

## Mass-independent Oxygen Isotope Variation in the Solar Nebula

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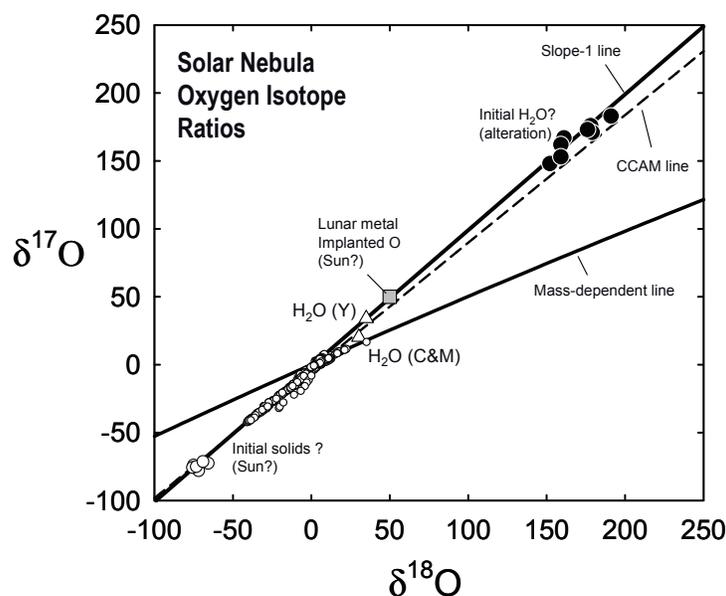
### ABSTRACT

In this chapter we compare and contrast chemical and photochemical pathways for mass-independent fractionation (MIF) of oxygen isotopes in the solar nebula. We begin by assessing the galactic evolution model for oxygen isotope variation in the Solar System in order to compare the predictions of a leading nucleosynthetic model with those of the chemical models. There are two fundamentally different classes of possible chemical mechanisms for mass-independent oxygen isotope fractionation in the early Solar System. One is symmetry-induced intramolecular vibrational disequilibrium of vibrationally excited reactant oxygen-bearing molecules. The other is isotope selective photodissociation of CO coupled with self-shielding and formation of H<sub>2</sub>O. Symmetry-induced fractionation is an experimentally verified process with solid theoretical foundations. It is observed to occur in Earth's atmosphere. It could have resulted in preservation of oxygen MIF effects only if mediated by dust grain surfaces. CO self-shielding is an attractive hypothesis for the origin of mass-independent oxygen isotope fractionation in the early Solar System because it appeals to a process that apparently occurs in the interstellar medium, but it lacks experimental verification. Three astrophysical settings for CO self-shielding are proposed as sites for generating  $\Delta^{17}\text{O}$  variability in the early Solar System. One is the inner annulus of the protostellar disk at relatively high temperature. Another is the surface of the disk high above the midplane where light from the central star grazes the

gas and dust of the disk, resulting in a zone of active CO predissociation and self-shielding. Interstellar light illuminating the disk at high incident angles causes a similar horizon of CO photodestruction. Variations in  $^{16}\text{O}$  could also have been inherited from self-shielding by CO in the molecular cloud that gave rise to the protosun. The overall consequence of CO self-shielding is conversion of CO gas to  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$ . A key difference between galactic evolution, chemically-induced MIF effects, and CO self-shielding is the predicted relative oxygen isotopic compositions of primeval dust and the Sun. Therefore, the oxygen isotopic composition of the Sun will be a crucial arbiter that may permit us to narrow the list of possible origins for oxygen MIF in the early Solar System.

## INTRODUCTION

Rocky bodies in the Solar System exhibit large variations in  $^{16}\text{O}$  relative to both  $^{17}\text{O}$  and  $^{18}\text{O}$  rather than the expected mass-dependent trend in which fractional changes in  $^{17}\text{O}/^{16}\text{O}$  are about half those in  $^{18}\text{O}/^{16}\text{O}$  (Fig. 1). This anomalous behavior among the isotopes of oxygen in primitive Solar System materials is one of the most pronounced isotopic features of the Solar System, and its cause has remained a mystery since it was first discovered (Clayton *et al.* 1973). Although there have been many mechanisms proposed (Clayton 1993), all can be classified as either nucleosynthetic or chemical in nature. The primary topics of this chapter are chemical and photochemical pathways for mass-independent fractionation (MIF) of oxygen isotopes in



**Figure 1.** Compilation of Solar System oxygen isotope ratios (‰). Chondrite mineral separate and whole-rock fluorination data from the laboratory of R. N. Clayton and ultraviolet laser-ablation fluorination data from E. Young's laboratory are shown as small open circles. Oxygen implanted in lunar iron metal (Ireland *et al.* 2006) is represented by the grey square. Calculated  $\text{H}_2\text{O}$  vapor compositions for the inner solar nebula after Clayton and Mayeda (1984) ( $\text{H}_2\text{O}$  (C&M)) and Young (2001) ( $\text{H}_2\text{O}$  (Y)) are shown as open triangles. Incipient aqueous alteration products in Acfer 094 (Sakamoto *et al.* 2007) are shown as black circles. Analyses of an extremely  $^{16}\text{O}$ -enriched chondrule (Kobayashi *et al.* 2003) is shown as large open circles. Also shown are the terrestrial mass-dependent fractionation line, the mass-independent carbonaceous chondrite anhydrous mineral (CCAM, dashed with slope = 0.94) and "primitive" slope-1.0 (solid with slope = 1.0) lines.

the solar nebula. However, evaluating the likelihood that such mechanisms apply should be done with reference to competing hypotheses, and so we begin by presenting galactic evolution calculations that allow one to compare the predictions of a leading nucleosynthetic model with those of the chemical models. Our discussion includes the possibility for inheritance of chemically-induced MIF from the placental molecular cloud that gave rise to the Sun, as well as chemical mechanisms within the disk itself.

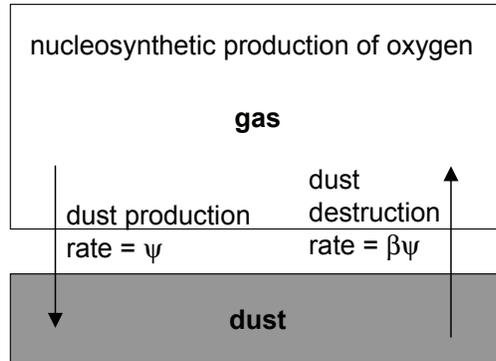
Throughout this chapter we will refer to plots of  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ . These “delta” values refer to the per mil (‰) difference from the ratio in a reference reservoir  $j$  such that  $\delta^i\text{O} = 10^3[(i\text{O}/^{16}\text{O})/(i\text{O}/^{16}\text{O})_j - 1]$  where  $i$  refers to either 17 or 18. The reference reservoir  $j$  is either the Standard Mean Ocean Water (SMOW) reference for oxygen isotope measurements, the average solar value for galactic evolution modeling or the initial solar value based on Ca-, Al-rich inclusions (CAIs) for MIF modeling. We will also refer to  $\Delta^{17}\text{O}$  (“big delta  $^{17}\text{O}$ ”), usually defined as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \delta^{18}\text{O}$ .  $\Delta^{17}\text{O}$  represents the degree of departure from mass-dependent fractionation relative to some reference reservoir of oxygen. See Criss and Farquhar (2008) for a more detailed treatment of the  $\delta$  and  $\Delta$  notations.

### GALACTIC OXYGEN ISOTOPE EVOLUTION— A NON-CHEMICAL PATH TO MASS INDEPENDENCE

Galactic evolution refers to increases in the abundances of the secondary nuclides  $^{18}\text{O}$  and  $^{17}\text{O}$  as a consequence of increasing stellar metallicity with time compared with the linear growth rate of the primary nuclide  $^{16}\text{O}$  (Timmes et al. 1995). Oxygen-16 is the most abundant product of *primary* galactic nucleosynthesis, in that only H and He are more abundant (Anders and Grevesse 1989). It is primarily produced in supernova explosions. Thus, for a simple model of uniform production, the  $^{16}\text{O}$  mass will increase linearly with time over the history of our Galaxy. In contrast,  $^{18}\text{O}$  and  $^{17}\text{O}$  are products of *secondary* nucleosynthesis (Clayton 1988; Meyer et al. 2008) in that their yields are approximately proportional to the existing galactic inventory of  $^{16}\text{O} + ^{12}\text{C}$ . Thus, for a uniform production model for  $^{16}\text{O}$ , it follows that the abundances of  $^{17}\text{O}$  and  $^{18}\text{O}$  are expected to depend on the square of time. This results in a linear increase of  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  over the history of our Galaxy. Oxygen is also unique among all the elements in that it is present in significant quantities in both the dust and the gas of the diffuse interstellar medium. It is therefore possible, in principle, to preserve “old galactic oxygen” in the dust of the interstellar medium, and this could contribute to the oxygen isotopic heterogeneity observed in Solar System materials. Jacobsen et al. (2007) have recently investigated this problem using a simple two-box model approach, shown schematically in Figure 2. Here we include a brief overview of their model and results.

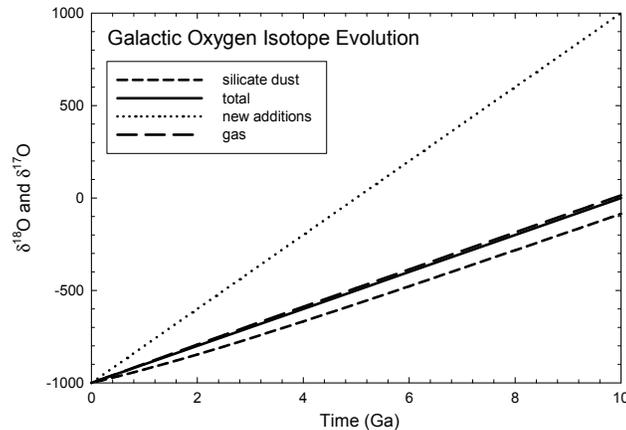
The model assumes that oxygen isotopes are produced by galactic nucleosynthesis injections into the gas phase of the interstellar medium. Some of this oxygen is isolated in dust grains (at a rate proportional to the amount of  $^{16}\text{O}$  in the gas) that may later be destroyed by various processes in the interstellar medium (dust destruction rate is proportional to the dust production rate). As a consequence, the dust reservoir may preserve a component of old galactic oxygen compared to the oxygen in the gas. We note that condensation of typical silicate dust sequestered about 14% of the total solar oxygen, while only ~1% was tied up as dust composed of the primitive CAIs found in chondrite meteorites. It is assumed that a steady-state distribution of oxygen is established between the gas and dust of the interstellar medium. We do not consider the molecular clouds as separate reservoirs for oxygen, as the matter in such clouds has a relatively short residence time of  $<10^8$  yr (Jacobsen 2005), which would not yield substantial isotopic heterogeneities.

For simplicity, we assume that the Solar System formed exactly 10 Ga after Galaxy formation. The evolution of oxygen isotope ratios in various reservoirs of this model as a



**Figure 2.** Simple galactic evolution model for oxygen isotopes (Jacobsen et al. 2007). Since oxygen is the only element that resides substantially both in silicate dust and the gas phase of the interstellar medium, it is essential that a first-order model take this into account. Oxygen isotopes are produced by galactic nucleosynthesis injections into the gas phase of the interstellar medium. Some of this oxygen is isolated in dust grains that may later be destroyed by various processes in the interstellar medium. The dust reservoir may thus preserve a component of old galactic oxygen compared to the oxygen in the gas.

function of time for this 10 b.y. period is shown in Figure 3 as  $\delta$ -values relative to the average solar composition. Note that in the  $\delta$ -notation, the time-evolution of  $^{17}\text{O}$  and  $^{18}\text{O}$  are identical, and therefore all these results will plot on the slope =1 line on the  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  diagram, which is referred to as the oxygen three-isotope plot. The average galactic evolution is labeled “total.” For the calculations illustrated in Figure 3, one assumes a difference between the gas and the dust of 100‰ ( $\delta^{18}\text{O}_{\text{dust}} = -86\text{‰}$ ), a value commensurate with the spread in oxygen isotope ratios in the Solar System. The 100‰ difference between gas and dust corresponds to a residence time of oxygen in the dust of 1.1 b.y. Note that the dotted curve is for new nucleosynthetic additions to the interstellar medium (ISM) as a function of time. It ends up at a value of +1000‰ for both  $^{17}\text{O}$  and  $^{18}\text{O}$  at the time of formation of the Solar System; this is the expected average value of new additions to the ISM at the time of formation of our Solar System, and it differs greatly from the average ISM material from which the Solar System was derived.

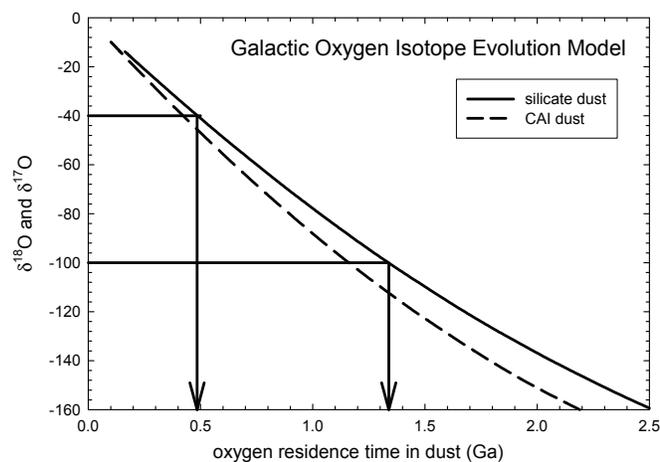


**Figure 3.** The evolution of oxygen isotope ratios (shown as  $\delta$ -values relative to the average solar composition) as a function of time for the model in Figure 2. The total time prior to Solar System formation is assumed to be 10 b.y. Note that in the  $\delta$ -notation the  $^{17}\text{O}$  and  $^{18}\text{O}$  evolutions are identical and therefore all these results will plot on the slope 1 line in the  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  diagram. The average galactic evolution is labeled “total”. For these calculations we assumed a difference between the gas and the dust of 100‰ and a residence time of oxygen in the dust of 1.1 b.y. Note that the dotted curve is for new nucleosynthetic additions to the interstellar medium as a function of time. It ends up at a value of +1000‰ for both  $^{17}\text{O}$  and  $^{18}\text{O}$  at 10 Ga, the time of formation of the Solar System.

The box-model gives a simple relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  ( $\delta$  relative to solar oxygen isotope ratios) and the mean oxygen residence time in the dust, shown in Figure 4. The  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  difference between the dust and the gas must be at least about 50‰ to generate the observed range of values in primitive meteorites. Ireland et al. (2006) reported an estimate of the present solar value of about +50‰ while others have estimated  $\text{H}_2\text{O}$  values that are also highly enriched in  $^{18}\text{O}$  and  $^{17}\text{O}$  (Clayton and Mayeda 1984; Young 2001).  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values of  $-40$  to  $-100$ ‰ in the dust result in a mean residence time of the oxygen in the dust of 0.5 to 1.5 b.y. (Fig. 4). Using CAI dust instead of magnesian silicate dust does not substantially change this result (Fig. 4). A residence time of 0.5 to 1.5 b.y. is reasonable for the coarse dust in the interstellar medium (Clayton et al. 1989). Most recently, Sakamoto et al. (2007) reported  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  values both approaching +200‰ in a poorly characterized phase (PCP) from the matrix of the carbonaceous chondrite Acfer 094. They argue that the PCP could have formed by interaction with solar nebular water and suggest that Solar System water was highly enriched in  $^{17}\text{O}$  and  $^{18}\text{O}$  ( $\delta^{17,18}\text{O}_{\text{SMOW}} = +180$ ‰). This means that the difference between the initial dust and gas in the Solar System could have been as large as 250‰. In that case the mean residence time of the oxygen in the dust would be about 4.5 to 5 b.y., suggesting very little recycling of oxygen in ISM grains. We treat this conclusion with caution because it is conceivable that the PCP aggregates are presolar in origin. A presolar silicate grain with a  $\delta^{17}\text{O}$  value of +400‰ was also reported by Sakamoto et al. (2007) in the matrix of the same meteorite, within  $\sim 40$   $\mu\text{m}$  of the PCP aggregate. More work is needed to evaluate this interesting discovery.

#### Testing the hypothesis – the oxygen isotopic composition of the Sun

The basic conclusion is that galactic evolution can produce the observed range in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  in the Solar System if it represents a difference in average age of oxygen of the gas phase and dust at the time the Solar System formed. Since oxygen in the Sun represents the gas phase, the galactic evolution model predicts that the Sun should be  $^{16}\text{O}$ -poor relative to the primeval solids of the Solar System. A test of the hypothesis is therefore whether or not the Sun is  $^{16}\text{O}$ -poor relative to planets and asteroids. Oxygen implanted in iron metal on the lunar surface is consistent with an  $^{16}\text{O}$ -poor Sun if the implanted oxygen is indeed representative of the Sun (Ireland et al. 2006). However, as discussed by Davis et al. (2008), there are two data



**Figure 4.** The model in Figure 2 gives a relationship between  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  ( $\delta$  relative to solar oxygen isotope ratios) in the dust and the mean oxygen residence time in the dust. Since  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  is most likely in the range  $-40$  to  $-100$  (see text) it means that that the mean residence time of the oxygen in the dust is in the range 0.5 to 1.3 b.y.

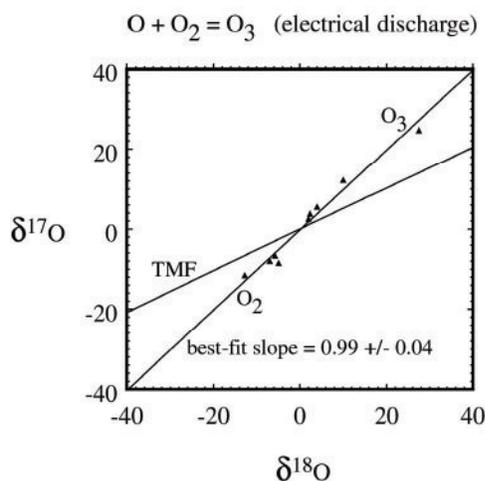
sets for implanted solar wind oxygen on the Moon, and the second set of data (Hashizume and Chaussidon 2005) implies that the Sun has oxygen isotope ratios similar to those of CAIs. This is inconsistent with the prediction of galactic evolution. Clearly, the oxygen isotopic composition of the Sun will be a key test of this hypothesis. Analysis of solar wind samples collected by the Genesis spacecraft are in progress and are expected to resolve the question of the oxygen isotopic composition of the Sun.

### CHEMICAL MASS-INDEPENDENT OXYGEN ISOTOPE FRACTIONATION

For more than two decades, symmetry-based kinetic MIF isotope effects have been posited as possible sources of the  $\Delta^{17}\text{O}$  variability in the Solar System (Thiemens 1992, 1996). Chemically-induced MIF effects were first identified as a consequence of ozone formation from molecular oxygen (Thiemens and Heidenreich 1983) and the archetypical MIF reaction remains  $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ . In the first experiments it was observed that  $\text{O}_3$  produced by dissociation of  $\text{O}_2$  gas was enriched in  $^{18}\text{O}$  relative to the residual  $\text{O}_2$ , with  $\delta^{17}\text{O}$  approximately equal to  $\delta^{18}\text{O}$  (Fig. 5). This MIF effect attending  $\text{O}_3$  formation was discovered to be the source of anomalous oxygen isotope fractionation in the stratosphere (Mauersberger 1987) and has proven to be an important tracer in Earth's atmosphere (e.g., Yung *et al.* 1991). Subsequent studies have shown MIF effects in reactions involving CO and  $\text{CO}_2$  (Röckmann *et al.* 1998; Bhattacharya *et al.* 2000).

Understanding the mass-independent isotope fractionation effect for ozone in the laboratory (Thiemens and Heidenreich 1983), stratosphere (Krankowsky *et al.* 2000), and for the earliest solids in the Solar System (Clayton *et al.* 1973) poses interesting challenges. These challenges are both in the intrinsic interest in the phenomena themselves and in understanding the new chemical physics responsible for the phenomena. Much is now understood about the MIF in ozone formation in the gas phase (Gao and Marcus 2001). Much less is known about the prospects for mass-independent isotope effects involving condensed phases (cf. Miller *et al.* 2002).

Recent experiments by Nuth *et al.* (2006) and Chakraborty *et al.* (2006) on the rapid formation of silicates from ignition of a mixture of  $\text{N}_2\text{O}$  or  $\text{O}_2$  (as sources of O atoms), silane,  $\text{Fe}(\text{CO})_5$  and  $\text{H}_2$  by a Tesla coil yielded run products that appear to show a slope of 0.68 on the three-isotope plot of  $\delta^{17}\text{O}$  against  $\delta^{18}\text{O}$ . This value exceeds the normal mass-dependent value of 0.52, though it is not as large as the mass-independent slope of 1.0. It appears, however, that the result was likely due to reaction with ozone formed when oxygen is present, as noted in Kimura *et al.* (2007).



**Figure 5.** Results of an experiment replicating the results first obtained and published by Thiemens and Heidenreich (1983). In this experiment,  $\text{O}_2$  gas at pressures of 44 to 101 torr was subjected to an electrical discharge. The product  $\text{O}_3$  is enriched in  $^{18}\text{O}$  and  $^{17}\text{O}$  and the residual  $\text{O}_2$  is depleted in these rare isotopes, and their compositions fall on a line with a slope of 1 on the  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  plot. TMF refers to the terrestrial mass fractionation line. Data collected by E. Young and T. Hoering (unpub.).

A surface chemical reaction mechanism for the oxygen isotope MIF in the earliest processed solids of the Solar System was explored recently (Marcus 2004). Here we describe two conditions necessary for a chemical MIF mechanism to be viable for early Solar System solids such as those that compose CAIs formed at high temperatures (~1500-2000 K) and low pressures (~  $10^{-7}$  bar). We first discuss a chemical mechanism for the MIF in ozone, and then for CAIs. The principles for both are similar, but the details are very different. For the CAIs, a gas phase mechanism, an analogue of the mechanism for ozone, was considered initially (Thiemens 1996, and later, Marcus unpublished). In detailed calculations, however, it was ruled out, and instead a reaction occurring on dust surfaces was described (Marcus 2004).

A chemical mechanism for producing the  $^{16}\text{O}/(^{17}\text{O}+^{18}\text{O})$  variability in Solar System solids is intrinsically attractive because of its simplicity compared with other mechanisms, in terms of transport, light sources, etc. However, as Lyons and Young (2005b) have pointed out and as Marcus (2004) has also noted, experimental evidence for a chemical explanation of MIF for the CAIs is presently lacking. In this chapter, specific laboratory experiments are proposed to test a suggested mechanism. One experiment is novel only in the reaction temperatures for which it is proposed.

### The MIF in ozone formation

We first summarize a theory applied initially to ozone formation (Hathorn and Marcus 1999; Gao and Marcus 2001, 2002; Gao et al. 2002). The theory was then adapted as a possible chemical MIF for the earliest solids. It involves several, though not all, concepts that are well established by many studies on the rates of unimolecular dissociation and bimolecular recombination reactions (Wardlaw and Marcus 1988; Gilbert and Smith 1990; Holbrook et al. 1995; Forst 2003). The main features of this theory are summarized below.

Oxygen atoms are typically formed in the stratosphere or laboratory by photodissociation (stratosphere, laboratory) of  $\text{O}_2$  or electric discharge in  $\text{O}_2$  (laboratory). O and  $\text{O}_2$  in the gas phase recombine on collision to form a vibrationally excited ozone molecule,  $\text{O}_3^*$ :



The  $\text{O}_3^*$  subsequently redissociates via Reaction (1) or is stabilized by collisions involving loss of vibrational energy to any molecule M:



After  $\text{O}_3^*$  formation in Equation (1), an energy redistribution (“intramolecular energy randomization”) occurs among the vibrations and rotations of the  $\text{O}_3^*$  molecule. This redistribution is typically assumed to provide, on the average, an equipartitioning of the excess energy among all the coordinates of the vibrationally hot  $\text{O}_3$ , subject to the constraint of the fixed total energy  $E$  and total angular momentum  $J$  of this  $\text{O}_3^*$  that exists prior to the next collision. The energy redistribution among the coordinates is due to anharmonic couplings of the molecular vibrations of  $\text{O}_3^*$  and to coriolis and other couplings of the vibrations and rotations. The standard theory used to treat bimolecular recombination and unimolecular dissociation reactions in the literature is a statistical theory, known as “RRKM” theory (Rice, Ramsperger, Kassel, Marcus) (Marcus 1952; Wardlaw and Marcus 1988; Gilbert and Smith 1990; Holbrook et al. 1995; Forst 2003). Symmetrical isotopomers such as  $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ ,  $^{16}\text{O}^{17}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  have fewer intramolecular dynamical couplings for an energy redistribution (fewer “quantum mechanical coupling matrix elements”), because of symmetry restrictions, as compared with asymmetric  $\text{O}_3$  isotopomers, such as  $^{16}\text{O}^{16}\text{O}^{17}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ . Because of the reduced number of coupling elements in the symmetric isotopomers, we have assumed that the symmetric isotopomers have less redistribution of the energy of the newly formed chemical bond among the other coordinates than do the asymmetric isotopomers. Thereby, the symmetric  $\text{O}_3^*$  occupy less “phase space” and, consequently, in terms of unimolecular reaction theory, have shorter

lifetimes than the asymmetric isotopomers. The shorter lifetime means that there is less chance of the symmetric  $O_3^*$  being stabilized by loss of energy in a collision, so the rate of formation of the stabilized molecule is less. This assumption of less energy redistribution in the symmetric isotopomers remains to be tested by *ab initio* quantum mechanical calculations and by a direct experiment noted below. This property of reduced number of coupling elements for symmetric systems is the same for all symmetrical isotopomers regardless of isotopic masses, since all have the same common symmetry property. The simultaneous formation of symmetric heavy atom isotopomers,  $^{16}O^{17}O^{16}O$  and  $^{16}O^{18}O^{16}O$ , dilutes the magnitude of the MIF by about 1/3 but does not eliminate it.

In summary, because of a dynamical consequence of symmetry, the vibrationally excited asymmetric isotopomers  $QOO^*$ , where Q is  $^{17}O$  or  $^{18}O$ , have approximately equal lifetimes that are longer than that of the symmetric isotopomers,  $OOO^*$  and  $OQO^*$ . At low pressures they thereby have an improved chance of being deactivated by a collision and of forming a stable ozone molecule, leading to an equal (mass-independent) excess of the heavy isotopes in the ozone.

This symmetry/asymmetry behavior is not restricted to  $O_3$  but would apply to all triatomic or larger molecules that have the possibility of forming symmetric and asymmetric isotopomers, although its extent will depend on the molecule and the temperature, e.g., it can differ in magnitude for  $O_3^*$ ,  $CO_2^*$ ,  $SiO_2^*$ , and  $O_4^+$ .

Experimental studies permit tests of these ideas. For example, the universality of the effect among all types of isotopomers is seen in oxygen mixtures heavily enriched in  $^{17}O$  and  $^{18}O$  (Mauersberger et al. 1999). The effect of pressure on the MIF (Morton et al. 1990; Thiemens and Jackson 1990) has been measured and the theory tested by comparison with the data (Gao and Marcus 2001, 2002). The effect of temperature has been studied (Morton et al. 1990) and at present is perhaps qualitatively understood: the higher the temperature, the higher the energy of the  $O_3^*$ , the shorter its lifetime, the less time there is for energy redistribution in the excited ozone, and so the greater the non-statistical effect and thereby the MIF. Missing, however, is a direct experiment: the dissociative lifetime behavior of the vibrationally excited  $O_3^*$  has not been studied under well-defined, collision-free conditions. Under suitable conditions,  $O_3^*$  could be prepared with a known vibrational energy and its time-evolution could be studied using a two laser “pump-dump” method in a molecular beam. A single-exponential decay of the  $O_3^*$  would indicate full statistical intramolecular mixing of the energy, while a more complex time decay would indicate incomplete mixing (“non-RRKM” behavior) (e.g., Marcus et al. 1984). Different isotopomers of  $O_3^*$  could be similarly studied, together with the effect of increased energy on the distribution of lifetimes. An increased energy is expected to increase the difference in the lifetimes of the symmetric and asymmetric isotopomers, based on an interpretation of the observed effect of temperature on the MIF.

There is a large body of experimental data on ozone formation obtained under very special experimental conditions (Mauersberger et al. 1999) in which the isotopic exchange (“isotopic scrambling”) is minor. In these experiments, the ratios of recombination rate constants, such as the ratio of  $k$ 's of  $[^{16}O + ^{18}O^{18}O]/[^{16}O + ^{16}O^{16}O]$ , are measured directly. These results show strikingly large isotope-specific quantum effects, very different from MIF but well understood in terms of differences of zero-point energies of the two competing modes of dissociation of an ozone molecule,  $^aO^bO^cO^* \rightarrow ^aO + ^bO^cO$  and  $^aO^bO + ^cO$ , e.g., Marcus and Gao (2001, 2002). However, as interesting as these special “exit-channel” effects are in their own right, it has been shown that because of a cancellation, contrary to some reports in the literature, they have no bearing on the MIF phenomenon (Hathorn and Marcus 1999). We have stressed this point, since occasionally the two very different effects, the mass-independent effect of “scrambled” systems and the anomalously large mass-dependent effect for reactions of the type  $Q + OO \rightarrow QOO^* \rightarrow QOO$  and  $QO + O$ , where Q denotes a heavy isotope, appear to have been confused

in the literature. This cancellation arises since both sides of the reaction,  $Q + \text{OO} \rightarrow \text{QOO}^* \rightarrow \text{QO} + \text{O}$ , contribute to the observable effect, not just one side.

Isotopic effects on the formation of ozone in the laboratory have been studied at temperatures ranging from  $\sim 100$  K to 373 K (Morton et al. 1990) and at pressures from  $10^{-2}$  to  $10^2$  bar (Morton et al. 1990; Thiemens and Jackson 1990). Such conditions are very different from the temperatures and pressures at which CAIs are presumed to have formed. With these remarks as background, we turn next to the MIF in CAIs.

### Conditions for a chemical MIF in the formation of CAIs

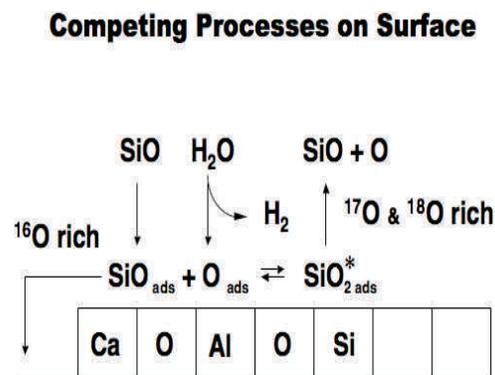
Detailed calculations have shown that at 1500-2000 K and  $10^{-7}$  bar, storage of the heavy O isotopes by purely gas phase recombination reactions in molecules such as  $\text{SiO}_2$  and  $\text{AlO}_2$  is not possible (Marcus 2004; Chen and Marcus, to be published); gaseous  $\text{SiO}_2$  and  $\text{AlO}_2$  are too unstable at the high temperatures to serve as storage reservoirs. When formed, they also immediately redissociate at these low pressures, since collisions occur too infrequently to stabilize them before redissociation.

Thus, any purely *chemical* explanation for MIF in the early solar nebula should invoke, instead, reactions on surfaces, such as on existing dust grains. Reaction on a surface instead of in the gas phase changes by many orders of magnitude the adverse entropy effect that occurs in a gas phase bimolecular recombination at low pressures, because of the concentrating effect of the surface (e.g., Marcus 2004). At the same time, by not requiring the existence of a long-lived, unstable triatomic molecule for a storage reservoir in an  $\text{H}_2$ -rich atmosphere, the surface reaction mechanism avoids a second major drawback of an MIF due to purely gas phase reactions (Marcus 2004). A recent study of dissociation of  $\text{O}_3$  on silica surfaces (Chakraborty and Bhattacharya 2003a,b; Janssen 2003) suggests that MIF effects can occur by surface-induced dissociation, lending experimental support for the concept of MIF with surface-mediated reactions.

### A possible chemical mechanism for MIF in CAIs

A purely chemical mechanism for the MIF in the CAIs is sketched schematically in Figure 6, using  $\text{SiO}$  as an example of a reacting diatomic molecule. In the case of minerals rich in Al, the deposition onto the surface would involve Al atoms, since  $\text{AlO}$  is expected to be too unstable in the gas phase to be a significant contributor. The Al atom deposition could be followed by reactions such as  $\text{Al}_{\text{ads}} + \text{O}_{\text{ads}} \leftrightarrow \text{AlO}_{\text{ads}}$  and  $\text{AlO}_{\text{ads}} + \text{O}_{\text{ads}} \leftrightarrow \text{AlO}_{2,\text{ads}}^*$ , where the  $\text{O}_{\text{ads}}$  has arisen from the reaction in Figure 6 or, under a more oxidizing atmosphere, from oxygen atoms,  $\text{O}_{\text{gas}} + \text{surface} \rightarrow \text{O}_{\text{ads}}$ .

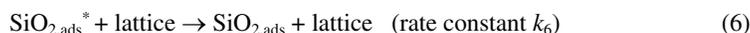
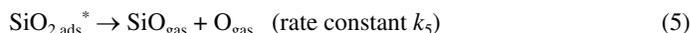
In the mechanism in Figure 6, the principal step for forming adsorbed  $\text{SiO}$  on the surface is the reaction of  $\text{H}_2\text{O}$  with the surface, the reverse of a possible reaction for accelerating the vaporization of forsterite by reaction with  $\text{H}_2$ . The  $\text{H}_2$  reaction with forsterite has been studied in the laboratory (Nagahara and Ozawa 1996; Tsuchiyama et al. 1998, 1999). The reason for choosing  $\text{H}_2\text{O}$  instead of  $\text{O}$  as the reactant in the Figure 6 case is based on estimated rate constants and concentrations (Marcus 2004; Chen and Marcus, to be published) using the data on the  $\text{H}_2$ -catalyzed vaporization.



**Figure 6.** Schematic diagram of competing processes on the surface of a growing CAI mineral.

In Figure 6, a vibrationally excited  $\text{SiO}_2$ ,  $\text{SiO}_{2,\text{ads}}^*$ , is formed on the surface by recombination of  $\text{O}_{\text{ads}}$  and  $\text{SiO}_{\text{ads}}$  (or  $\text{AlO}_{2,\text{ads}}^*$  from  $\text{AlO}_{\text{ads}} + \text{O}_{\text{ads}}$ ). These  $\text{O}_{\text{ads}}$  and  $\text{SiO}_{\text{ads}}$  undergo two competitive reactions: (a) recombination on the surface to form the vibrationally excited  $\text{SiO}_{2,\text{ads}}^*$ ; and (b) entrance into the crystal lattice, together with other species such as Ca, Mg and Al, to form a Ca-, Al-rich mineral. The  $\text{SiO}_{2,\text{ads}}^*$  itself undergoes two competing reactions in Figure 6: (a) redissociation into  $\text{SiO}_{\text{ads}} + \text{O}_{\text{ads}}$ ; and (b) evaporation into  $\text{SiO}$  and  $\text{O}$  in the gas phase.

We next adapt the argument used for interpreting the MIF in  $\text{O}_3^*$  formation in the gas phase to the system in Figure 6. There are conditions, however, for a viable MIF by a mechanism of this type to produce  $\text{SiO}$  (gas) +  $\text{O}$ (gas) that is mass-independently enriched in  $^{17}\text{O}$  and  $^{18}\text{O}$  and  $\text{SiO}_{\text{ads}} + \text{O}_{\text{ads}}$  that is mass-independently enriched in  $^{16}\text{O}$  upon entering the lattice of a proto-CAI. These conditions are expressed with reference to the following reactions:



where  $k_3$  and  $k_{-3}$  are the rate constants of the forward and reverse, respectively, of Equation (3). The conditions are pre-equilibrium of  $\text{SiO}_{2,\text{ads}}^*$ ,  $\text{SiO}_{\text{ads}}$ , and  $\text{O}_{\text{ads}}$ , corresponding to  $k_3 \gg k_4$ , and  $k_{-3} \gg k_5, k_6$ , where the Ca and Al surface concentrations have been absorbed into the definition of  $k_4$ . Laboratory experiments can test these conditions. Analogs of Eqs. (3) through (5) for an Al-bearing mineral such as  $\text{MgAl}_2\text{O}_4$  are



The available data on deactivation of vibrationally hot molecules on surfaces are sparse. A study using complex molecules suggests that the efficiency of deactivating vibrationally excited molecules on surfaces decreases with increasing temperature (Flowers *et al.* 1981). In addition, the intrinsic lifetime of the  $\text{SiO}_{2,\text{ads}}^*$  or  $\text{AlO}_{2,\text{ads}}^*$  with respect to dissociation decreases with increasing energy and hence with increasing temperature, according to unimolecular reaction rate theory. Both factors favor the possibility that the desired surface pre-equilibrium Reaction (3) and (3') *may* occur.

There is also the question of time scale. If the overall processes are very slow, some equilibration of the isotopic separation might occur in some form before the species are stabilized by permanently entering the crystal lattice. There is presently no information on this time scale, since a study of the formation of solids from  $\text{SiO}$ ,  $\text{H}_2\text{O}$ , Ca (atoms) and Al (atoms) at 1500 to 2000 K remains to be made.

### Consequences of chemical mechanism for MIF in the early water

We consider here the consequence of the chemical reaction scheme in Equations (2a)-(5') and Figure 6 for the early water formed in the Solar System. In this scheme there would be an equal enrichment of  $^{17}\text{O}$  and  $^{18}\text{O}$  (MIF) in water formed as a byproduct of CAI formation. To see this result we add to the Equations (2a)-(5') the fast Reactions (6') and (7') that would inevitably accompany that scheme:



the O atoms coming from the  $O_{\text{ads}}$  in Reactions (5) and (5') and Figure 6, and also ultimately from recycling of the  $\text{SiO}_{\text{gas}}$  or  $\text{AlO}_{\text{gas}}$  emitted in Reactions (5) and (5'). All are enriched in  $^{17}\text{O}$  and  $^{18}\text{O}$  in an MIF manner. As noted in Appendices B and E of Marcus (2004), Reactions (6') and (7') are very rapid, Reaction (6') occurring at every collision at  $\sim 2000$  K and Reaction (7') occurring at 1 of every 10 collisions. In this way, the heavy O atom enrichment in the early  $\text{H}_2\text{O}$  formed in this scheme balances their MIF deficiency in the formation of the CAIs in the scheme.

#### Testing the hypothesis: experiment to test gas phase MIF at high temperature

Prior to testing any postulated surface chemical reaction scheme for the MIF effect in solids, it is desirable to know, in what appears to be a simpler experiment, if an MIF is even chemically possible in the gas phase at the high temperatures (1500 to 2000 K) relevant for CAI formation. In laboratory experiments on ozone formation at much lower temperatures (100 to 373 K), the magnitude of the MIF was observed to increase with increasing temperature (Morton et al. 1990). Thus, it is possible that an MIF will exist at high temperatures.

If an MIF does not occur in the gas phase at these high temperatures, it is unlikely to occur on a surface at those temperatures. For this reason, an initial exploration of a possible chemical MIF at 1500-2000 K in a gas phase experiment is particularly desirable, since the corresponding surface experiment and its interpretation will be more difficult.

In such a gas phase experiment, the newly-formed, vibrationally-excited molecules that have subsequently been collisionally stabilized have to be extracted from the reaction system quickly, before these product molecules redissociate. One example of a possible reaction is  $\text{CO} + \text{O} \rightarrow \text{CO}_2^*$  in an  $\text{H}_2$ -free atmosphere (Bhattacharya and Thiemens 1989), with pressures high enough for there to be some collisional stabilization of the vibrationally hot  $\text{CO}_2^*$  together with reaction times short enough for the back-reaction  $\text{CO}_2^* + \text{M} \rightarrow \text{CO}_2 + \text{M}$  to be negligible.

Further, the source of the O atoms should be such that any complicating transient species (such as  $\text{O}_3$ ) are absent. One potential source of the O atoms is the photodissociation of  $\text{N}_2\text{O}$  to yield  $\text{N}_2 + \text{O}$ . If, as an example, CO is used as the second reactant, the subsequent isotopic scrambling of the O atoms, via  $\text{O} + \text{CQ} \rightleftharpoons \text{OCQ}^* \rightleftharpoons \text{OC} + \text{Q}$ , would eliminate any isotopic fractionation resulting from the photodissociation itself. The recombination reaction  $\text{CO} + \text{O} \rightarrow \text{CO}_2$  has been studied isotopically (Bhattacharya and Thiemens 1989), though not yet under high-temperature conditions.

At first glance, a potential objection (that is easily dismissed) to observing an MIF in a reaction such as  $\text{CO} + \text{O} \rightarrow \text{CO}_2^*$ , is that the desired reaction is electronically spin-forbidden (singlet CO + triplet O  $\rightarrow$  singlet  $\text{CO}_2$ ). The presence of an odd-numbered nucleus,  $^{17}\text{O}$ , in a reactant reduces the spin-forbidden impediment for this reaction, due to electron spin-nuclear spin coupling, and so catalyzes the recombination and destroys any mass-independence. However, this effect would occur both in the formation,  $\text{CO} + \text{O} \rightarrow \text{CO}_2^*$ , and in the redissociation,  $\text{CO}_2^* \rightarrow \text{CO} + \text{O}$ , of the  $\text{CO}_2^*$ . Since the redissociation of the  $\text{CO}_2^*$  dominates over collisional stabilization of the  $\text{CO}_2^*$  at low pressures, this spin-spin effect favoring formation of  $\text{CO}_2^*$  containing  $^{17}\text{O}$  also favors this reverse process, relevant here, however, there would be little redissociation of the  $\text{CO}_2^*$  because of collisional deactivation, and then the spin-spin coupling would indeed favor  $^{17}\text{O}$  enrichment of the  $\text{CO}_2$ .

To see if any MIF exists in gas-phase reactions at 1500 to 2000 K, it would be useful to explore the low-pressure behavior of a gas-phase reaction such as the above. Further, undertaking such studies at sufficiently low pressures, in conjunction with unimolecular reaction rate theory, provides information in the deactivational effect of the surface at these temperatures. It will be interesting to see from such experiments whether a chemically-based MIF can occur in the gas phase at 1500-2000 K, and also to explore the surface experiments.

At room temperature, a surface causes the MIF associated with  $O_3$  formation to disappear at pressures  $< 7 \times 10^{-3}$  bar (Morton *et al.* 1990). There is thus a contrast with the scheme in Figure 6, since now there is no competition with oxygen entering into a lattice. When in a surface study of ozone formation at high temperatures most of the  $O_3^*$  formed on the surface is deactivated on the surface, then a pre-equilibrium  $O + O_2 = O_3^*$  needed for an MIF cannot exist. Only when most of the  $O_3^*$  is not deactivated, either on the surface at low pressures or in the gas phase at high pressures, can a pre-equilibrium needed for an MIF exist.

### PHOTOCHEMICAL MASS-INDEPENDENT OXYGEN ISOTOPE FRACTIONATION: CO SELF-SHIELDING

Isotope-selective photodissociation of molecules (especially CO and  $O_2$ ) combined with self-shielding has long been regarded as a possible explanation for the anomalous oxygen isotope distribution in Solar System rocks (Kitamura and Shimizu 1983; Thiemens and Heidenreich 1983; Navon and Wasserburg 1985), but the idea languished until recently, primarily because of the likelihood that back reactions among products at high temperatures (e.g., Navon and Wasserburg 1985) would erase the isotopic effects. A revival of the concept as it pertains to CO and  $N_2$  is in full swing, however, as a result of a suggestion by Clayton (2002b) that self-shielding by CO at the inner annulus of the proto-solar circumstellar disk might be the cause of the slope-1 trend of CAI data on plots of  $\delta^{17}O$  vs.  $\delta^{18}O$ . Doubt has been raised about the efficacy of CO self-shielding at the disk inner annulus (Lyons and Young 2003), though more experimental and computational work is required to fully assess the model. Nonetheless, the idea has spawned two additional models. One model supposes that the oxygen isotope effects of CO self-shielding are inherited from the placental molecular cloud (Yurimoto and Kuramoto 2004) while the other considers CO self-shielding at the surfaces of the disk (Lyons and Young 2005a). In either case, the  $^{18}O$  and  $^{17}O$  liberated by photodissociation of CO is most likely sequestered in water ice (Young and Lyons 2003; Yurimoto and Kuramoto 2004; Lyons and Young 2005a). These models predict that one should see an excess of  $C^{16}O$  relative to  $C^{18}O$  and  $C^{17}O$  in protoplanetary disks as a consequence of self-shielding by  $C^{16}O$ . The prediction offers the prospect of a direct test of the CO self-shielding hypotheses in their various forms. In this section we will consider all three proposed astrophysical settings for mass-independent oxygen isotope fractionation by CO photodissociation and self-shielding in the early Solar System: 1) the inner annulus of the protostellar disk; 2) the surfaces of the protostellar disk; and 3) the placental molecular cloud of the disk.

Although not yet verified by laboratory experiments, CO self-shielding, especially at low temperatures, is an attractive explanation for  $\Delta^{17}O$  variability in the Solar System because it is a process observed in the interstellar medium and, perhaps, in disks as well (see below). It also has the advantage that a principle by-product is  $^{16}O$ -depleted  $H_2O$ . The latter appears to be an important feature of the distribution of oxygen in the early solar nebula (Clayton and Mayeda 1984; Young 2001, 2007a; Sakamoto *et al.* 2007).

#### CO photodissociation and self-shielding

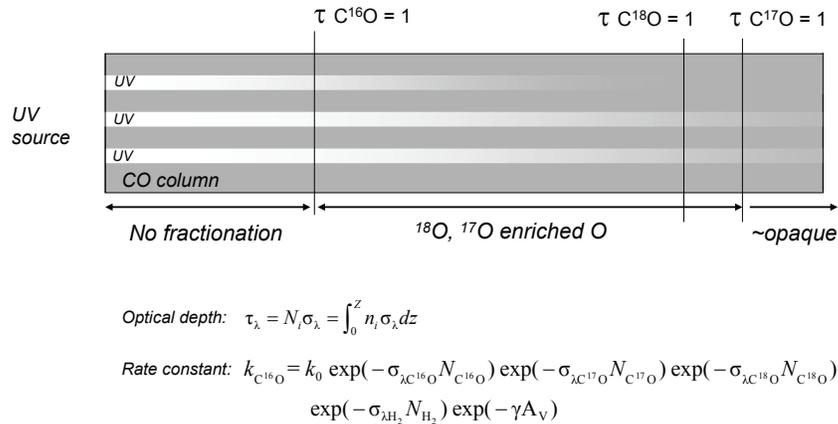
Carbon monoxide experiences destruction by photodissociation induced by far-UV (FUV) stellar radiation at wavelengths of 91 to 110 nm. Photodestruction takes place primarily through predissociation. Predissociation involves passage to bound excited states prior to dissociation. Since the excited molecules have well-defined rovibrational states, photolysis by predissociation is isotope-specific.

In particular, rovibrational lines in the UV absorption bands of the  $^{17}O$  and  $^{18}O$  CO oxygen isotopologues are red-shifted by  $\sim 25 \text{ cm}^{-1}$  per amu relative to the lines for  $C^{16}O$  (e.g., Ubachs *et al.* 2000). The observed shifts are consistent with the prediction based on an assumption of a relatively strong C-O bond in the excited state, where the shifts in frequency are  $\nu_{CO} -$

$\nu_{C^iO} = [1 - (\mu_{CO}/\mu_{C^iO})^{1/2}]\omega_e$ , where  $\omega_e$  is the vibrational constant and  $\mu_i$  is the reduced mass for isotopologue  $i$ . Line spacings for a given isotopologue are on the order of  $3.6 \text{ cm}^{-1}$  as prescribed by the dependence of rotational constants on reduced mass. The result of these isotope-specific shifts is a tight intermingling of lines (e.g.,  $C^{17}O$  R and  $C^{16}O$  P transitions) with separations on the order of  $1 \text{ cm}^{-1}$ . This separation can be compared with line widths. If linewidths are less than the separation of intercalated lines, then absorption will be isotope-specific. Excited lifetimes ( $\tau$ ) for CO are  $> 3 \times 10^{-11} \text{ s}$  (Eikema et al. 1994) but may be as long as  $2 \times 10^{-10} \text{ s}$  (Ubachs et al. 2000), resulting in natural line widths  $\Gamma$  (FWHM) of  $< 0.16 \text{ cm}^{-1}$ , and perhaps as narrow as  $0.03 \text{ cm}^{-1}$  ( $\Gamma = 1/(\tau 2 \pi c)$ ). A purely Lorentzian line shape suggests that the wings of a  $0.16 \text{ cm}^{-1}$  FWHF peak extend  $7 \text{ cm}^{-1}$  from the peak center out to intensities of 1‰ relative to the maximum intensity. Wings for a  $0.03 \text{ cm}^{-1}$  line extend  $2.2 \text{ cm}^{-1}$  from the peak center at the 1‰ threshold. These figures serve to demonstrate that the FUV absorption spectra of the CO isotopologues are sufficiently distinct that CO dissociation is profoundly wavelength-dependent.

As a result of the distinct UV absorption spectra of  $C^{16}O$ ,  $C^{17}O$  and  $C^{18}O$ , CO will absorb FUV wavelengths in proportion to the column densities of the constituent oxygen isotopologues (Fig. 7). Because solar and interstellar  $^{16}O/^{18}O$  and  $^{16}O/^{17}O$  ratios are  $\sim 500$  and  $\sim 2600$ , respectively, spectral lines for  $C^{16}O$  will be more optically thick than  $C^{17}O$  and  $C^{18}O$  lines (van Dishoeck and Black 1988). This process of saturation of the photodissociating lines of the abundant isotopologue is referred to as self-shielding and is a process known to be important in the interstellar medium (ISM) (Bally and Langer 1982; Sheffer et al. 2002). However, as the separation between intercalated lines from the different isotopologues are separated by distances smaller than the full baseline widths of the peaks themselves, there is mutual shielding of one isotopologue on another; the isotope specificity is not simple (van Dishoeck and Black 1988; Lyons and Young 2005a). More work on the specifics of the mutual

### CO photodissociation self shielding



**Figure 7.** Schematic illustration of the process of CO self-shielding. Optical depths for the relevant wavelengths of far ultraviolet light (zig-zag arrows),  $\tau$ , depend upon the wavelength-specific absorption cross sections  $\sigma_\lambda$  and column depths of  $N_i$  of CO isotopologues  $i$ . The column unit optical depths depend largely on the number densities  $n_i$  of the isotopologues. The rate constant for photodissociation of each of the isotopologues,  $k_i$ , is a product of shielding functions of form  $\exp(-\sigma_{\lambda,i} N_i)$  and the visual extinction of dust,  $A_v$ , modified for the FUV ( $\gamma$ ). Atomic oxygen liberated by photodissociation of CO between the unit  $\tau$  for  $C^{16}O$  and  $C^{17}O$  is enriched in  $^{18}O$  and  $^{17}O$  relative to the reactant CO.

shielding effect is required as the slope of the self-shielding effect in oxygen three-isotope space depends on these relationships.

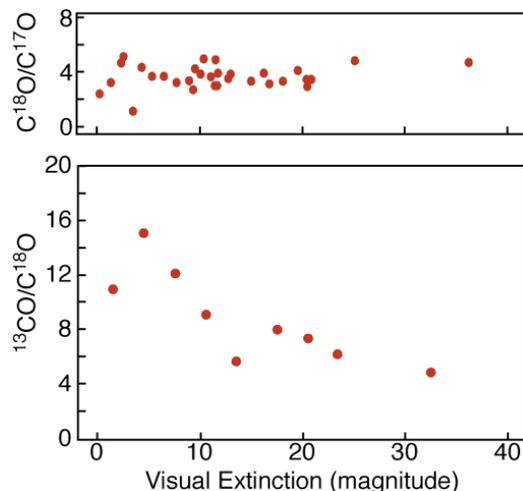
By assuming a solar-like ratio of CO to H<sub>2</sub> in the gas phase (e.g., gas in an accretion disk or in a molecular cloud in the interstellar medium), one can use the FUV shielding functions for CO (Lyons and Young 2005a; van Dishoeck and Black 1988) to derive a general rule relating hydrogen column density (N<sub>H</sub>, see Fig. 7) to oxygen isotope-specific photodissociation of CO. The result is that oxygen isotope fractionation by CO photodissociation is expected in regions where N<sub>H</sub> ~ 10<sup>19</sup> to 10<sup>22</sup> cm<sup>-2</sup>. One can also use typical relationships between N<sub>H</sub> and extinction of visible light, or A<sub>v</sub>, expressed in magnitudes ( $\Delta m = \text{mag} = 2.5 \log(I_2/I_1)$  where I<sub>2</sub> and I<sub>1</sub> are two different intensities of light), by ~ 0.1 micron-sized dust grains (Lee et al. 1996) to show that mass-independent oxygen isotope fractionation by CO photodestruction is expected where A<sub>v</sub> ranges from ~ 5×10<sup>-3</sup> to 5. Larger-sized dust grains, such as might be found in a disk, reduce A<sub>v</sub> in CO self-shielding regions by 10 fold. These ranges in N<sub>H</sub> and A<sub>v</sub> serve as general guides for assessing the likely locations for CO isotope-selective photodissociation.

#### Astronomical observations of oxygen isotope fractionation by CO self-shielding

**Molecular clouds.** Carbon monoxide is the second most abundant molecular gas in molecular clouds and also the most abundant oxygen-bearing species. Anomalously high C<sup>16</sup>O/C<sup>18</sup>O in molecular clouds was first attributed to isotope-selective CO photodissociation and self-shielding by Bally and Langer (1982). Since then, large mass-independent oxygen isotope fractionation effects attributed to CO self-shielding in interstellar clouds have been observed. Indeed, evidence for isotopic fractionation between the relatively abundant isotopologues <sup>13</sup>CO and C<sup>18</sup>O (composing ~1 and ~0.3% of total CO, respectively, if solar isotopic abundances are used) in molecular clouds has been accumulated for more than two decades (e.g., Frerking et al. 1982; Lada et al. 1994). Mass-independent fractionation of CO in molecular clouds based on observations of C<sup>17</sup>O as well as C<sup>18</sup>O has been reported (e.g., White and Sandell 1995; Bergin et al. 2001; Wouterloot et al. 2005). Sheffer et al. (2002), for example, using UV spectroscopy, report <sup>12</sup>C<sup>16</sup>O/<sup>12</sup>C<sup>17</sup>O and <sup>12</sup>C<sup>16</sup>O/<sup>12</sup>C<sup>18</sup>O approximately five times (i.e., δ<sup>18</sup>O ~ δ<sup>17</sup>O ~ 4000‰) the ambient values for the local interstellar medium on a line of sight towards X Persei. Enrichments in both heavy oxygen isotopologues are consistent with a slope of 1 on a plot of δ<sup>17</sup>O vs. δ<sup>18</sup>O, within large uncertainties.

Many such observations are conducted by cross-correlating visual extinction (A<sub>v</sub>) with column density of CO isotopologues along the lines of sight. As noted above, A<sub>v</sub> reflects the column density of dust grains that are the primary absorber of visual light in a molecular cloud. Hence the visual extinction also provides a measure of the attenuation of interstellar UV in clouds. The column densities of CO isotopologues can be determined from the intensity of mm-wave emission due to the transition of rotational energy state. Each isotopologue has its own rotational energy levels that can be used to obtain column densities for each of the isotopologues.

In Figure 8, CO isotopologue ratios observed in the dark cloud IC5146 (Lada et al. 1994; Bergin et al. 2001) are shown as a function of visual extinction. The <sup>13</sup>CO/C<sup>18</sup>O ratio depends on visual extinction, decreasing with increasing visual extinction with a peak at several mag. This represents the isotopic fractionation across the molecular cloud. On the other hand, the C<sup>18</sup>O/C<sup>17</sup>O ratio is nearly constant independent of visual extinction, meaning that the isotopic fractionation in CO is “mass independent.” Note that the column density of C<sup>16</sup>O is difficult to determine directly because the intensity of line emission from this abundant isotopologue is saturated and no longer proportional to its column abundance. Note also that the fractionation between <sup>13</sup>CO and <sup>12</sup>CO is expected to be significantly diluted because of the exothermic reaction <sup>13</sup>C<sup>+</sup> + <sup>12</sup>CO → <sup>12</sup>C<sup>+</sup> + <sup>13</sup>CO (van Dishoeck and Black 1988; Warin et al. 1996). The mass-independent isotopic fractionation of CO in Figure 8 is interpreted to be the result of self-shielding by CO isotopologues (e.g., van Dishoeck and Black 1988; Viala et al. 1988; Warin et al. 1996).



**Figure 8.** The isotopomeric ratios of gaseous CO as a function of visual extinction in the dark cloud IC5146.  $^{13}\text{CO}/\text{C}^{18}\text{O}$  is after Lada et al. (1994) and  $\text{C}^{18}\text{O}/\text{C}^{17}\text{O}$  is after Bergin et al. (2001).

**Circumstellar disks.** Observations of at least one circumstellar gaseous disk provide a hint of  $\text{C}^{16}\text{O}$  overabundance. HL Tau is a low-mass, pre-main sequence star with a disk that is regarded as a prototype for the solar nebula. The surrounding disk extends out as far as 1400 AU from the star. Accretion is occurring at a rate of  $10^{-5} M_{\odot} \text{ yr}^{-1}$  (Brittain et al. 2005). Brittain et al. (2005) presented high-resolution infrared spectra of the embedded star showing broad CO emission lines and narrow CO absorption lines. The broad emission lines represent the hot ( $\sim 1500$  K) inner portion of the circumstellar disk while the absorption lines originate from the disk gas at an effective temperature of about 100 K. In general, one expects CO in the distal regions of a circumstellar disk ( $R > 100$ 's of AU) to represent the canonical oxygen isotope ratios, e.g.,  $\text{C}^{16}\text{O}/\text{C}^{18}\text{O} = 560 \pm 25$  (Wilson and Rood 1994). Brittain et al. found instead that the ratio of column densities for  $\text{C}^{16}\text{O}$  and  $\text{C}^{18}\text{O}$ ,  $N_{\text{C}^{16}\text{O}}/N_{\text{C}^{18}\text{O}}$ , is  $800 \pm 200$ . These authors suggest that the overabundance of  $\text{C}^{16}\text{O}$  (albeit at only the  $2\sigma$  level) could be the result of isotope-selective photodissociation resulting from the HL Tau UV field.

Detection of high  $\text{C}^{16}\text{O}/\text{C}^{18}\text{O}$  in the HL Tau disk ( $\text{C}^{16}\text{O}/\text{C}^{18}\text{O} = 800 \pm 200$  vs.  $560 \pm 25$ ) in gas in the outer disk is tantalizing evidence that CO self-shielding of stellar or interstellar FUV may be a feature of the chemical evolution of disks.

Enrichments in  $\text{C}^{16}\text{O}/\text{C}^{18}\text{O}$  (and  $\text{C}^{16}\text{O}/\text{C}^{17}\text{O}$ ) in other protoplanetary disks around young stellar objects have not been identified, but neither have the observations been made with this explicit goal in mind. Sensitive measurements of several lines of all three oxygen isotopologues in several objects of various masses would permit a systematic investigation of oxygen isotope ratios in the disks. One would require high signal-to-noise ratio in order to use line shape information to control for optical depth effects in the main isotope, as well as to make sensitive measures of the two rare isotopes.

### The pivotal role of $\text{H}_2\text{O}$

The importance of  $\text{H}_2\text{O}$  in the isotopic evolution of the solar nebula is suggested by numerous studies showing that  $\Delta^{17}\text{O}$  of water during chondrite formation was substantially greater than that of the rock component (Clayton and Mayeda 1984; Choi et al. 1998; Young et al. 1999; Lyons and Young 2005b; Sakamoto et al. 2007). This is an important observation because water plays a pivotal role as a carrier of  $^{16}\text{O}$ -poor oxygen in CO self-shielding models. Here we review briefly predictions and evidence for high and variable  $\Delta^{17}\text{O}$  of water in the inner ( $R < 5$  AU) solar protostellar disk.

Solar abundances of the elements and the kinetics of gas phase reactions indicate that approximately half of the total oxygen in a protoplanetary disk resides in CO. Another one-third is contained in H<sub>2</sub>O, with the remainder as lithophile oxides (Anders and Grevesse 1989; Fegley 2000). Water plays a central role as the carrier of the <sup>16</sup>O-depleted oxygen in models for CO self-shielding described below. Clayton and Mayeda (1984) recognized the importance of H<sub>2</sub>O as a reservoir for <sup>16</sup>O-poor oxygen in the solar nebula based on the isotopic compositions of secondary minerals in chondrites. Yurimoto and Kuramoto (2002, 2004) pointed out that there should have been a reciprocity in  $\Delta^{17}\text{O}$  between H<sub>2</sub>O and CO in the protosolar molecular cloud. Lyons and Young later showed that the same isotopic reciprocity likely existed between H<sub>2</sub>O and CO in cold portions of the protosolar accretion disk high above the midplane (Young and Lyons 2003; Lyons and Young 2005a).

Water is the most likely driver for the oxygen isotopic evolution of the Solar System because H<sub>2</sub>O forms readily from O liberated by CO photodissociation, and because H<sub>2</sub>O vapor exchanges oxygen isotopes with silicate rapidly while CO does not. Yu *et al.* (1995) showed that 50% oxygen isotope exchange occurs between molten silicate and H<sub>2</sub> + H<sub>2</sub>O gas at 1773 K and 1 bar after 5 minutes. These authors argued that at nebular pressures ( $\sim 10^{-5}$  to  $10^{-8}$  bar), 50% exchange would take 10 hours, demonstrating that exchange of oxygen between molten silicate and H<sub>2</sub>O gas is efficient. Conversely, analogous experiments involving CO and silicate show no evidence of isotopic exchange under similar conditions (Bosenberg *et al.* 2005).

A protoplanetary disk is born as an accretionary gas disk, where gas is transported toward the central star, and subsequently evolves to a quiescent disk. During disk evolution, chemical heterogeneity is caused by gas-dust fractionation within (e.g., Morfill *et al.* 1985). Fractionation of gas and dust includes the sedimentation of dust grains toward the disk midplane and the preferential inward migration of dust grains. In particular, the latter process may have caused significant change in the mean isotopic composition of the inner disk (Yurimoto and Kuramoto 2004).

Radial migration of dust grains occurs in response to gas drag. Gas composing the circumstellar disk rotates around the central star slightly slower than the Keplerian rate at each radial distance because of the outward pressure gradient. Solid grains immersed in the gas tend to follow the Keplerian rotation, resulting in gas drag and loss of angular momentum. Loss of angular momentum causes inward migration. Such inward migration of dust grains occurs during active accretion (Weidenschilling and Cuzzi 1993). Assuming the profile of density and temperature of disk gas follows those of the minimum-mass solar nebula, mm- to m-sized grains migrate most rapidly inward. The scenario is robust and is not sensitive to disk parameters such as surface density profile (Cuzzi and Zahnle 2004; Kuramoto and Yurimoto 2005).

Because the disk temperature increases inward, a migrating dust grain releases volatiles upon encountering the appropriate sublimation temperature. Under the realistic range of disk gas density, the sublimation temperature of H<sub>2</sub>O is about 150 K (Lewis 1972). The annulus region where H<sub>2</sub>O sublimates is called the snow line. The snow line migrates inward with time as the disk cools. It may have been as close as 3 AU from the proto-sun at some interval based on a minimum-mass solar nebula model (Hayashi *et al.* 1985). After the passage of the snow line, dust grains leave behind H<sub>2</sub>O vapor in the surrounding gas which may accrete inward more slowly. This causes enrichment of H<sub>2</sub>O vapor within the inner disk. Numerical analyses show that enrichments of H<sub>2</sub>O of more than 2 $\times$  relative to the solar proportion defined by solar C/O/H are possible inside the snow line, using realistic physical parameters (Cuzzi and Zahnle 2004; Kuramoto and Yurimoto 2005).

Numerous studies of meteorites suggest that the inner solar nebula became enriched in <sup>17</sup>O, <sup>18</sup>O with time (e.g., Choi *et al.* 1998; Wasson *et al.* 2004), and there is plentiful evidence for oxygen isotopic exchange between surrounding nebular gas and meteoritic constituents, including CAIs (Yurimoto *et al.* 1998; Fagan *et al.* 2004; Yoshitake *et al.* 2005) and chondrules

(Maruyama et al. 1999; Wasson et al. 2004). These observations appear consistent with the scenario of gradual H<sub>2</sub>O enrichment in the inner disk during disk evolution.

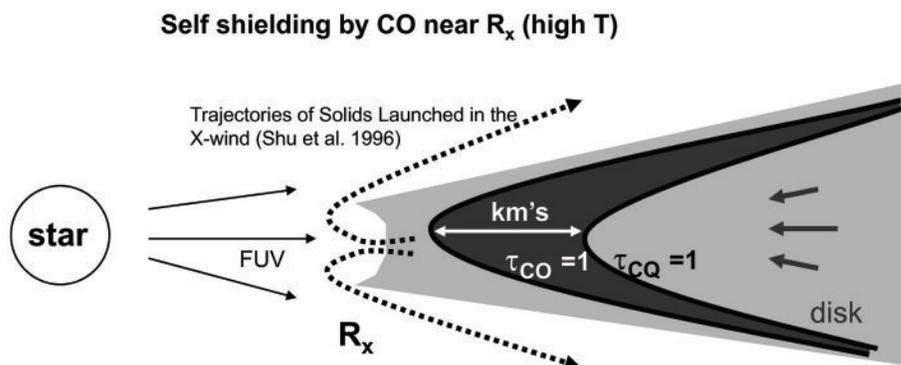
Previous studies attempting to use the oxygen isotopic compositions of minerals produced by aqueous alteration of carbonaceous chondrites to infer the original isotopic composition of H<sub>2</sub>O in the early Solar System (Clayton and Mayeda 1984; Choi et al. 1998; Clayton and Mayeda 1999; Young 2001) were hindered by the fact that waters from which these minerals grew were likely to have already exchanged oxygen with rock (Young et al. 1999). The recent findings by Sakamoto et al. (2007) of incipient aqueous alteration in a phase in a carbonaceous chondrite with  $\delta^{18}\text{O} \sim \delta^{17}\text{O} \sim 180\text{‰}$  appears to circumvent this hindrance. The oxygen isotope data for aqueously altered chondrites strongly supports the hypothesis that H<sub>2</sub>O in the inner regions of the solar protoplanetary disk was severely depleted in <sup>16</sup>O and enriched in <sup>17</sup>O and <sup>18</sup>O.

#### CO self-shielding at the inner annulus of the solar circumstellar disk

R. N. Clayton (2002b) argued that self-shielding by CO at the inner annulus of the solar circumstellar disk might be the origin of mass-independent oxygen isotope fractionation in the Solar System (Fig. 9). This hypothesis is based on the assumption that solar  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are coincident with the low end of the data trend shown in Figure 1 (i.e., <sup>16</sup>O-rich) and that the signal incurred by self-shielding by CO could be exported back to distal regions of the disk as material entrained in the X-wind described by Shu et al. (2001).

Self-shielding by CO in the region of the X-wind of the protostellar disk is attractive as an hypothesis to the extent that the X-wind itself was responsible for forming and/or modifying primitive solids like CAIs and chondrules in the early Solar System.

There are three potential difficulties associated with the scenario in Figure 9. The first is that at the high temperatures that prevail in the  $R_x$  region ( $T > 1500\text{ K}$ ), one might expect line broadening to cause substantial overlapping of the predissociation spectra of the CO isotopologues, and thus eliminate the isotope selectivity. Recent calculations, however, suggest that line broadening may be insufficient to preclude the effect, even at the high temperatures that obtain in the inner annulus of the disk (Lyons et al. 2007). The second possible difficulty is that at high temperatures and number densities, back reaction between liberated O and other



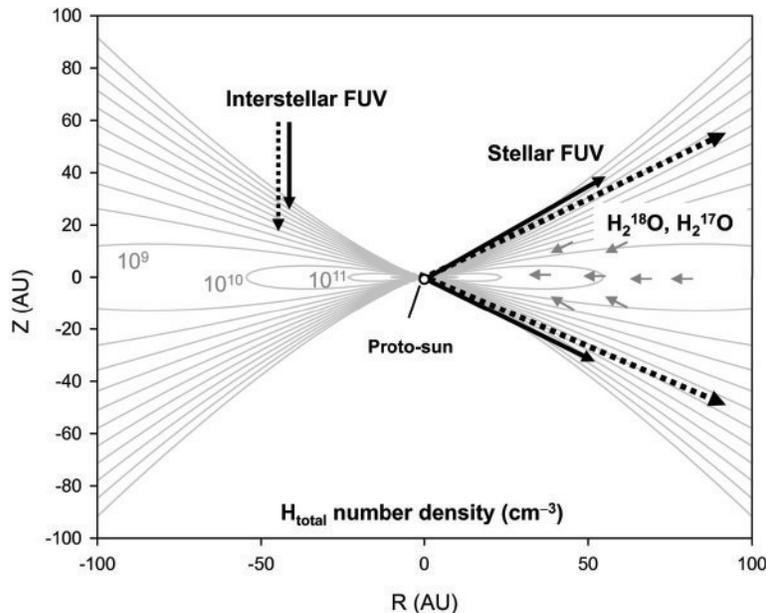
**Figure 9.** Schematic illustration of the Clayton hypothesis for CO self-shielding at the inner annulus of the solar circumstellar disk. Circumstellar radius  $R_x$  marks the inner edge of the disk. Here material flowing inward (dark grey arrows) in the disk is periodically ejected from the  $R_x$  region back out into the disk in the magnetically-driven “X wind” (Shu et al. 1996) (dotted lines). The region of CO self-shielding between the  $\tau = 1$  surfaces for  $\text{C}^{16}\text{O}$  and  $\text{C}^{17}\text{O}$  and  $\text{C}^{18}\text{O}$ , together denoted CQ, (heavy black lines) is calculated to be on the order of km in scale based on typical disk number densities (Lyons and Young 2003).

species may well eliminate the possibility of preserving the isotopic consequences of self-shielding in a reservoir of oxygen. The preservation of  $^{16}\text{O}$ -poor O as  $\text{H}_2\text{O}$  at high temperatures requires further investigation. The third potential difficulty is that where FUV fluxes are high, CO is destroyed so rapidly that there is no substantial isotope fractionation (see the next section for a fuller explanation of this last issue).

### CO self-shielding at the surfaces of the solar circumstellar disk

Possible difficulties with preserving the isotopic signal of CO self-shielding at high temperatures are overcome where CO photodissociation occurs at low temperatures (e.g.,  $< 100$  K), as in the interstellar medium clouds. Within the circumstellar disk that was the solar nebula, the surfaces of the disk at  $\text{H}_2$  number densities of  $\sim 10^5$  to  $10^6$   $\text{cm}^{-3}$  (pressure  $\sim 10^{-14}$  bar) are prime locations for preserving the isotopic effects of CO self-shielding (Fig. 10).

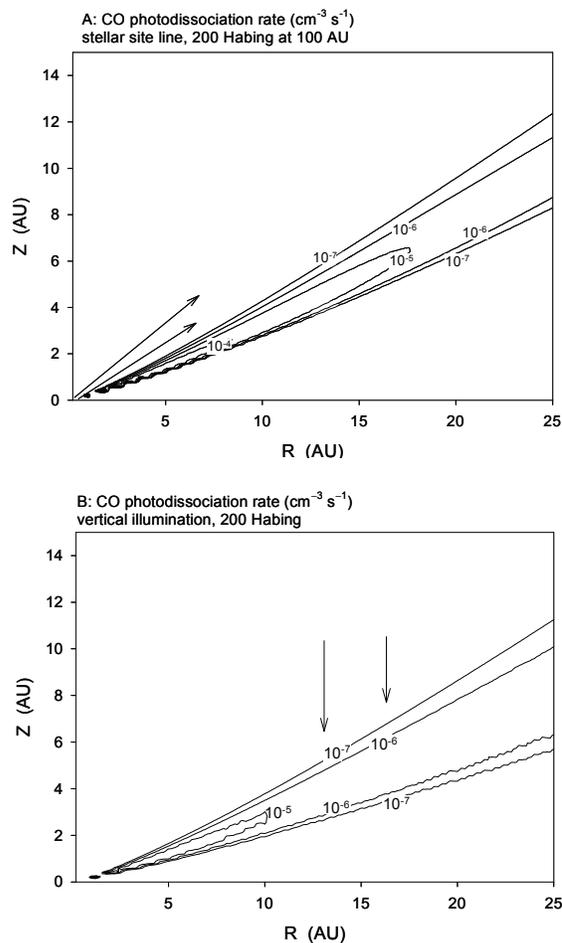
There are two sources of FUV at the surfaces of a circumstellar disk. One is ambient UV from the surrounding environs entering the disk at a high incident angle. The other is the central star itself where light travels on a line of sight from the star through the disk. A flared geometry, as shown in Figure 10, is thought to be typical of many disks (Kenyon and Hartmann 1987). A disk such as that in Figure 10, with concave upper surfaces relative to the midplane, intercepts more light along a sight line to the central star than a non-flaring disk. This effect increases with distance from the central star (Kenyon and Hartmann 1987) and maximizes the potential for photochemistry within the optically thin surfaces, especially in the outer regions of the disk.



**Figure 10.** Contour map of a model circumstellar disk as viewed edge-on. The disk model is the “Kyoto” model used to describe the accretion disk surrounding DM Tau (Aikawa and Herbst 2001). The model is appropriate for a relatively evolved protoplanetary circumstellar disk. Grey contours show H nuclei number densities, increasing inward in single decade increments. The model discussed in the text, in which either stellar or interstellar FUV, entering the disk along sight lines to the central star or at high angle, respectively, is shown schematically. Dashed lines refer to the optically thin FUV wavelengths that dissociate  $\text{C}^{18}\text{O}$  and  $\text{C}^{17}\text{O}$ . Black arrows represent the optically thick  $\text{C}^{16}\text{O}$  dissociation wavelengths.  $\text{H}_2\text{O}$  enriched in  $^{18}\text{O}$  and  $^{17}\text{O}$  is formed near the  $10^6$  contour region as a product of CO photodestruction (see text). This isotopically heavy water is then transported by turbulent forces to the inner disk (grey arrows).

As described above, isotope-specific photodissociation of CO occurs at gas column densities of  $10^{19}$  to  $10^{22}$   $\text{cm}^{-2}$  when  $\text{CO}/\text{H}_2$  is approximately  $10^{-4}$  (i.e., for solar  $\text{C}/\text{O}$ ). As a result, liberation of  $^{18}\text{O}$ - and  $^{17}\text{O}$ -enriched O from CO will be focussed along surfaces in the disk where  $Z \sim 1/4$  to  $1/3 R$  ( $Z$  is altitude of the midplane,  $R$  is circumstellar radius) with either high incident angle of illumination or along a sight line from the central star (Fig. 11). In the treatment that follows, no explicit adjustments of gas temperatures due to ionization (e.g., Glassgold et al. 2005) have been made. More work is needed in this area, but self-shielding apparently occurs just below the height of dramatic heating above the midplane in the disk.

**Simulating chemical evolution.** The chemistry of the diffuse and cold regions of circumstellar disks is a consequence of kinetics involving interactions between ions, neutral species, and cosmic ray particles. A quantitative model for the oxygen isotopic consequences of CO self-shielding in the solar circumstellar disk was presented by Lyons and Young (2005a). In that work, the authors produced a one-dimensional (1-D) calculation in which a UV flux perpendicular to the surfaces of the disk caused liberation of  $^{16}\text{O}$ -depleted O by CO photodissociation. The code includes 375 reactions among 96 species and gas-grain reactions that permitted  $\text{H}_2\text{O}$  to form on grain surfaces from the liberated O. Vertical mixing from



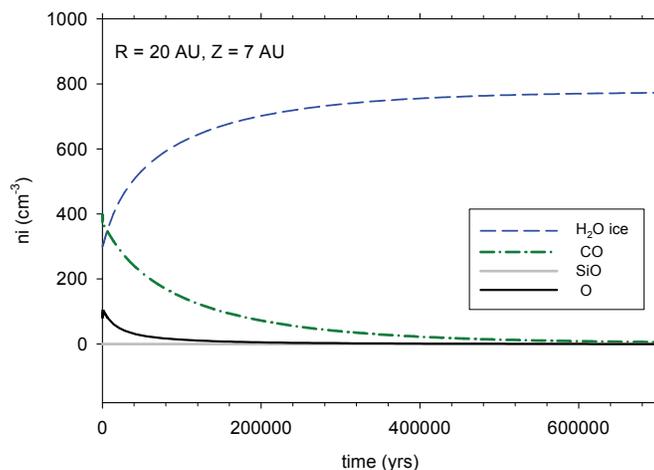
**Figure 11.** Map of CO photodissociation rate for the disk in Figure 10. Rates were obtained from the CO photodissociation rate constant from the UMIST data base, shielding functions described by Lyons and Young (2005a), and stellar (A) and interstellar (B) UV fluxes (arrows) 200x local ISM at  $R = 100$  AU. The flux for the stellar sight line varies with  $1/R^2$ . Arrows indicate direction of illumination.

the disk photoactive zone to the midplane was included by approximating a turbulent eddy diffusion coefficient with the turbulent viscosity  $\nu_t = \alpha cH$  where  $c$  is the sound speed,  $H$  is the vertical scale height and  $\alpha$  is the parameter that prescribes the strength of turbulent mixing.

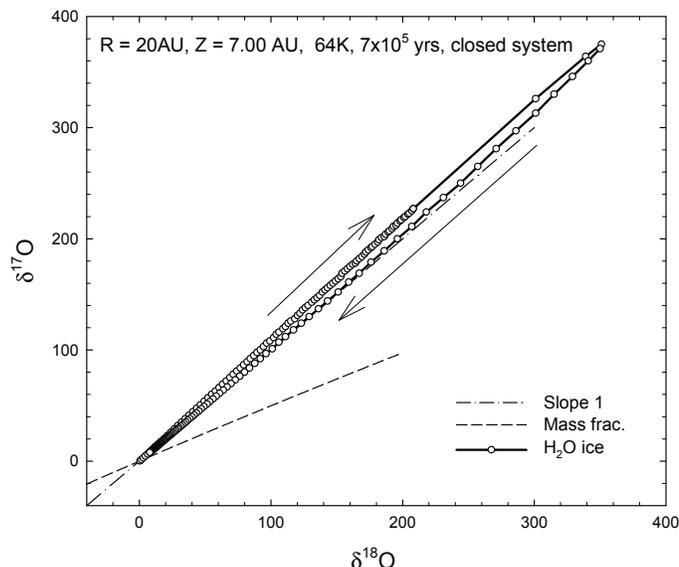
Calculations presented in this chapter are based on a larger astrochemical reaction network code constructed for the purpose of investigating photochemical effects involving CO at the surfaces of the solar protoplanetary disk (Young 2006, 2007b). More than 500 species and 7600 reactions are available in this new reaction network. The code utilizes a modification of the University of Manchester Institute of Technology data base for astrochemistry (UMIST, rate99) (Le Teuff *et al.* 2000). The reaction network is convolved with a simple model for number densities and temperatures as a function of circumstellar radial distance  $R$  and height above the midplane  $Z$  in a disk (Aikawa and Herbst 2001). Details of the reaction network are given elsewhere (Young 2007b). For the results presented below, an FUV flux coming from the central star of  $200\times$  local ISM (200 Habing) at  $R = 100$  AU was used (except where otherwise specified). The extinction from dust assumes grains with a radius of  $3 \mu\text{m}$ . The precise dust grain size has limited influence on final results.

**Calculation results-UV flux.** Rates of CO photodissociation with a uniform vertical FUV flux and rates due to FUV illumination along stellar sight lines toward the central star (with the same flux at 100 AU, the low end of estimates for a T-Tauri star field) are similar at large radial distances  $R$  from the star (Fig. 11). Differences become substantial, however, as the FUV flux rises sharply in the latter case with proximity to the star.

At  $R > 10$  AU, the net result of CO photodissociation is wholesale conversion of CO gas to  $\text{H}_2\text{O}$  ice in the photoactive layers of the disk (Fig. 12). Yurimoto and Kuramoto (2004) suggested that  $\text{H}_2\text{O}$  formation is mediated primarily on dust grain surfaces, but the calculations shown here demonstrate water ice forms efficiently in the gas phase as well. The reactions leading to gas-phase  $\text{H}_2\text{O}$  are described by Herbst (2000). The timescale for  $\text{H}_2\text{O}$  ice formation from CO is on the order of  $10^5$  yr (Fig. 12). At  $R \sim 10$  AU a steady state is achieved at disk surfaces such that reactions that produce CO are balanced by the conversion of CO to  $\text{H}_2\text{O}$  ice. At  $R > 5$  AU,  $\text{H}_2\text{O}$  ice produced by CO photodissociation forms with compositions that fall along a slope-1 line on a plot of  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  (Fig. 13). This is true even in the presence of the large mass-dependent fractionations.



**Figure 12.** Plot of number densities of species for the calculated conversion of CO to  $\text{H}_2\text{O}$  ice in surface layers of a model disk at  $R = 20$  AU. Timescale for net reaction is  $10^5$  yrs.

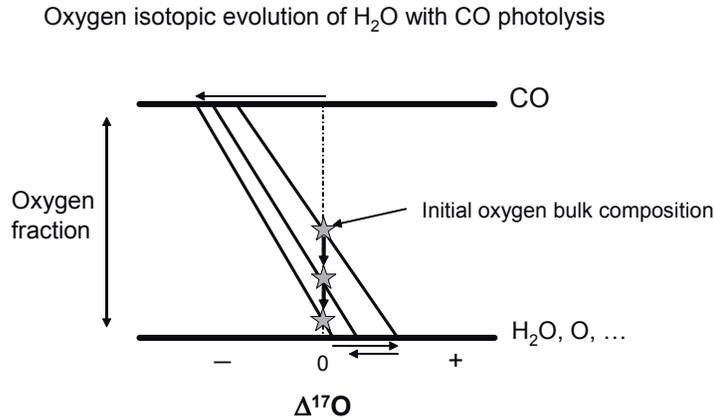


**Figure 13.** Isotopic evolution of H<sub>2</sub>O ice in the CO self-shielding region of a disk at  $R = 20$  AU. Arrows show time evolution. Dots show  $\Delta t = 70$  yr and then 7000 yr. The  $\delta$  values are with respect to the initial bulk material.

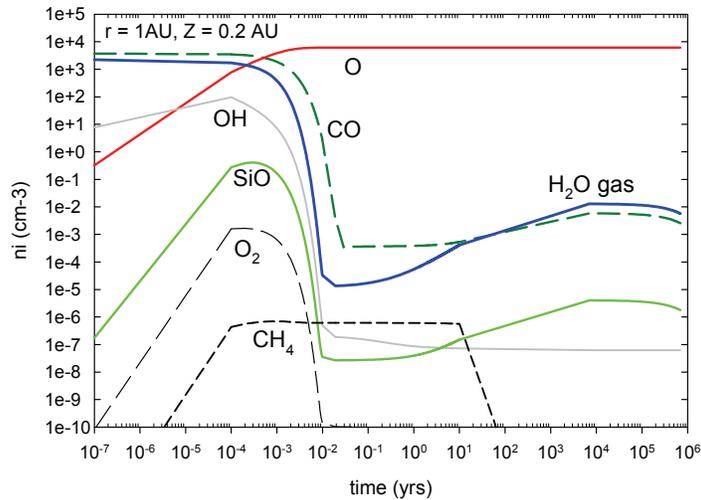
At  $R \leq 5$  AU, reaction timescales are too rapid to preserve the isotopic effects of CO photodissociation and self-shielding due to the high FUV flux. This can be understood with reference to Figure 14. The initial condition of the system is one in which oxygen is partitioned subequally between CO and H<sub>2</sub>O + O + other O-bearing species. As CO is destroyed, a larger fraction of oxygen is present as H<sub>2</sub>O + O + other O-bearing species. Eventually, as the oxygen fraction of CO becomes negligible, the remaining species (primarily H<sub>2</sub>O and O) return to the original isotopic composition of the system (Fig. 14). This process explains the loop traversed by H<sub>2</sub>O in Figure 13. If the rate of photodestruction of CO is too rapid in comparison to the redistribution of oxygen in the reaction network, product H<sub>2</sub>O never experiences a significant increase in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  because it is effectively always the dominant reservoir of O. In such cases, like that shown in Figure 15 at  $R = 1$  AU, mass-dependent fractionation dominates over the isotopic effects of CO self-shielding in species other than CO because of the rapid destruction of CO (Fig. 16). This result suggests that CO self-shielding in regions of high UV flux ( $R \leq 5$  AU) is not likely to be the explanation for  $\Delta^{17}\text{O}$  variations in the Solar System. In other words, it appears that the isotopic effect of CO self-shielding is an outer disk phenomenon.

**Transport of H<sub>2</sub>O to the inner Solar System.** Once <sup>16</sup>O-poor H<sub>2</sub>O is produced in the region of CO self-shielding, it quickly freezes onto dust grain surfaces. Radial transport of these grains to the inner portions of the disk would ultimately result in sublimation of the H<sub>2</sub>O ice and enhancement of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of H<sub>2</sub>O vapor there (Young and Lyons 2003; Cuzzi and Zahnle 2004). Oxygen isotopic exchange between H<sub>2</sub>O vapor and silicate melts is known to be relatively efficient, unlike exchange between CO and melts, allowing for transfer of the <sup>16</sup>O-poor signal contained in water to be transferred to silicate. Some aspects of delivering <sup>16</sup>O-poor H<sub>2</sub>O are discussed in the section on CO self-shielding in molecular clouds.

A major problem is the timescale over which oxygen isotope signals incurred in the outer regions of the solar nebula might have been transported to the region of terrestrial planet formation. Simple box models have been constructed (Young 2007b) that capture the essence

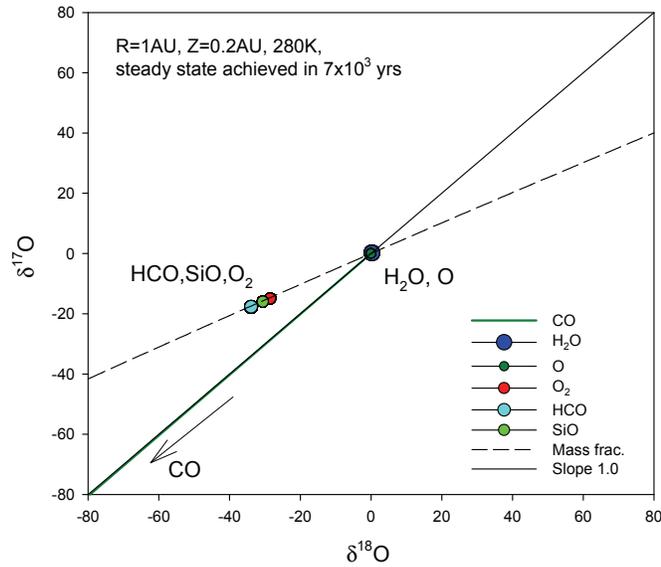


**Figure 14.** Schematic diagram showing the influence of oxygen fraction (ordinate) on  $\Delta^{17}\text{O}$  (abscissa) of reactant CO and product H<sub>2</sub>O + O + ... during photodissociation of CO. Stars mark the bulk composition of the gas phase in terms of oxygen fractions of CO and H<sub>2</sub>O+O+... at three different time steps. Black lines are tie lines connecting coexisting compositions of CO and H<sub>2</sub>O + O + ... As CO is burned away, more and more oxygen is retained in H<sub>2</sub>O + O and other O-bearing molecules. The net result is an initial rise in  $\Delta^{17}\text{O}$  of H<sub>2</sub>O + O that offsets the decrease in  $\Delta^{17}\text{O}$  of residual CO, followed by a decrease in  $\Delta^{17}\text{O}$  of product molecules.



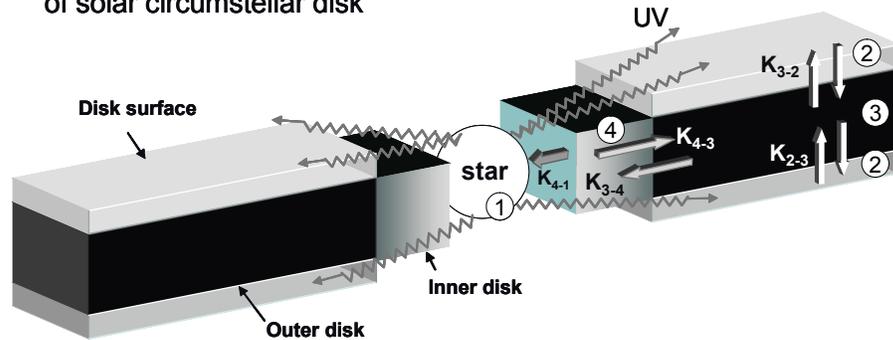
**Figure 15.** Number densities of species calculated at  $R = 1\text{ AU}$  and  $Z = 0.2\text{ AU}$  (in the CO photolysis zone) in a model disk. Note the rapid timescale of evolution compared with reactions at  $R = 20\text{ AU}$  (Fig. 12).

of the time evolution of oxygen isotope ratios in the circumstellar disk. Figure 17 summarizes the model calculation scheme. Here CO photodestruction and H<sub>2</sub>O formation reactions in the disk surfaces are approximated as a single reaction that converts CO to H<sub>2</sub>O in the presence of H<sub>2</sub> with a rate constant,  $k_{\text{photo}}$ , of  $10^{-5}\text{ yr}^{-1}$ . The reaction network calculations constrain the ratios of the effective rate constants for the <sup>18</sup>O and <sup>16</sup>O isotopologues [e.g.,  $k_{\text{photo}}(^{16}\text{O})/k_{\text{photo}}(^{18}\text{O}) = 0.22$ ]. The effective reaction rates are combined with rates of transport between the surface regions of the disk, the outer disk, the inner disk (terrestrial planet formation region), and the growing star (Fig. 17). Transport is described by first-order rate equations with



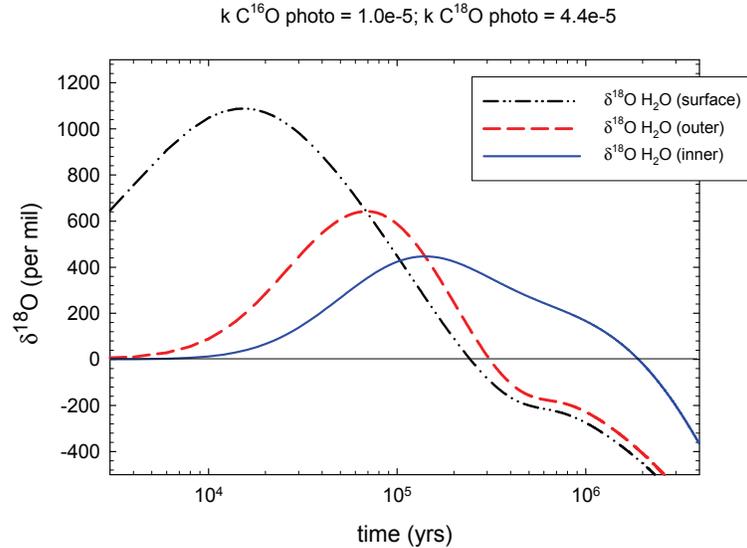
**Figure 16.** Isotopic evolution of O-bearing species at  $R = 1\text{AU}$  in the CO self-shielding layer of a circumstellar disk. Oxygen isotope fractionation is all mass-dependent with the exception of CO.

**Box model  
of solar circumstellar disk**



**Figure 17.** Schematic showing a box model for the evolution of oxygen isotope ratios in the early Solar System. Numbers refer to boxes representing reservoirs in the circumstellar disk and star. The  $k_{ij}$  are rate constants for transport while  $k_{\text{photo}}$  (not shown) is the rate constant for conversion of CO to H<sub>2</sub>O at the disk surfaces.

rate constants derived from the physics of disk evolution and stellar accretion as described in the literature. With a vertical transport timescale obtained from  $1/(\Omega\alpha)$ , where  $\Omega$  is the mean orbital frequency and  $\alpha$  is the alpha prescription for viscosity (i.e.,  $k_{2,3} = k_{3,2} = 1.5 \times 10^{-4} \text{ yr}^{-1}$ ; see Fig. 17), an estimate of the timescale of inward radial transport in a disk ( $k_{3,4} = 1 \times 10^{-5} \text{ yr}^{-1}$ ), a stellar accretion rate ( $10^{-7} M_{\odot} \text{ yr}^{-1}$ ,  $k_{4,1} = 10^{-7} \text{ yr}^{-1}$ ), and modest return flows, one obtains the result shown in Figure 18. The result shows that one expects a diachronous oxygen isotopic evolution across the disk with  $\Delta^{17}\text{O}$  rising first in the outer disk and later in the inner disk. The  $\Delta^{17}\text{O}$  of the inner disk rises on a timescale of hundreds of thousands of years to one million years.



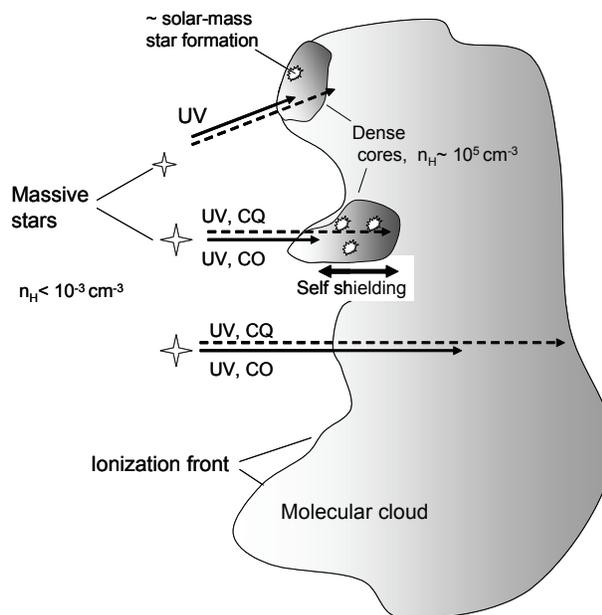
**Figure 18.** Box model for  $\delta^{18}\text{O} = \delta^{17}\text{O}$  evolution of the solar circumstellar disk.  $\Delta^{17}\text{O}$  is  $\sim 1/2$  of the  $\delta^{18}\text{O}$  values shown. Curves show the time evolution of  $\text{H}_2\text{O}$  in the disk surfaces, outer disk including midplane, and inner disk.

### CO self-shielding in molecular clouds and inheritance in the Solar System

The molecular cloud that produced the Sun is another viable place for CO self-shielding at low temperatures and has been proposed as the site of origin of  $\Delta^{17}\text{O}$  variability in the Solar System (Yurimoto and Kuramoto 2004). Since dust grains are efficient absorbers of photons with IR wavelength or shorter, molecular clouds are often recognized as dark clouds in the clear night sky. Formation of a star and an associated planetary system starts from the gravitational collapse of a molecular cloud core, a dense region in a molecular cloud (Fig. 19). In this model, interstellar FUV photons, perhaps from proximal massive stars (Fig. 19), illuminate cloud cores and cause CO photodissociation and self-shielding.

**Supporting observations.** A molecular cloud complex contains  $\sim 10^2$  to  $10^6$  solar mass of gas with a small proportion of dust (van Dishoeck *et al.* 1993). The gas species in molecular clouds are dominated by  $\text{H}_2$  and He. The dust grains are typically submicron in size and consist mainly of amorphous silicates and  $\text{H}_2\text{O}$  ice, probably with silicate cores and icy mantles (e.g., Langer *et al.* 2000). As in the outer regions of circumstellar disks, low temperatures (typically 10 to several 10K) and low gas densities ( $10^2$  to  $10^9$  hydrogen molecules/ $\text{cm}^3$ ) require that chemistry in molecular clouds is dominated by kinetics rather than thermochemistry (e.g., van Dishoeck *et al.* 1993; Langer *et al.* 2000). The gas-phase chemistry is triggered by formation of radicals and ions due to irradiation of interstellar UV and cosmic rays followed by ion-molecule reactions. Surface reactions on the dust grains are also important for promoting exothermic reactions, including the formation of  $\text{H}_2$  molecules and  $\text{H}_2\text{O}$  ice from absorbed radicals, because dust grains can buffer the generated heat (Gould and Salpeter 1963; Watson and Salpeter 1972; Boogert and Ehrenfreund 2004).

In molecular clouds, CO predissociation line spacing is much larger than the broadening due to thermal and turbulent motions and collisions. UV wavelengths that dissociate the major isotopologues attenuate at the surfaces of the clouds by self-shielding, whereas UV corresponding to absorption by the rare isotopologues can penetrate deeply into the cloud



**Figure 19.** Schematic illustration of CO photodissociation and self-shielding in molecular cloud cores. Shades of grey depict relative gas number densities. Denser cloud cores are sites of solar-mass star formation. Far ultraviolet light with wavelengths corresponding to predissociation of  $C^{16}O$  (solid arrows) and  $C^{18}O,^{17}O$  (CQ, dashed arrows) comes from massive stars that “burn” away the original molecular cloud. Self-shielding by CO is localized in cloud cores where the gas is optically thick with respect to CO but optically thin for CQ. The diagram is based on a summary by Hester and Desch (2005).

interiors. Therefore, the minor isotopologues are selectively photo-dissociated within cloud interiors. Because  $C^{18}O$  and  $C^{17}O$  are minor, their photo-dissociation occurs at nearly the same rate. This explains the constancy of  $C^{18}O/C^{17}O$  ratios in Figure 8.

In the dark cloud IC5146, young stars are scarce. However, similar fractionation patterns have been reported for the clouds with abundant young stars such as the  $\rho$  Oph dark cloud (Wouterloot et al. 2005) and the Orion molecular cloud OMC1 (White and Sandell 1995). Both clouds are known as the nearest sites actively forming low-mass (nearly solar mass or less) stars and high-mass (more massive than the sun) stars, respectively. The similar depletions of  $C^{17}O$  and  $C^{18}O$ , keeping  $C^{18}O/C^{17}O$  constant, has also been observed for the more diffuse interstellar medium by using UV spectroscopy (Sheffer et al. 2002), as described above. Hence, the mass-independent fractionation in CO is a common feature of interstellar clouds independent of astrophysical setting.

**Calculations.** Isotopic fractionation of CO in molecular clouds has been reproduced by numerical models based on the assumption of a stationary state of gas phase chemistry in a quiescent cloud (van Dishoeck and Black 1988; Warin et al. 1996; Marechal et al. 1997). These models predict that the isotopologue ratio  $^{13}CO/C^{18}O$  peaks at a visual extinction of 2-3 or less with a tail beyond 10. This result is largely consistent with the results of astronomical observations, although the observations tend to show larger fractionation at large visual extinction. This is partly due to the uncertainty in UV radiation field in cloud (e.g., van Dishoeck and Black 1988). Gradual thickening of cloud gas, i.e., evolution from a diffuse to a dense cloud, or gas mixing between the cloud surface and interior would also contribute to the observed larger fractionation.

***H<sub>2</sub>O formation and transport to the inner Solar System.*** H<sub>2</sub>O is the most abundant oxygen-bearing molecule in molecular clouds other than CO, and isotopic fractionation of CO likely propagates to H<sub>2</sub>O ice. A primary mechanism for forming the H<sub>2</sub>O molecule is hydrogenation reactions on grain surfaces (Tielens and Hagen 1982; Jones and Williams 1984; Boogert and Ehrenfreund 2004). The selective dissociation of the minor CO isotopologues produced in a molecular cloud setting should liberate oxygen atoms enriched in heavy isotopes. These oxygen atoms almost certainly become trapped and converted to H<sub>2</sub>O on grain surfaces. Hence, H<sub>2</sub>O ice in molecular clouds is expected to be enriched in heavy oxygen isotopes as the primary counterpart of CO gas (Yurimoto and Kuramoto 2004).

H<sub>2</sub>O ice is formed in clouds with total visual extinction greater than  $\sim 3$ , and the change in dust extinction properties associated with the ice formation appears to occur sharply with increasing visual extinction (Whittet et al. 2001). Star formation is initiated by the collapse of cloud cores with visual extinctions of 5 to 25 (van Dishoeck et al. 1993). The lower threshold corresponds to the range where isotopic fractionation in CO gas is expected. Therefore, the materials forming a planetary system are likely to be inherently fractionated in oxygen isotopes in a mass-independent sense as a consequence of CO photodissociation and H<sub>2</sub>O formation.

The oxygen isotopic compositions of CO gas and H<sub>2</sub>O ice in a cloud are estimated based on the results of numerical studies (explained above). For clouds with typical physical conditions for star formation,  $\delta^{17,18}\text{O}$  in CO gas and in H<sub>2</sub>O ice are expected to be  $-60$  to  $-400$  and  $+100$  to  $+250\%$ , respectively, relative to the mean isotopic composition of the parent molecular cloud (Yurimoto and Kuramoto 2004). The enrichment of heavy oxygen isotopes in H<sub>2</sub>O is consistent with the analysis of H<sub>2</sub>O-altered minerals in primitive meteorites, as described above (Clayton and Mayeda 1984; Clayton 1993; Choi et al. 1998; Young 2001; Sakamoto et al. 2007). The inherent isotopic fractionation between gas and ice in molecular clouds is expected to result in development of large-scale heterogeneity in oxygen isotopic composition within an evolving planetary disk derived from the cloud. Enrichment of water inside the snowline of the protosolar disk would have caused significant enrichment of heavy isotopes of oxygen in the inner disk. This is because H<sub>2</sub>O occupies a significant proportion of total oxygen in the system ( $\sim 1/3$  of the total oxygen should have been present as H<sub>2</sub>O prior to enrichment by H<sub>2</sub>O ice sublimation). A conservative estimate shows that the mean  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  values of the inner disk (including gas and solid grains) should have risen several tens of  $\%$  or more from the original average oxygen isotopic composition by virtue of H<sub>2</sub>O enrichment (Yurimoto and Kuramoto 2004).

#### **Testing the hypotheses: predictions of the CO self-shielding models**

The CO self-shielding models predict that oxygen isotopic ratios in the Sun should be indistinguishable from those of solids representative of primitive dust in the protoplanetary disk. The galactic evolution model posits that the Sun should be <sup>16</sup>O-poor relative to primeval dust, and the chemically-induced MIF model predicts primitive solid oxygen isotope ratios that straddle the solar value (see above). Some recent measurements of the oxygen isotopic composition of solar wind implanted in iron metal from lunar soils suggest solar oxygen isotope ratios coincident with primitive CAI ratios, consistent with the predictions of the CO self-shielding models (Hashizume and Chaussidon 2005). However, other measurements suggest depletion of <sup>16</sup>O in solar wind oxygen and are consistent with the galactic evolution model (Ireland et al. 2006). Here again, the true solar oxygen isotope ratios will go a long way toward validating one of the various genera of hypotheses for the origin of the <sup>16</sup>O anomaly in the Solar System.

Many observations are consistent with photodissociation of CO in the diffuse regions of the solar nebula or in molecular clouds as an explanation for the slope-1 line in oxygen isotope space. These models account for the fact that H<sub>2</sub>O was almost certainly depleted in <sup>16</sup>O (enriched in <sup>18</sup>O and <sup>17</sup>O, H<sub>2</sub>Q) relative to silicates and other metal oxides in the Solar System. Production in the outer solar nebula also provides a natural explanation for the correlation between <sup>16</sup>O and the refractory nature of solids; refractory minerals should have retained their

original  $^{16}\text{O}$ -rich compositions because they would have had limited opportunity for reaction with  $\text{H}_2\text{O}$  during transit through the nebula.

The isotopic compositions of the Sun,  $\text{H}_2\text{O}$  and primeval silicates cannot be used to distinguish between the various CO self-shielding models. In all three models described above, CO is expected to be enriched in  $^{16}\text{O}$ ,  $\text{H}_2\text{O}$  is predicted to be depleted in  $^{16}\text{O}$  and silicate dust should have the same isotopic composition as the Sun. A prediction of all three models is that  $\text{H}_2\text{O}$  should have been extremely depleted in  $^{16}\text{O}$ , with compositions similar to that inferred from the  $^{16}\text{O}$ -depleted incipient alteration in a carbonaceous chondrite reported by Sakamoto et al. (2007). The best opportunity for identifying the oxygen isotopic composition of primeval dust and, possibly, CO, might come from the analysis of the constituents of comets. However, the results of the recent Stardust mission (McKeegan et al. 2006) show that comets can include materials processed in the inner Solar System, and are not necessarily simply vessels for pristine pre-solar ices and dust.

Oxygen isotopic compositions of primitive Solar System rocks (CAIs) define a line of slope 1 on a plot of  $\delta^{18}\text{O}$  vs.  $\delta^{17}\text{O}$ . In evaluating the plausibility of CO self-shielding as the cause of the  $^{16}\text{O}$  variability of the Solar System, it is important to know if the slope of 1.0 on this plot is preserved in the face of the potential for large mass-dependent isotope fractionations at the low temperatures that prevail in the outer disk. A slope-1 ( $\sim 1.0 \pm 0.05$ ) relation between  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  signifies variability in  $^{16}\text{O} \gg ^{18}\text{O} \sim ^{17}\text{O}$ . The first calculations by Lyons and Young (2005a) suggested that a slope of 1.0 is to be expected, but mass-dependent fractionation was not included in those calculations. The subsequent calculations (e.g., Fig. 13) suggest that a slope of 1.0 is produced even with mass fractionation. In addition, one would wish to include other competing MIF mechanisms, such as that proposed by Marcus (2004) and described in the previous section of this chapter.

An important criterion for judging success or failure for matching models to the meteorite record will be the degree to which derived timescales can be squared with the meteorite data. For example, transport times of the  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  produced in models (e.g., Fig. 18) can be compared with timescales determined from decades of cosmochemical research characterizing  $^{16}\text{O}^{18}\text{O}_{-1}$  and  $^{16}\text{O}^{17}\text{O}_{-1}$  exchange reactions evidenced in objects like CAIs. If, for example, the timescales of  $^{16}\text{O}^{18}\text{O}_{-1}$  and  $^{16}\text{O}^{17}\text{O}_{-1}$  exchange in CAIs as determined using short-lived nuclides (primarily radiogenic  $^{26}\text{Mg}$  produced by decay of  $^{26}\text{Al}$ ) are too short or too long in comparison to the model timescales for shifting  $\Delta^{17}\text{O}$ , then we will have to reconsider either the models or the meaning of the CAI data.

A collateral consequence of this, and indeed any, CO self-shielding model may be that  $\text{N}_2$  should also exhibit the isotopic consequences of FUV illumination, as suggested previously (Kitamura and Shimizu 1983; Clayton 2002a).  $\text{N}_2$  is an important N-bearing species in the interstellar medium and, apparently, in the distal regions of disks (Knauth et al. 2004). Isotope-specific photodissociation of  $\text{N}_2$  may lead to N isotope effects in more readily observable species like  $\text{N}_2\text{H}^+$  and HCN in disks. Future observations of the isotope ratios for these N-bearing species may serve as tests of the importance of photodissociation in the isotope systematics of circumstellar disks in general and in the early Solar System in particular. This is important because, in the absence of photochemistry, large  $^{15}\text{N}/^{14}\text{N}$  ratios in meteoritic materials would seem to require inheritance from the interstellar medium, with profound implications for the origins of organic materials in the Solar System (Busemann et al. 2006).

## SUMMARY

A simple galactic evolution model can account for the observed variations of oxygen isotopes in primitive meteorites. In such a scenario, silicate dust in the ISM has a life-time of about 0.5 to 1.5 b.y., values that are consistent with the estimates of Clayton et al. (1989) for coarse

dust. The Galactic evolution model is consistent with the solar oxygen isotope composition of Ireland et al. (2006) but inconsistent with that of Hashizume and Chaussidon (2005).

There are two fundamentally different chemical classes of mechanisms that are candidate progenitors of mass-independent oxygen isotope fractionation in the early Solar System. One is symmetry-induced intramolecular vibrational disequilibrium of vibrationally excited reactant oxygen-bearing molecules. The other is isotope-selective photodissociation of CO coupled with self-shielding and formation of H<sub>2</sub>O.

Symmetry-induced fractionation should only have resulted in preservation of oxygen MIF effects if mediated by dust grain surfaces. Experiments, some of which are suggested here, are needed to establish the viability of surface-mediated MIF processes relevant to the early Solar System. The principle attraction of this hypothesis is that it is intrinsic to the rock-forming process itself and would therefore be expected to pervade all primitive rock materials.

CO self-shielding is an attractive hypothesis for the origin of mass-independent oxygen isotope fractionation in the early Solar System because it appeals to a process known to occur in the interstellar medium and, possibly, in disks. Three astrophysical settings for CO self-shielding are proposed as sites for generation of  $\Delta^{17}\text{O}$  variability in the early Solar System. One is the inner annulus of the protostellar disk at relatively high temperature. Another is at the surfaces of the disk high above the midplane, where light from the central star grazes the gas and dust of the disk, resulting in a zone of active CO predissociation and self-shielding. Interstellar light illuminating the disk at high incident angles causes a similar horizon of CO photodestruction. The last site for CO self-shielding relevant to Solar System formation is in the molecular cloud that gave rise to the protosun. The overall consequence of CO self-shielding is conversion of CO gas to <sup>16</sup>O-poor H<sub>2</sub>O. Timescales for transferring this signal from the outer disk to the inner disk in the region of terrestrial planet formation would have been on the order of one million years. Experiments are required to understand in detail the influence of temperature on CO self-shielding. If CO self-shielding is a natural consequence of circumstellar disk evolution, we should be able to test the hypothesis directly by searching for C<sup>16</sup>O excesses in other protostellar disks with new, high-spatial-resolution observations of young stellar objects.

A key difference between galactic evolution, chemically-induced MIF effects, and CO self-shielding is the predicted relative oxygen isotopic compositions of primeval dust and the Sun. Therefore, the oxygen isotopic composition of the Sun will be a crucial arbiter that may permit us to narrow the list of possible origins for oxygen MIF in the early Solar System.

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