacuum
4. Degassing during the waning stages of the magma ocean stage following the Giant Impact (Boyce et al., 2015; Barnes et al., 2016).

Each of these ideas has merits and all are not mutually exclusive. Clearly the cause or causes of the enormous enrichment in ^{37}Cl in lunar samples is unique and is not well understood.

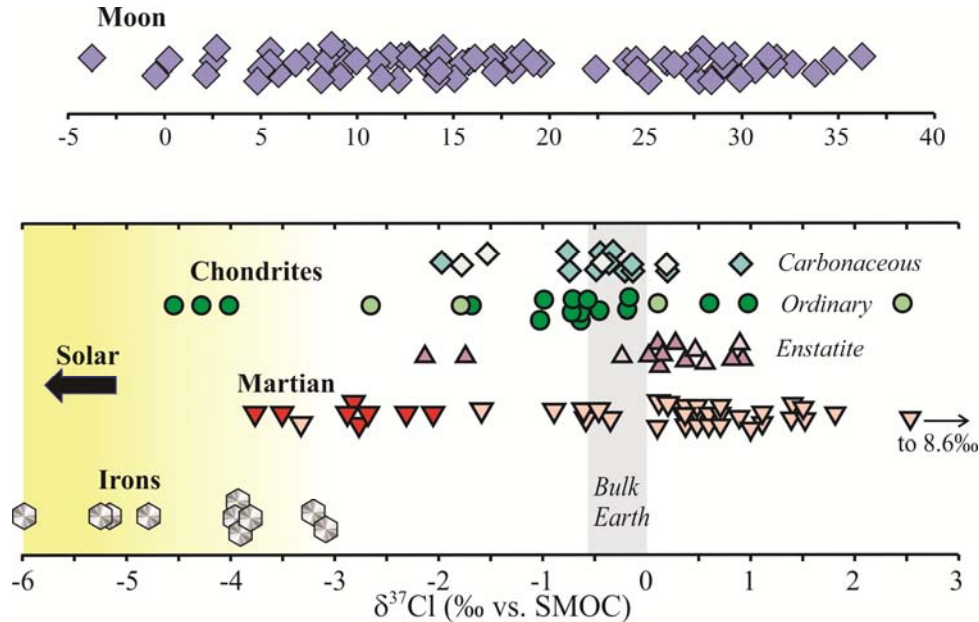


Fig. 13.12. Chlorine isotope composition of extraterrestrial materials. The lowest $\delta^{37}\text{Cl}$ values probably reflect the composition of the protonebular disk and Sun. Iron meteorites, mantle-derived Martian meteorites (deep red) and several ordinary chondrites preserve this signature. The other samples have been contaminated by a ^{37}Cl -enriched HCl-bearing ice or have lost light isotopes through vaporization. Each of these possibilities drives the $\delta^{37}\text{Cl}$ values of the residue to higher values. Lunar samples show a huge range of $\delta^{37}\text{Cl}$ values (note different scale for lunar materials). The high $\delta^{37}\text{Cl}$ values are due to vaporization of Cl during degassing.

Other isotope systems have been used to study extraterrestrial materials including Li, Mg, Si, Ti, Cr, Fe, Ni, Zn, and Mo. These are not normally considered as traditional stable isotopes and will not be considered here. Readers are referred to the recent book “*Non-Traditional Stable Isotopes*” (2017) which is a general overview of some of the recent developments of the non-HCNOS isotope systems.

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