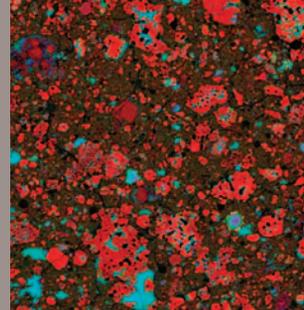


Stable Isotope Cosmochemistry and the Evolution of Planetary Systems

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Stable isotopes record the evolution of planetary systems, beginning with stars coalescing from molecular clouds, followed by the nucleosynthesis of elements in stars, and proceeding to the accretion and differentiation of planets. Current stable isotope measurements range in scale from isotopic mapping of the Milky Way Galaxy with spectrographs on telescopes to the analysis of stardust with ion probes.

KEYWORDS: Solar System, oxygen isotopes, silicon isotopes, iron isotopes, meteorites

INTRODUCTION

Stable isotope cosmochemistry has been successful in revealing how a molecular cloud located in an arm of the Milky Way Galaxy collapsed to form a flattened spiral nebula from which the Sun and its planets, asteroids, and comets accreted. The history of these violent processes stretches more than 4.5 billion years into the past. The decay of radioactive isotopes (“unstable isotopes”) gives an indispensable calibrated timeline for the birth of the Solar System. But it is the analysis of stable isotopes in ancient meteorites that unlocks the record of physical and chemical processing leading to the formation of our habitable planet.

As far back in time and as deep in space as astronomers can see, there were and are stars forming and dying, molecular clouds collapsing, and planets accreting. The scale on which these processes take place is unimaginably vast. And yet, evidence of stellar nucleosynthesis and planetary evolution can be found in the stable isotope composition of a meteorite or a piece of Earth’s mantle nestling comfortably in one’s hand. Stars burn hydrogen and helium, creating ¹²C, ¹⁶O, and heavier isotopes, and writing tell-tale isotopic signatures as time passes. Eventually, stars explode, dispersing their newly minted elements into molecular clouds. Raw radiation from young stars drives photochemical fractionation of stable isotopes in the clouds. Explosions of supernovae trigger gravitational collapse, a circumstellar nebula coalesces, and planetesimals accrete, incorporating isotopic records of their progenitors. As protoplanets grow, radioactivity from short-lived isotopes heats them. Space rubble melts, magmas flow and cool, crust forms, and stable isotopes strive for equilibrium fractionation between various solids, liquids, and gases. Planets emerge from the violence. None of these successive processes erase fully the record of what came before. Remnants of earlier events remain, even if only as the tiniest of relics. Stable isotopes record stellar nucleosynthesis, photochemical fractionation, volcanic eruptions, and yesterday’s rainstorm.

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The outline of this article follows a timeline from the birth of the Sun to the accretion, alteration, and differentiation of planetary bodies. We highlight new results in stable isotope cosmochemistry from a variety of techniques but do not present a complete history of research or a systematic inventory of isotope results.

ORIGINS INFERRED FROM PRESOLAR GRAINS AND ASTRONOMICAL STUDY OF YOUNG STELLAR OBJECTS AND MOLECULAR CLOUDS

Stable isotopes provide a primary tool for placing our Solar System in the context of star formation in the Galaxy. Comparing isotope ratios of presolar grains extracted from meteorites with those in protoplanetary systems forming today elsewhere in the Galaxy presents exciting new possibilities for learning about the early history of our Solar System.

Presolar grains, typically less than 20 micrometers in size, consist of diamond, silicon carbide, graphite, silicate and oxide minerals, nitride, carbide, and metal. They are found embedded in chondritic meteorites. The grains are samples of interstellar dust produced by dying stars. Their stable isotope ratios of Xe, Ne, ¹⁵N/¹⁴N, ¹³C/¹²C, ²⁹Si/²⁸Si, ³⁰Si/²⁸Si, ¹⁸O/¹⁶O, and ¹⁷O/¹⁶O differ by tens of percent (thousands per mil) from Solar System values. The anomalous stable isotope abundances can be related to the patterns of nucleosynthesis of elements and isotopes in different types of stars (Zinner 2007; Nguyen and Messenger 2011 this issue).

Oxygen is of particular value as a tracer of processes in the early Solar System and in other nascent planetary systems because it occurs in great abundance. O comprises ~50% by mass of most rocky materials and ranks behind only hydrogen and helium in abundance in the gas phase of molecular clouds. With the advent of improved instrumentation, astronomical measurements of stable isotope ratios are becoming a powerful new tool for probing the chemistry of young stellar objects (YSOs), making comparisons with the Solar System possible. Oxygen and carbon are both especially promising because their primary host, CO, is the most abundant molecular species in circumstellar disks after H₂.

Young stellar objects (YSOs) are young stars together with their envelopes of collapsing molecular cloud material and circumstellar disks. These objects serve as analogs for the early Solar System.

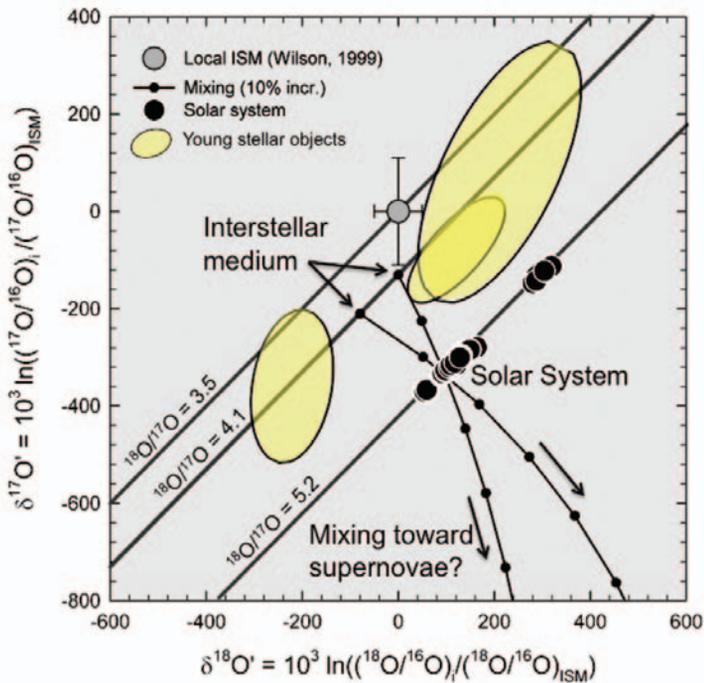


FIGURE 1 Oxygen isotope map of the Milky Way Galaxy in logarithmic coordinates (modified after Young et al. 2011). The Solar System's $^{18}\text{O}/^{17}\text{O}$ ratio of 5.2 is explained as the result of mixing between typical interstellar medium (ISM) material with one or more exploding type-II supernovae tens of millions of years prior to formation of the Solar System. Possible mixing trends are shown by the black curves with dots.

The $^{18}\text{O}/^{17}\text{O}$ Enigma

The Solar System has an $^{18}\text{O}/^{17}\text{O}$ ratio of 5.2, in contrast to values of 4.1 to 3.5 for measurements of the local interstellar medium and YSOs (Fig. 1). Theories of Galactic chemical evolution (GCE) predict that the $^{18}\text{O}/^{17}\text{O}$ ratio should remain constant over time because both rare O isotopes are secondary nuclides. Production of secondary nuclides in stars requires the existence of nuclides heavier than H and He (e.g. ^{12}C and ^{16}O) as fuel. As stars synthesize new elements and then return them to the interstellar medium when they lose mass and die, the abundances of the heavier elements that feed ^{17}O and ^{18}O production grow with time in the Galaxy. Accordingly, the abundances of both ^{17}O and ^{18}O should rise linearly with time relative to ^{16}O , a primary nuclide that does not rely on the existence of elements heavier than H and He for its synthesis. Until recently, the disparity between Solar System and galactic $^{18}\text{O}/^{17}\text{O}$ ratios was regarded as the product of poor sampling and/or systematic errors between astronomical observations and mass spectrometry measurements. This explanation appears less likely now in view of new measurements of $^{18}\text{O}/^{17}\text{O}$ in protostars by infrared absorption spectroscopy (Fig. 2; Smith et al. 2009). By virtue of these measurements, systematic errors in the previous radio astronomy measurements are excluded as the cause (Young et al. 2011). A physical explanation is now required. Such deviations in $^{18}\text{O}/^{17}\text{O}$ could reflect a starburst caused by a galactic merger. Alternatively, enrichment of ^{18}O relative to ^{17}O could have been produced in the Sun's parental molecular cloud by one or more exploding type-II supernovae of appropriate composition and size from a generation of stars formed tens of millions of years prior to the Solar System. If true, comparisons between the O isotope ratios of our Solar System and the rest of the Galaxy will provide a tracer of the astrophysical environment in which our Solar System formed.

Silicon and Supernova Enrichment

Presolar grains provide context for the Solar System birth environment because in some cases their isotopes record the ratios that prevailed in the interstellar medium at the time the Sun was born. The vast majority of presolar grains, including SiC and oxides, derive from dust ejected by asymptotic giant branch (AGB) stars. These stars are highly evolved red giants that expel prodigious quantities of dust in "stellar winds" as they die, greatly enriching their circumstellar envelopes in SiC and amorphous silica. Processing in these stars has little effect on Si isotopes in general, so one expects the Si emitted by AGB stars to reflect the interstellar medium at the time the progenitors of these red giants formed. Since the grains from AGB stars that we find in meteorites must be from stars that predate the Sun, in many cases by billions of years, we should expect that a comparison between solar $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ ratios and the values for presolar grains should reflect the process of GCE whereby both ratios increase linearly with time. In fact, the opposite is observed (Nittler and Dauphas 2006): the Sun has lower $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ ratios than presolar SiC grains. The anomalous solar $^{30}\text{Si}/^{28}\text{Si}$ and $^{29}\text{Si}/^{28}\text{Si}$ ratios could be linked to injection of supernova ejecta. Explaining differences between the isotopic composition of our Solar System and the isotopic composition of other stars should provide important clues to our origins.

EVIDENCE OF SOLAR NEBULA EVOLUTION DEDUCED FROM CAIs AND CHONDRULES

The Origin of the $\delta^{18}\text{O}$ versus $\delta^{17}\text{O}$ slope = 1 Line

The mass-independent distribution of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values defining the slope-1 line is arguably the most distinctive chemical signature of the Solar System's rocky bodies and its most puzzling feature (Fig. 3). The cause of mass-independent oxygen isotope fractionation in the early Solar System has remained a mystery since its discovery decades ago in the calcium-aluminum inclusions (CAIs) of chondritic meteorites (Clayton et al. 1973). Isotopically selective photodissociation of molecules (especially CO) combined

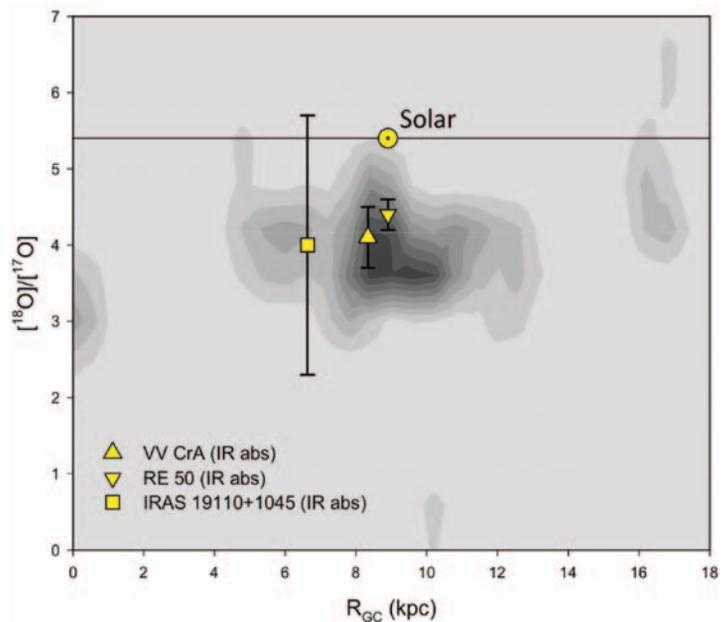


FIGURE 2 Astronomical infrared absorption spectroscopy measurements of $^{18}\text{O}/^{17}\text{O}$ in CO molecules in the circumstellar environment of young stars (Smith et al. 2009). Y-axis is $^{18}\text{O}/^{17}\text{O}$ ratio. X-axis is galactocentric radius, R_{GC} , in kiloparsecs. VV CrA is a binary star in the Corona Australis molecular cloud. RE 50 (Reipurth 50) is an intermediate-mass star in the Orion Molecular Cloud. IRAS 19110+1045 is a massive young stellar object.

with self-shielding has long been regarded as one possible explanation of the slope-1 line (Thiemen and Heidenreich 1983), and this idea has gained popularity in recent years (Clayton 2002; Lyons and Young 2005).

Calcium–aluminum-rich inclusions (CAIs) are aggregates of refractory minerals, including mellilite, Ti–Al-rich pyroxene, spinel, and hibonite, micrometers to millimeters in size, found in chondrule-bearing meteorites. The $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ values of CAIs lie along a line of slope approximately 1 (Fig. 3). The CAI O isotope analyses extend from the composition of the solar wind (presumably the composition of the Sun) towards the terrestrial mass-fractionation line (MacPherson 2007; McKeegan et al. 2010).

Carbon monoxide molecules are destroyed when they absorb far-ultraviolet (FUV) photons with wavelengths of 91 to 110 nm. But before they disassociate, the molecules enter a transient, energetically excited state with sharp absorption lines, well defined in wavelength. The wavelengths of the absorption lines depend on the isotopic composition of the molecules. The chemical bond $^{12}\text{C}-^{16}\text{O}$ vibrates at different frequencies than $^{12}\text{C}-^{18}\text{O}$: consequently, the wavelengths of FUV absorption for isotopically labeled molecules are different. Now consider a CO-bearing molecular cloud illuminated by a nearby star or a circumstellar disk lighted by a central star. The CO molecules will filter light from the star in an isotopically specific fashion. The most abundant CO species, $^{12}\text{C}^{16}\text{O}$, will absorb more of its characteristic wavelength than either of the rare molecules $^{12}\text{C}^{17}\text{O}$ or $^{12}\text{C}^{18}\text{O}$. The wavelength capable of dissociating $^{12}\text{C}^{16}\text{O}$ will be attenuated more rapidly with distance from the star than wavelengths destructive to $^{12}\text{C}^{17}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. The optical depth of $^{12}\text{C}^{16}\text{O}$ -destroying wavelengths of UV light will be much greater than that for the wavelengths that destroy the rare isotopologues (molecules that differ only in their isotopic composition). In this way, $^{12}\text{C}^{16}\text{O}$ is depleted in the gas nearest the star, but an overabundance of this molecule accumulates deep

in the column of gas where the ultraviolet light is attenuated. Such an isotopic fractionation due to optical depth effects, during which molecules are optically shielded, is termed *self-shielding*. Astronomers have observed isotopic fractionation of CO taking place in molecular clouds, providing observational evidence for the mechanism of self-shielding (Sheffer et al. 2002).

The isotopic heterogeneity of CO self-shielding is ephemeral: it will be eliminated by isotope exchange reactions between dust, molecules, atoms, and ions in the cloud or disk as time goes by. The spatial heterogeneity in O isotope ratios established by self-shielding is likely preserved by the formation of water ice. The O atom released by preferential destruction of CO reacts with ubiquitous H, forming H_2O that is frozen in the deep chill of space onto the surfaces of dust grains (Fig. 4). Later on, as dust is warmed by the accreting Sun, H_2O vapor sublimates from water ice. Reactions between H_2O vapor and rock dust will then produce a mixing line—the slope-1 line in $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ space between the ^{16}O -poor water reservoir and the ^{16}O -rich rock reservoir (Lyons and Young 2005).

Analysis of the O isotope composition of solar wind implanted in the Genesis mission collector plates suggests the Sun has a composition near -50‰ in both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$, forming the anchor point at the ^{16}O -rich end of the slope-1 line (McKeegan et al. 2010). These results are consistent with the self-shielding model. The site at which self-shielding took place is debated: did FUV photolysis occur in the placental molecular cloud and did the solar nebula inherit isotopic heterogeneity? Or, did the nascent Sun irradiate its own nebula, causing isotope fractionation as the circumstellar disk began to congeal? Photodissociation of CO is a complicated process, however, and it has been suggested that FUV illumination of CO may not result in a slope of 1 in a plot of $\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$. Deviations from slope-1 behavior will occur if the effects of self-shielding are overwhelmed by large differences in the rates of photodissociation of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ that have nothing to do with optical depth, as suggested by Chakraborty et al. (2008). Much exciting research remains to be done!

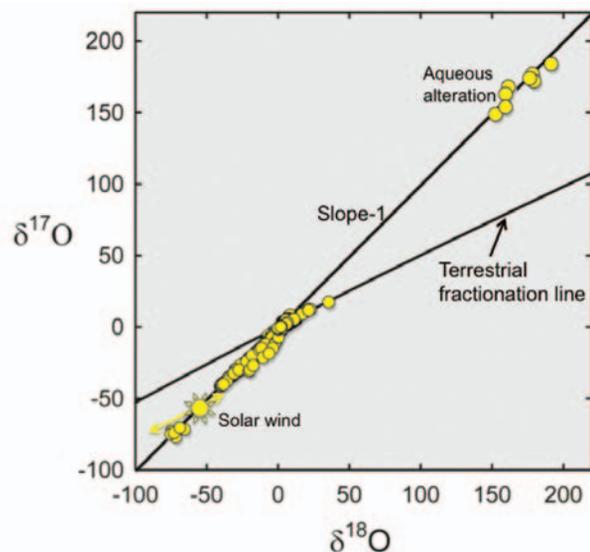


FIGURE 3 Oxygen isotope map of the Solar System. $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values of meteorites are in units of per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water). The terrestrial fractionation line (TFL) has a slope of approximately 0.52. All of Earth's rocks and minerals plot on the TFL except for arid surface deposits formed by atmospheric deposition of aerosol particles that interacted with ozone. Note that the carbonaceous chondrite anhydrous mineral line (not illustrated) has a slope of 0.94 and lies slightly to the right of the slope-1 line.

AQUEOUS ALTERATION IN PLANETARY EVOLUTION

Asteroids, comets, and gas-giant planets that accreted far from the radiant heating of the young Sun accumulated water ice from the solar nebula. When icy bodies were heated by decaying radioactive isotopes such as the now extinct ^{26}Al or ^{60}Fe , their ice melted. Water infiltrated throughout the parent bodies, reacting with anhydrous minerals (including chondrules and CAIs) to form phyllosilicate, oxide, sulfide, sulfate, and carbonate minerals. The isotopic compositions of these secondary minerals provide evidence of their early Solar System age and the conditions under which aqueous alteration took place.

Recent development of a “carbonate clumped-isotope thermometer” (Ghosh et al. 2006) provides new opportunities for reconstructing the aqueous alteration temperatures on carbonaceous chondrite parent bodies. This new geothermometer has a great advantage over traditional isotope geothermometers since it is independent of the isotopic compositions of coexisting phases. Furthermore, when one couples the formation temperature estimated through the carbonate clumped-isotope thermometer with the O isotope composition of the carbonate minerals, the O isotope composition of the parent water from which carbonates precipitated can also be derived.

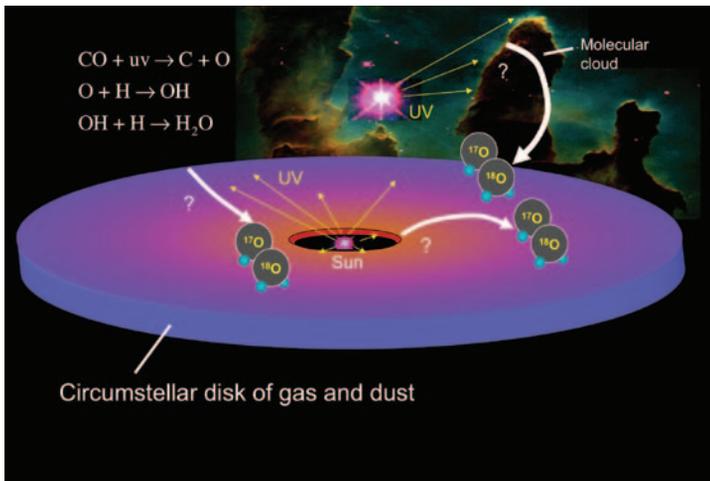


FIGURE 4 The photolytic decomposition of CO molecules by UV light and self-shielding in a molecular cloud or circumstellar disk leads to heterogeneity in oxygen isotope compositions. Three suggested locations for this process are depicted here. Heterogeneity is preserved by the formation of isotopically labeled water ice that freezes on dust grains.

The carbonate clumped-isotope thermometer constrains carbonate formation temperatures based on a homogeneous equilibrium within the carbonate lattice itself: $M^{13}C^{16}O^{16}O + M^{12}C^{18}O^{16}O = M^{13}C^{18}O^{16}O + M^{12}C^{16}O^{16}O$, where M is a metal (Eiler 2007). As opposed to being randomly dispersed, ^{13}C and ^{18}O in a thermodynamically equilibrated carbonate mineral tend to “clump” into the same carbonate ion group to form $^{13}C^{18}O^{16}O^{2-}$, due to the lower zero-point energy of this doubly substituted isotopologue compared to nonsubstituted or singly substituted isotopologues. This preferential clumping of ^{13}C and ^{18}O produces abundances of $^{13}C^{18}O^{16}O^{2-}$ higher than expected from a statistical distribution of isotopes. The magnitude of this abundance excess increases with decreasing temperature and is determined by measuring anomalous enrichments of mass-47 CO_2 (mainly $^{13}C^{18}O^{16}O$) in the CO_2 derived from phosphoric acid digestion of carbonate minerals.

Application of carbonate clumped-isotope geothermometry to calcite in CM chondrites demonstrates that aqueous alteration of CM chondrite parent bodies occurred at 21 °C to 71 °C from fluids with $\delta^{18}O_{VSMOW}$ of 1.8‰ to 7.8‰ and $\delta^{17}O_{VSMOW}$ of -0.2‰ to 2.9‰. A negative correlation between $\delta^{13}C$ of the carbonates and $\delta^{18}O$ of the alteration fluids is taken as evidence of methane generation on the parent body during aqueous alteration, which in turn indicates a reducing and alkaline alteration environment ($Eh \leq -0.67$ and $pH \geq 12.5$) (Guo and Eiler 2007). In the context of fluid-flow models of aqueous alteration, these estimated alteration temperatures suggest aqueous alteration occurred within an approximately 250 m thick zone, 1.8 km from the surface of a 9 km radius body. Clumped-isotope geothermometry in other carbonaceous chondrites coupled with Mn–Cr chronometry of carbonate minerals makes it possible to estimate the thermal history of aqueous alteration. Preliminary results indicate that aqueous alteration started within 1–2 million years after the accretion of those parent bodies and that the alteration temperatures decreased from 34 °C to 18 °C in the first ~4 million years and further to -20 °C after a total of ~6.5 million years (Guo 2008).

NONTRADITIONAL STABLE ISOTOPES, THE EARLY SOLAR NEBULA, AND PLANETARY DIFFERENTIATION

Stable isotopes of the elements Li, Mg, Si, Cl, Ca, Cr, Fe, Zn, Cu, etc. have also been investigated in cosmochemistry. These nontraditional isotope systems offer insights into a wide variety of nebular and planetary processes because they participate in suites of chemical reactions and physical mechanisms different from those involving H, C, N, O, and S. Investigations using the heavier stable isotopes as tracers were regarded skeptically because the magnitudes of the fractionations of stable isotopes between minerals were expected to fall to immeasurably small values. Such skepticism was justified on the grounds that isotope fractionation between minerals scales with $\Delta m/m^2$, where Δm is the difference between the masses and m is the average atomic mass of the element. No instruments were available at the time that could reliably measure the fractionations to the necessary precision. Development of the multiple-collector inductively coupled plasma mass spectrometer (MC-ICPMS), which ionizes elements across the periodic table efficiently in a hot plasma for analysis with high precision and accuracy, opened a new and productive line of research in stable isotope cosmochemistry.

The primitive constituents of chondritic meteorites, including CAIs and chondrules, were like canaries in the mine, reacting swiftly to changing environmental conditions, where the mine in this case is the circumstellar disk of gas and dust from which the planets were formed. CAIs and chondrules come in many forms, but in many cases they were obviously melted. However, the conditions attending the melting of these two distinct kinds of objects were very different, and stable isotope ratios provide the crucial evidence of this fact.

Chondrules are spherical intergrowths of olivine and pyroxene that crystallized from molten nebular droplets 1–2 million years after the condensation of CAIs (Krot et al. 2009). The presence of chondrules is the defining feature of most of the chemically primitive classes of meteorites, the chondrites (the CI chondrites being the notable exception). The O isotope compositions of chondrules scatter along the slope-1 line, with the ordinary chondrites extending above the terrestrial fractionation line to ^{16}O -poor values (FIG. 3). The colinearity of CAI and chondrule $\delta^{17}O$ versus $\delta^{18}O$ values with the inferred composition of the Sun distinguishes them as ancient products of nebular processing.

Chondrules generally have the same Mg and Si isotope ratios as most meteorites and other bodies in the Solar System, including Earth, Moon, Mars, and the asteroid Vesta. CAIs that melted, on the other hand, generally have higher $^{25}Mg/^{24}Mg$ and $^{30}Si/^{28}Si$ than other objects in the Solar System. This enrichment in the heavy isotopes of these major rock-forming elements is the consequence of evaporation of the molten CAIs at low pressures in the circumstellar disk. As with the evaporation from Earth’s oceans of $H_2^{16}O$ compared with $H_2^{18}O$, the lighter isotopes evaporate more readily than the heavier isotopes, leaving the residues enriched in the heavy isotopes. Recent work has characterized the physical chemistry of this process to the point where it is possible to model the evaporation of CAIs to determine the timescales and pressures (partial pressures of the H_2 gas that dominates circumstellar disks) during evaporation (Shahar and Young 2007). Results suggest timescales of days to weeks at realistic astrophysical pressures (FIG. 5). The fact that the CAIs were molten for only a matter of days or weeks places tight constraints on

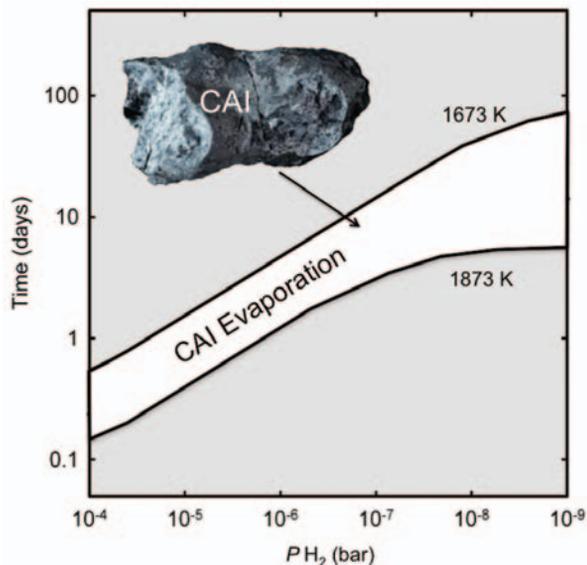


FIGURE 5 Calculated duration (in days) of melting of a type-A CAI as a function of temperature (in kelvins, K) and pressure (p_{H_2}) based on reconstructing the evaporative enrichment of $^{25}Mg/^{24}Mg$ and $^{30}Si/^{28}Si$ in the object (after Shahar and Young 2007). Inset is an image of an unusually large type-B CAI, 0.5 cm in size, from the Allende meteorite. Objects like this one were molten in the early solar nebula for days to weeks.

the astrophysical environments in which these objects were melted. For example, they could not have been heated simply as a consequence of being in a hot portion of the inner disk (heated by energy dissipation by inward accretion) because they would have remained molten for much longer periods of time. An abrupt episode of heating is required, perhaps as a result of shock waves passing through the disk.

Why did the chondrules not evaporate while the CAIs did? Current thinking is that chondrules were melted in large clusters in which the objects were closely spaced (Young 2004; Cuzzi and Alexander 2006). CAIs, on the other hand, must have melted in comparative isolation, with spacings between them of greater than several meters (Shahar and Young 2007). Such detailed information about the mechanisms that melted these millimeter- to centimeter-sized objects more than 4.5 billion years before present is a direct consequence of our understanding of how stable isotopes partition during phase changes.

While it has been known for some time that there is a chemical heterogeneity between differentiated objects and chondrites (for example, volatile-element budgets, Mg/Si, refractory-element contents), it has been assumed that the Earth formed from a chondritic bulk composition. Therefore, the origin of this heterogeneity has been debated heavily, and discussion focuses on either planetary differentiation processes or disk-related mechanisms as the primary cause. Three of the four most abundant elements in the terrestrial planets—Mg, Si, and Fe—follow mass-dependent fractionation laws in three-isotope space, providing evidence for efficient mixing at some stage in the evolution of protoplanetary material. Due to this observation, an isotopic fractionation in these elements between Earth and chondrites is highly unexpected, but it would have many implications for the formation of the Earth (and other planetary bodies) if found.

The observation that basalts from Earth are enriched in ^{57}Fe relative to chondrites has led to a myriad of explanations for why this difference exists. The possibilities include fractionation caused by evaporation and condensation

during the Moon-forming giant impact, partial melting, magmatic differentiation, metasomatism, and planetary differentiation (FIG. 6). Theoretical calculations by Polyakov (2009) show that $\delta^{57}Fe$ changes as a function of pressure. Based on the difference between $\delta^{57}Fe$ of Fe-metal and Fe-perovskite, he concluded that the Earth obtained its nonchondritic $\delta^{57}Fe$ due to equilibrium Fe isotope fractionation during segregation of Earth's core. This study was the first to consider the role of pressure in iron isotopic fractionation processes. Further experimental work needs to be done to confirm this mechanism—an exciting research opportunity for high-pressure science.

The Si isotope ratio of the bulk silicate Earth is homogeneous, but recent studies found a measurable difference between Earth and carbonaceous chondrites, though the value is still debated (Georg et al. 2007; Fitoussi et al. 2009). The authors argue, in both studies, that the difference between bulk silicate Earth $\delta^{29}Si$ and carbonaceous chondrite $\delta^{29}Si$ values reflects the fractionation that occurred during core segregation on Earth. While the Earth was segregating, small molten-Fe droplets were equilibrating with the surrounding silicate melt and alloying with Si during their descent through the mantle towards the core. This process left the silicate Earth enriched in ^{29}Si relative to chondrites. Theoretical and experimental work (Georg et al. 2007; Shahar et al. 2009) shows that ^{28}Si dissolves in metal more readily than ^{29}Si , adding more evidence that Si isotope ratios measured today record processes of planetary differentiation that occurred billions of years ago. This work requires that the Earth went through a magma-ocean stage under highly reducing conditions so that Si would alloy easily with the metal (FIG. 6).

The Mg isotope compositions of Earth and chondrite meteorites have also been measured, but there is no consensus as to whether the values are the same within error. Wiechert and Halliday (2007) found that all differentiated planets measured have a higher $^{25}Mg/^{24}Mg$ ratio than chondrite meteorites, with the terrestrial mantle approximately 0.13‰ greater in $\delta^{25}Mg$ than chondrites. Young et al. (2009) also came to the conclusion that the Earth is nonchondritic, but decreased the magnitude of the

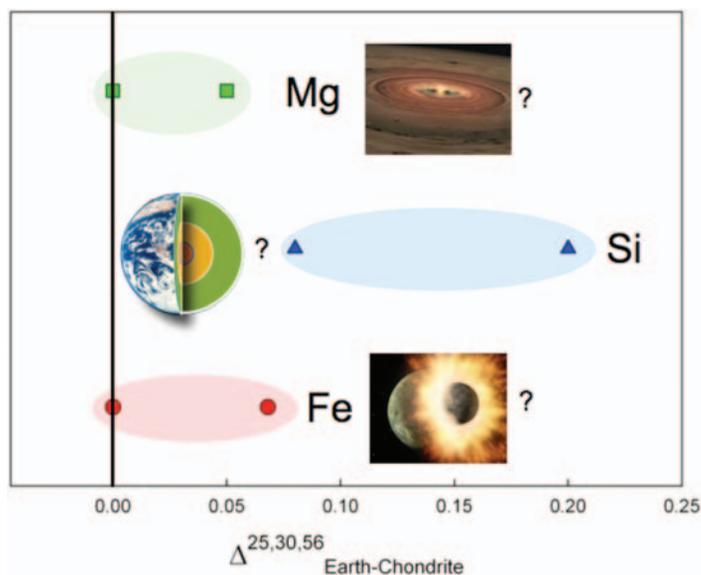


FIGURE 6 Range of values measured for $\Delta^{25}Mg$, $\Delta^{30}Si$, and $\Delta^{56}Fe$ between Earth and chondrite. The straight line at 0.00‰ reflects the expected value if no process fractionated the isotopic reservoirs. Several possible isotope-fractionation mechanisms are shown, including sorting of dust and molten drops for Mg, core segregation for Si, and a giant impact for Fe.

difference to $\leq 0.05\%$. Chakrabarti and Jacobsen (2010), however, find that the Earth has the same $\delta^{25}\text{Mg}$ value as chondrites. If a difference in $\delta^{25}\text{Mg}$ between Earth and chondrite meteorites exists, it is difficult to explain. Fractionation of $^{25}\text{Mg}/^{24}\text{Mg}$ by a mechanism of core segregation is ruled out because Mg is too large to dissolve into iron metal and therefore is not usually considered a plausible light element in the core (though the size difference decreases with pressure). If there is agreement that Earth and chondrites are dissimilar in $\delta^{25}\text{Mg}$, then the difference would imply a process occurring prior to Earth formation, presumably in the circumstellar disk from which the planets formed. Possible mechanisms for producing heterogeneity include physically sorting molten chondrules from dust within the disk and a heterogeneous Mg isotope composition of the inner Solar System due to inefficient mixing (Fig. 6).

CONCLUSIONS

The state of the art in stable isotope cosmochemistry is one of a constant influx of new ideas, new techniques, and new investigators. Who would have predicted that measure-

ment of the isotope ratios of molecular clouds by astronomers on a scale of 10^{19} meters would reinforce the observations of cosmochemists analyzing stardust grains 10^{-6} meters in diameter, a range of 25 orders of magnitude in size? Or that the invention of inductively coupled plasma ion sources would revolutionize analysis of elements in the middle of the periodic table by mass spectrometry? Or that the successful measurement of infinitesimally small abundances of molecules containing two rare isotopes would open a new discipline of geo-cosmo-thermometry? We offer no conclusions. Every one of the sentences in this review is subject to revision in the light of new research. But we earnestly invite interested readers to stay tuned. Don't miss the coming excitement!

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REFERENCES

- Chakrabarti R, Jacobsen SB (2010) The isotopic composition of magnesium in the inner Solar System. *Earth and Planetary Science Letters* 293: 349-358
- Chakraborty S, Ahmed M, Jackson TL, Thiemens MH (2008) Experimental test of self-shielding in vacuum ultraviolet photodissociation of CO. *Science* 321: 1328-1331
- Clayton RN (2002) Self-shielding in the solar nebula. *Nature* 415: 860-861
- Clayton RN, Grossman L, Mayeda TK (1973) A component of primitive nuclear composition in carbonaceous meteorites. *Science* 182: 485-488
- Cuzzi JN, Alexander CMOD (2006) Chondrule formation in particle-rich nebular regions at least hundreds of kilometers across. *Nature* 441: 483-485
- Eiler JM (2007) "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. *Earth and Planetary Science Letters* 262: 309-327
- Fitoussi C, Bourdon B, Kleine T, Oberli F, Reynolds BC (2009) Si isotope systematics of meteorites and terrestrial peridotites: implications for Mg/Si fractionation in the solar nebula and for Si in the Earth's core. *Earth and Planetary Science Letters* 287: 77-85
- Georg RB, Halliday AN, Schauble EA, Reynolds BC (2007) Silicon in the Earth's core. *Nature* 447: 1102-1106
- Ghosh P, Adkins J, Affek H, Balta B, Guo W, Schauble EA, Schrag D, Eiler JM (2006) ^{13}C - ^{18}O bonds in carbonate minerals: A new kind of paleothermometer. *Geochimica et Cosmochimica Acta* 70: 1439-1456
- Guo W (2008) Carbonate Clumped Isotope Thermometry: Application to carbonaceous chondrites and effects of kinetic isotope fractionation. Unpublished PhD thesis, Caltech
- Guo W, Eiler JM (2007) Temperatures of aqueous alteration and evidence for methane generation on the parent bodies of the CM chondrites. *Geochimica et Cosmochimica Acta* 71: 5565-5575
- Krot AN and 15 coauthors (2009) Origin and chronology of chondritic components: A review. *Geochimica et Cosmochimica Acta* 73: 4963-4997
- Lyons JR, Young ED (2005) CO self-shielding as the origin of oxygen isotope anomalies in the early solar nebula. *Nature* 435: 317-320
- MacPherson GJ (2007) Calcium-aluminum-rich inclusions in chondritic meteorites. In: Davis AM (ed) *Meteorites, Comets, and Planets. Treatise on Geochemistry 1*, Elsevier, chapter 1.08, 47 pp
- McKeegan KD, Kallio APA, Heber VS, Jarzebinski G, Mao PH, Coath CD, Kunihiro T, Wiens R, Allton J, Burnett DS (2010) Genesis SiC concentrator sample traverse: Confirmation of ^{16}O -depletion of terrestrial oxygen. 41st Lunar and Planetary Science Conference, abstract 2589
- Nittler LR, Dauphas N (2006) Meteorites and the chemical evolution of the Milky Way. In: Lauretta DS, McSween HY Jr (eds) *Meteorites and the Early Solar System II*. University of Arizona Press, Tucson, AZ, pp 127-146
- Nguyen AN, Messenger S (2011) Presolar history recorded in extraterrestrial materials. *Elements* 7: 19-24
- Polyakov VB (2009) Equilibrium iron isotope fractionation at core-mantle boundary conditions. *Science* 323: 912-914
- Shahar A, Young ED (2007) Astrophysics of CAI formation as revealed by silicon isotope LA-MC-ICPMS of an igneous CAI. *Earth and Planetary Science Letters* 257: 497-510
- Shahar A, Ziegler K, Young ED, Ricolleau A, Schauble EA, Fei Y (2009) Experimentally determined Si isotope fractionation between silicate and Fe metal and implications for Earth's core formation. *Earth and Planetary Science Letters* 288: 228-234
- Sheffer Y, Lambert DL, Federman SR (2002). Ultraviolet detection of interstellar $^{12}\text{C}^{17}\text{O}$ and the CO isotopomeric ratios toward X Persei. *The Astrophysical Journal Letters* 574: L171-L174
- Smith RL, Pontoppidan KM, Young ED, Morris MR, van Dishoeck EF (2009) High-precision C^{17}O , C^{18}O and C^{16}O measurements in young stellar objects: Analogues for CO self-shielding in the early Solar System. *The Astrophysical Journal* 701: 163-175
- Thiemens MH, Heidenreich HE III (1983) The mass-independent fractionation of oxygen: A novel isotope effect and its possible cosmochemical implications. *Science* 219: 1073-1075
- Wiechert U, Halliday AN (2007) Non-chondritic magnesium and the origins of the inner terrestrial planets. *Earth and Planetary Science Letters* 256: 360-371
- Wilson TL (1999) Isotopes on the interstellar medium and circumstellar envelopes. *Reports on Progress in Physics* 62: 143
- Young ED (2004) Isotopic cosmobarometry – A synthesis of concepts and implications for chondrule and CAI formation mechanisms. 35th Lunar and Planetary Science Conference, abstract A1300
- Young ED, Tonui E, Manning CE, Schauble E, Macris CA (2009) Spinel-olivine magnesium isotope thermometry in the mantle and implications for the Mg isotopic composition of Earth. *Earth and Planetary Science Letters* 288: 524-533
- Young ED, Gounelle M, Smith RL, Morris MR, Pontoppidan KM (2011) Astronomical oxygen isotopic evidence for supernova enrichment of the solar system birth environment by propagating star formation. *The Astrophysical Journal*, in press
- Zinner E (2007) Presolar Grains. In: Davis AM (ed) *Meteorites, Comets, and Planets. Treatise on Geochemistry 1*, Elsevier, chapter 1.02, 33 pp ■