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OXYGEN-16 VARIATIONS IN THE SOLAR SYSTEM: THE POSITIVES AND NEGATIVES. T. R. Ireland, Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia <Trevor.Ireland@anu.edu.au>.

Introduction: The ^{16}O isotopic variations in oxygen from refractory materials have colored meteoritics research for over 30 years [1]. While isotopic anomalies in titanium and magnesium can be ascribed to nucleosynthetic processes (producing enhanced ^{50}Ti and ^{26}Al), the systematics of oxygen isotopic variations have not been so easy to delineate. While initially portrayed as a nucleosynthetic component, the lack of correlation with other isotopic anomalies, makes this an unsatisfactory explanation [e.g. 2]. The discovery of chemically-induced mass independent isotope fractionation and similar variations in Earth's atmosphere [3] opened a new way of looking at the anomalies, but the specific mechanism that might operate in the early solar system has been lacking. Most recently, production of ^{16}O variations through predissociation mechanisms, both in the molecular cloud and in the solar nebula, have attracted attention [4-6].

^{16}O -enrichments and depletions: A prediction of any of the chemical isotope fractionation models is the production of complementary ^{16}O -enriched and ^{16}O -depleted components. In Earth's atmosphere, oxygen becomes isotopically lighter, while ozone is heavy. In the UV photochemistry models, predissociation of CO leads to isotopically light CO, and isotopically heavy O radicals that react with protons to form water ice, or react with solids surfaces to produce local oxidation. For example, it is predicted that cometary water ice should be isotopically very heavy [4] and variations in dust/gas ratios in the early solar system may produce reservoirs with heavy oxygen [7].

^{16}O depletions in lunar metals: Oxygen with a 5% depletion in ^{16}O exists in lunar metals grains [8]. This oxygen signal is preserved approximately 2nm below the surface in metals grains from lunar soil 10084. After removal of isotopically normal surface oxidation (either lunar or terrestrial), the oxygen concentration decreases, but the composition in terms of ^{16}O excess remains constant until the signal has decayed after a few hundred nanometers. The depth control is provided by the sputter rate of Cs^+ ions into Fe-rich matrices (metals and oxides), but the depth calibration for the metal grains is complicated because the grain geometry is altered when the grains are pressed in to gold. The preservation of an anomalous oxygen component below the surface and the constancy of the composition with depth

(notwithstanding possible changes in mass-dependent fractionation) suggest solar wind implantation.

Hashizume and Chaussidon [9] have also measured lunar metal grains and find extensive surface oxidation with isotopically normal oxygen persisting to depths of over 1000 nm. In a few cases, the apparent ^{16}O excess rises with depth, that is, there appears to be an un-mixing of the surface isotopically normal oxygen and a component preserved at depth that is enriched in ^{16}O , and attributable to ^{16}O -rich solar energetic particles. Hashizume and Chaussidon [9] therefore conclude that the solar composition is, at a minimum, enriched in ^{16}O by 4%.

These two data sets, from [8] and [9] respectively, are therefore at odds with each other and require explanation. The difference in the data is very marked. The grains analyzed by Ireland et al. [8] had very shallow effects of surface oxidation (order 10 wt% of oxygen to a few nm) while the metal grains analyzed by Hashizume and Chaussidon show persistent surface oxidation (oxygen concentration of over 10 wt % persisting to near 200 nm). The anomalous composition measured by [8] was constant with depth, the anomalous composition measured by [9] was seen in only 5 grains of 134 and persistently changed with depth. These are clearly different samples from the Moon reflecting dramatically different histories. But, they are both from the Moon, and the differences between the data sets offer the prospect of resolving some long-standing issues concerning the preservation of solar wind on the Moon.

The key questions for resolving the issues between the lunar metal data sets are: 1) how widespread is the ^{16}O depleted composition in lunar soils? 2) Is surface oxidation produced on the Moon and under what conditions? 3) Is the Sun isotopically heavy by 5 % or is another source possible?

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DENSITIES OF THE SATURNIAN SATELLITES AND THE C/O CHEMISTRY OF THE SOLAR NEBULA

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The composition of material condensed from a solar composition nebula is highly dependent on the abundance of oxygen, the dominant solid forming element (silicates and water ice), and carbon, roughly half as abundant. These abundances, and the partition of gaseous C between CO and CH₄, determine the relative abundances of water ice and rock/metal in the solid condensates. The mean densities of satellites made from this material reflect the rock, metal and ice abundances, corrected for the effects of pressure and porosity. Recently proposed changes to the solar abundance values for carbon and oxygen have a large effect on the expected density solar composition condensates. The effects of these changes on the interpretation of new satellite density determinations from the Cassini mission include: 1. Solar composition condensates have higher mean densities regardless of the state of gas phase carbon, 2. Phoebe is significantly denser, for plausible porosities, than the regular icy satellites and is likely representative of solar nebular condensates in CO-rich conditions in the outer solar system rather than circum-Saturn planetesimals, 3. The mass-weighted average icy satellite density ($\sim 1220 \text{ kg m}^{-3}$) is too low for a solar composition condensate from either the solar nebula or a circumplanetary nebula unless significant amounts of carbon were incorporated as low density solids, and 4. Large variations in mean density among the icy satellites imply post-formation fractionation processes that result in significant differences in current ice to rock/metal proportions. A portion of this work was done at the Jet Propulsion Laboratory, Caltech, under a grant from NASA.

TRANSITION ELEMENT (Fe, Cr, AND Mn) OXIDATION STATES RECORDED IN PRIMITIVE INTERPLANETARY DUST. Lindsay P. Keller¹ and Akiko Takayama², ¹ARES, Mail Code KR, NASA Johnson Space Center, Houston, TX 77058, ²Faculty of Science, 1-1, Rokkodai, Nada-ku, Kobe JAPAN 657-8501 (Lindsay.P.Keller@jsc.nasa.gov).

Introduction: Anhydrous interplanetary dust particles (IDPs) contain abundant presolar materials including silicate stardust [1] and preserved molecular cloud organic matter [2, 3]. Other primitive characteristics include high porosity, higher abundances of carbon, nitrogen, and volatile trace elements than CI chondrites, and an anhydrous mineralogy dominated by Mg-rich crystalline silicates such as enstatite and forsterite along with abundant amorphous silicates. Some of these anhydrous IDPs are linked directly to cometary sources based on estimates of their atmospheric entry velocities [4]. The anhydrous IDPs are likely representative samples of the building blocks of the solar system – a complex mixture of nebular and presolar materials largely unperturbed by secondary processing.

Results and Discussion: Enstatite and forsterite grains in IDPs typically contain minor Cr and Mn contents (up to 5 wt.% as oxides) and in many cases their abundance exceeds that of Fe (Fig. 1). Low-Fe, Mn-rich forsterites were identified in IDPs by Klöck *et al.* [5] and have also been observed in some primitive meteorites [5, 6]. The Mn-rich forsterite and enstatite are believed to have formed via gas-solid condensation in the nebula [5, 6], with forsterite forming at higher temperatures than enstatite. It is not known whether the Cr in these silicates is di- or trivalent, but Na is not detected in the pyroxenes, so the charge balanced substitution NaCr^{3+} for 2Mg does not appear to be operating – this suggests Cr^{2+} substitution for Mg, in both pyroxene and olivine. Minor diopside grains in anhydrous IDPs tend to be more Cr-rich than enstatite in the same particles.

Amorphous silicates (GEMS, glass with embedded metal and sulfides) are abundant in these primitive IDPs and also record variable oxidation states. We proposed that most GEMS grains are non-equilibrium condensates that formed after high temperature crystalline silicates (forsterite, enstatite, diopside) condensed, but prior to the main phase of sulfide formation/condensation [7]. In this scenario, conditions during condensation were sufficiently reducing to keep Fe in the metallic state to at least temperatures below $\sim 1000\text{K}$ (the upper stability limit for the preservation of the amorphous silicate matrix before it anneals [8]) and Fe^{2+} only became abundant when sulfidization reactions began at $\sim 700\text{K}$. Individual GEMS grains can contain both nanophase kamacite and taenite,

however, their compositions are not in equilibrium [9]. In our X-ray mapping experiments, we have also identified Fe- and Cr-rich grains within GEMS – detailed transmission electron microscope measurements are underway to determine if these are nanophase metal or chromite grains [9]. Our mapping experiments also show that the amorphous silicate matrix of GEMS grains tends to be highly SiO_2 normative with much of the Fe present as metal. However, we have measured Fe oxidation states in some FeS-free GEMS grains and have documented a mixture of Fe metal and Fe^{2+} in the amorphous silicate matrix [7].

Sulfides in IDPs are predominantly pyrrhotite and occur as large single crystal grains and as nanophase grains attached to the surfaces of GEMS grains. Rare grains of Zn-rich sulfide occur in these IDPs and suggests that Zn behaves as a chalcophile element.

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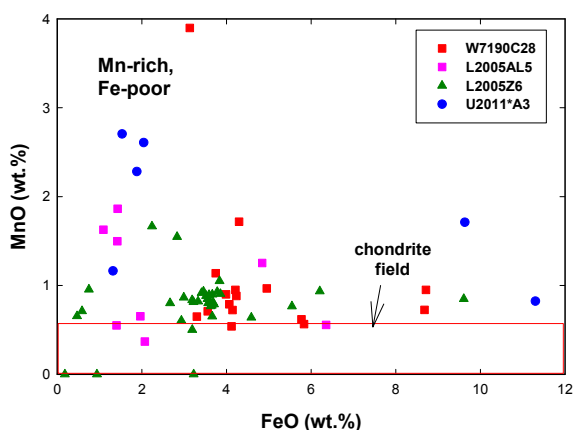


Figure 1. Compositions of pyroxene grains in anhydrous IDPs with unusual Mn-rich compositions – also plotted is the field for meteoritic pyroxene compositions from [5].

OXYGEN ISOTOPIC COMPOSITIONS OF CHONDRULES. A. N. Krot¹, R. H. Jones², M. Yoshitake³, and H. Yurimoto⁴, ¹University of Hawai'i at Manoa, USA (sasha@higp.hawaii.edu). ²University of New Mexico, USA. ³Kobe University, Japan. ⁴Hokkaido University, Japan.

It is generally believed that chondrules formed by varying degrees of melting of dense aggregates of Fe-Mg silicate, metal, and sulfide grains during repetitive flash-heating events in the dusty solar nebula. O-isotopic compositions of chondrules may have recorded various stages of chondrule evolution: the assemblage of isotopically heterogeneous precursor grains, O-isotopic exchange with the surrounding gas during chondrule melting, and O-isotopic exchange during postcrystallization alteration. Conventional bulk and *in situ* ion microprobe measurements of O-isotopic compositions of chondrules and chondrule minerals [1-19], in combination with O-isotopic diffusion and exchange experiments on chondrule-like melts and minerals [20-22] and theoretical modeling [23-28] provide important constraints on the evolution of O-isotopic compositions of the inner solar nebula, the nature of chondrule-forming processes, and the genetic relationship between refractory inclusions and chondrules, and are reviewed here.

Bulk O-isotopic compositions of chondrules show large diversity both among and within the various chondrite groups [29-34]. On a three-oxygen diagram, bulk O-isotopic compositions of most chondrules in ordinary (O), enstatite (E), and carbonaceous (C) chondrites plot above, along, and below terrestrial fractionation line, respectively. These observations are commonly interpreted as a result of stochastic sampling of isotopically heterogeneous precursor materials and O-isotopic exchange with a common gaseous reservoir with $\Delta^{17}\text{O}$ of +2‰ to +8‰ [29,35]. In addition, bulk O-isotopic compositions of chondrules were probably modified to various degrees during postcrystallization alteration, most likely in an asteroidal setting [e.g., 36].

Ion microprobe measurements of O-isotopic compositions of chondrules have been reported for O, E, and C chondrites [1-19]. Most analyses of Fe-Mg chondrules are limited to olivine grains; measurements of multiple mineral phases within a single chondrule are exceptionally rare [3,10,25]. Al-rich chondrules with relict CAIs have been studied in greater details [4,6,9,10,13,14,16,25].

Most chondrules are ¹⁶O-depleted ($\Delta^{17}\text{O} \geq -7\text{‰}$) relative to AOAs and most CAIs ($\Delta^{17}\text{O} \leq -20\text{‰}$), suggesting formation in isotopically distinct reservoirs [24,27,28]. The only exceptions are chondrules and CAIs in the metal-rich CH and CB chondrites. In the CB chondrites Hammadah al Hamra 237 and QUE94411, the CAIs appear to have been melted; they are uniformly ¹⁶O-depleted ($\Delta^{17}\text{O} = -10\text{‰}$ to -6‰) and overlap in composition with chondrules ($\Delta^{17}\text{O} = -7\text{‰}$ to -1‰) [7]. This anomaly may be due to a planetary formation mechanism of the CB chondrites [37]. Some CAIs in CH chondrites are uniformly ¹⁶O-depleted to a level observed in most CH chondrules [18,38,39]. The uniformly ¹⁶O-rich chondrules ($\Delta^{17}\text{O} \leq -20\text{‰}$) are exceptionally rare and have been found only in CH chondrites [5,18].

Most Fe-Mg chondrules from primitive chondrites are isotopically uniform (within 2-3‰ in $\Delta^{17}\text{O}$); O-isotopic heterogeneity is due to the presence of relict grains which appear to represent either chondrules of earlier generations or incompletely melted refractory inclusions [3,10,11,19,25]. The Al-rich chondrules with relict CAIs have heterogeneous O-isotopic compositions ($\Delta^{17}\text{O}$ from -20‰ to 0‰), with the relict grains being ¹⁶O-enriched compared to the chondrule phenocrysts and mesostasis. The Al-rich chondrules without relict CAIs are iso-

topically uniform and have ¹⁶O-poor compositions similar to those of Fe-Mg chondrules.

We infer that O-isotope compositions of chondrules from primitive chondrites resulted from two major processes: homogenization of isotopically heterogeneous materials during chondrule melting, and O-isotopic exchange between chondrule melt and ¹⁶O-poor nebular gas. In contrast to most refractory inclusions, chondrules appear to have largely originated from ¹⁶O-poor precursors and were subsequently melted in the presence of ¹⁶O-poor nebular gas. If the initial composition of the solar nebula was ¹⁶O-rich [40], chondrule precursors must have been thermally processed in an ¹⁶O-poor gas. Because chondrules without relict grains in CR carbonaceous chondrites are isotopically uniform [10] and distinct from those in O chondrites, O-isotopic exchange with a common gaseous reservoir seems unlikely.

These observations can be interpreted in terms of isotopic self-shielding during UV photolysis of CO in the initially ¹⁶O-rich ($\Delta^{17}\text{O} \sim -25\text{‰}$) protoplanetary disk or parent molecular cloud [25,26,28,40]. According to these models, the UV photolysis preferentially dissociates C¹⁷O and C¹⁸O in the peripheral zones of the protoplanetary disk or the parent molecular cloud. If this process occurs in the stability field of water ice, the released atomic ¹⁷O and ¹⁸O are incorporated into water ice, while the residual CO gas becomes enriched in ¹⁶O. The inner solar nebula had initially solar H₂O/CO ratio and was ¹⁶O-rich. During this time, the ¹⁶O-rich CAIs and AOAs, and some chondrules formed. Subsequently, the inner solar nebula became H₂O-enriched and ¹⁶O-depleted, because meter-size icy bodies, which were enriched in ^{17,18}O, agglomerated outside the snowline (~5 AU), drifted rapidly towards the Sun and evaporated. During this time, which may have lasted for ~ 3 Myr, most of the chondrules and ¹⁶O-depleted igneous CAIs formed [25].

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OXYGEN ISOTOPES OF MATRIX OF PRIMITIVE METEORITES AND IMPLICATIONS TO

NEBULAR DUST. T. Kunihiro¹, K. Nagashima², A. Brearley³, and H. Yurimoto⁴, ¹University of California, Los Angeles, CA 90095 (tky@ess.ucla.edu), ²University of Hawaii at Manoa, Honolulu, HI 96822, ³University of New Mexico, Albuquerque NM 87131, ⁴Hokkaido University, Sapporo 0600810 Japan.

Introduction: Since the sun contains >99% of the mass of the solar system, its composition is considered representative of the solar nebula. The similar abundances of the carbonaceous chondrite nonvolatile elements to those of the solar photosphere are a major reason why the carbonaceous chondrites are of such great interest in modeling of the formation and early evolution of planetary materials in the solar nebula. The carbonaceous chondrites are comprised of three major components: refractory inclusions, chondrules, and fine-grained matrix. As a major component of carbonaceous chondrites, the matrix plays an important role in the search for pristine fine-grained nebular material in the solar nebula.

After oxygen isotopic anomalies were observed in refractory inclusions [1] many O-isotope studies have been made on refractory inclusions and chondrules; however, the fine-grained nature of the matrix was a limiting factor in determining O-isotope compositions of the specific constituents of the matrix.

Mineralogy and bulk O-isotope compositions of matrices: Matrix materials are diverse in character and vary from one chondrite group to another; however, in general, the matrix is largely composed of a complex assemblage of highly unequilibrated material consisting of silicates (dominantly FeO-rich olivine), oxides, sulfides, sulfates, carbonates, Fe-Ni metal, phyllosilicates, and amorphous and carbonaceous materials [2]. Matrix of highly pristine chondrites, such as Acfer 094, lacks phyllosilicates and consists largely of small crystalline silicates that are embedded in amorphous material [3]. The grain sizes of its constituent minerals range from ~5 μm down to 10 nm. Although the disequilibrium nature of the matrix would lead one to expect heterogeneous O-isotope distribution among minerals, the bulk O-isotope compositions of the matrix in several carbonaceous chondrites plot as a cluster on the CCAM line or slightly below, with $\delta^{18}\text{O}$ varying from 0 to 15‰ [4]. The distinct differences in the bulk O-isotope composition between matrices and chondrules (or refractory inclusions) imply that they were not derived directly from one another.

Micro-distribution of O-isotope compositions: Recently an in-situ and high-precision isotopic imaging technique (isotopography) has been developed [5] and applied to the matrix of Vigarano

[6-7] and Acfer 094 [8]. The O-isotopes are distributed heterogeneously in the matrix on a micrometer-scale. They plot along the CCAM line with $\delta^{18}\text{O}$ varying from ~-50 to ~10‰, consistent with O-isotope variations observed in chondritic components. Some 2 μm grains are ¹⁶O-rich and others are ¹⁶O-poor, and they are dispersed throughout the matrix. The O-isotopes in most of the matrix are ¹⁶O-poor and are distributed homogeneously. Submicron presolar-silicates with distinct O-isotope compositions are also embedded in the matrix of Vigarano and Acfer 094 although the abundances are extremely low (<30 ppm [7-8]). The degree of aqueous alteration is more extensive in Vigarano than in Acfer 094 [3, 9]. The existence of preserved submicron presolar-silicates in both Vigarano and Acfer 094 matrices with similar O-isotope distribution suggests that O-isotopes in the matrices are not completely modified by aqueous alteration and that the matrices retain O-isotope distributions of the nebular dust.

Implications to nebular dust: O-isotopes show that the matrix is a mechanical aggregate of fine-grained materials mainly formed in the solar system; small amounts of presolar grains also are dispersed in the matrix. More than 95% of matrix grains are depleted in ¹⁶O and equivalent to the bulk matrix. The rest are mainly ¹⁶O-enriched grains related to refractory inclusions. The low abundance of presolar grains indicates that most of presolar grains cannot survive in the solar nebula, i.e., they had been destroyed during nebular processes. O-isotopic equilibration with nebular gas is a probable explanation for the predominance of ¹⁶O-depleted materials in the matrices. If so, the gas-solid equilibration was almost completed before chondrite parent-body accretion in the solar nebula.

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OXYGEN ISOTOPIC EVOLUTION DURING THE FORMATION AND EVOLUTION OF THE SOLAR NEBULA: MOLECULAR CLOUD ORIGIN HYPOTHESIS FOR THE ISOTOPIC ANOMALY AND ITS IMPLICATIONS. Kiyoshi Kuramoto and Hisayoshi Yurimoto, *Hokkaido University, Sapporo 060-0810, Japan, (keikei@ep.sci.hokudai.ac.jp).*

Observations and theory strongly suggest that significant mass-independent isotopic fractionation occurs between CO and H₂O molecules within a molecular cloud core from which a proto-planetary system forms. Such isotopic anomalies may be transported to proto-planetary disk and trapped into heterogeneously into rocky components in the inner disk. This model provides a plausible explanation for the origin of heterogeneous oxygen isotope compositions among meteorites and their inclusions, and also some predictions which would become testable in future.

Molecular cloud chemistry: Since stars form in clustered environment, star-forming molecular cloud is irradiated by the energetic photons emitted from young stellar objects and possibly from massive stars if they coexist. Observational data [1,2] and numerical models [3] reveal selective ultra-violet dissociation of C^{17,18}O isotopomers by the self-shielding effect of C¹⁶O, the dominant O-bearing gas species in molecular clouds. Since released atomic oxygen is likely adsorbed and then hydrogenated to H₂O on dust grains, H₂O ice produced in molecular cloud is expected to be ¹⁶O-depleted. A mass balance consideration predicts that H₂O ice and CO have ¹⁶O-poor ($\delta^{17,18}\text{O}_{\text{MC}} = 100 \sim 250\%$) and ¹⁶O-rich ($-60 \sim -400\%$, which is consistent with observational constraint) compositions relative to the bulk molecular cloud, respectively [4]. This naturally explains the ¹⁶O-depleted nature of H₂O in the early solar nebula inferred from meteoritic minerals altered by H₂O [5].

Dust-gas fractionation in an accreting proto-planetary disk: A dust grain immersed in a proto-planetary disk has relative motion against ambient disk gas which rotates with speed slightly lower than the Keplerian owing to the support of radial pressure gradient. The frictional loss of angular momentum due to their relative motion causes the drift of grain toward the central star. Considering the gradual growth of dust grains from interstellar sub μm size by coagulation as well as the decay of gas accretion, a proto-planetary disk should have experienced a stage during which solid grains preferentially infall toward the central star. During this stage, solid grains release H₂O vapor to disk gas after the passage of the snow line and thereby enhance the H₂O vapor content in the inner disk. A two-fluid disk model predicts that enrichment with factor of several is possibly achieved in an inner disk when the disk accretion rate decreases to $10^{-8} M_{\odot}/\text{yr}$ (typical for classical T-tauri star) or below and the dust grains grow to mm-size [6]. This means that the inner solar nebula may become ¹⁶O-poor by several tens permils in average during such stage because H₂O is predicted to be significantly ¹⁶O-poor. Such moderate H₂O enhancement is sufficient to explain the relative depletion in ¹⁶O (difference in $\delta^{17,18}\text{O} \approx +50\%$) seen for the major part of the meteoritic materials relative to typical ¹⁶O-rich CAIs, assuming that the latter have formed before the development of H₂O enrichment [4]. This is consistent with the maintenance

of CAI and chondrule reprocessing after the main phase of ¹⁶O-rich CAI formation [7,8]. Above interpretation predicts that the Sun is ¹⁶O-rich, which is consistent with the ¹⁶O-rich composition of implanted solar wind extracted from lunar soil [9].

Relationship with diversity in redox state of primitive meteorites: The preferential infall of dust grains is also expected to cause a heterogeneous enrichment of reduced C-bearing vapors in the innermost disk through the vaporization of organic matters contained in dust grains. In particular, the change in disk accretion rate possibly causes large variation of C/O ratio as well as H₂O content within the inner disk. Before the H₂O-enriched nebular gas is transported to the disk center, the innermost disk possibly has high C/O ratio allowing the formation of SiC, which might play an important role in the Si/Mg fractionation as well in the control of redox state inferred from the chemical systematics of chondrites [6,10].

Outer planets as diagnostics to test models: Our model predicts that the outer planets have ¹⁶O-depleted compositions because they are enriched in heavy elements originally coexisted with H₂O ice as nebular dust components. The depletion increases with increasing heavy element enrichment. On the basis of chemical composition of their atmospheres, Jupiter, Saturn and Uranus/Neptune are estimated to have bulk isotopic compositions more than +35, 50, and 65‰ difference in $\delta^{17,18}\text{O}$ relative to the Sun, respectively [6]. The outer planets and their satellites may provide key diagnostics to test the models which attempt to explain the O-isotopic heterogeneity in the meteorites and rocky planets. This is because alternative models predict different O-isotopic composition for the outer planets. For instance, the model assuming the CO self-shielding at the inner edge of the solar nebula [11] implies little depletion in ¹⁶O relative to the Sun and that assuming the CO self-shielding at the surface skin layer of the solar nebula [12] implies poor correlation between the isotopic composition and heavy element enrichment.

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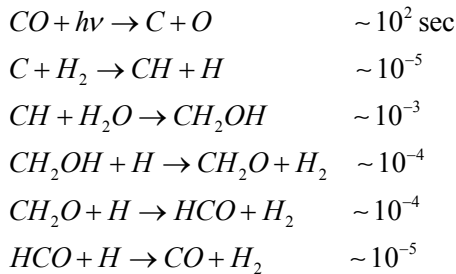
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CO SELF-SHIELDING IN THE SOLAR NEBULA J. R. Lyons¹, ¹Institute of Geophysics and Planetary Physics, and Department of Earth and Space Sciences, UCLA, Los Angeles, CA 90095; jrl@ess.ucla.edu

Introduction: Clayton's suggestion [1] that CO self-shielding in the X-point region of the nebula was the source of a ¹⁶O-depleted H₂O reservoir, as required by the two-component mixing model for CAIs [2], has led to recent work on the topics of self-shielding [3,4] and the oxygen isotope composition of the solar wind [5]. Here I will present a review of CO self-shielding in the solar nebula.

CO self-shielding in the inner solar nebula: Self-shielding of CO in the inner solar nebula is advantageous for two reasons: 1) a very high flux of far ultraviolet (FUV) photons was available from the protosun, and 2) the transport timescales to go from ~ 0.1 AU to ~ 2 AU are fairly short, especially if particles were carried by the X-wind. The disadvantages of CO self-shielding in the inner solar nebula are several [6]: 1) high temperatures reduce the effectiveness of self-shielding [7], 2) strong continuum absorption due to gas-phase H₂O, and 3) high temperature reactions of C with H₂ and H₂O eventually reforms CO, erasing the anomalous isotope signature produced by CO self-shielding.

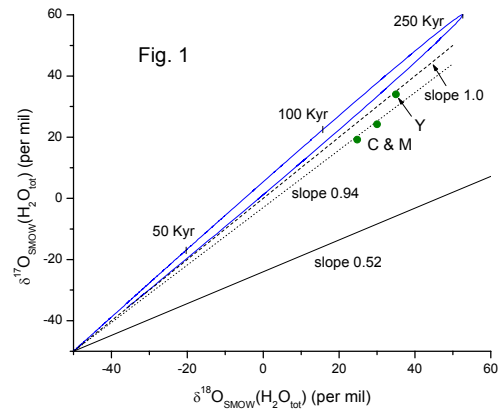
At 2000 K and 10 mbar, the following reaction sequence will occur (the chemical loss timescale for left-most reactant is shown) [6]:



Such short chemical loss timescales imply that CO is reformed from H₂O much more rapidly than CO is photolyzed, and so preservation of a self-shielding derived isotope anomaly is unlikely. However, 2000 K and 10 mbar may not be representative of the inner solar nebula. These calculations will be repeated for 1500 K and 0.1 mbar and the results presented.

CO self-shielding in the outer solar nebula: Self-shielding in the outer solar nebula is similar to that in molecular clouds (e.g., [8]). At temperatures < 120 K (approximately) reactions on grain surfaces involving H atoms and O atoms produced during CO photolysis yield ¹⁶O-depleted H₂O. The low temperatures inhibit isotopic equilibration of residual CO and

H₂O. Incorporating CO photolysis and self-shielding into a photochemical model for the solar nebula [4] yields the 3-isotope results for total nebular water shown in Figure 1. These results are for a distance R = 30 AU, Z = 0 (nebula midplane), a turbulent viscosity parameter $\alpha = 10^{-2}$, and a FUV flux = 500 times the local interstellar medium flux, all of which are plausible parameter values. Inclusion of differential absorption by H₂ reduces the slope of the trajectory shown in Fig. 1 from 1.1 to about 1.0, making the model calculations consistent with measurements of CAI slopes [9,10].



The timescale required for total nebular water to reach the isotopic values inferred from Murchison [2,11] is ~ 10⁵ years, which is comparable to the radial transport timescale inward from 30 AU. The implications of these fairly long timescales will be discussed.

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MASS-INDEPENDENT GAS PHASE AND SURFACE REACTIONS OF GEOCHEMICAL AND COSMOCHEMICAL INTEREST. R. A. Marcus¹, ¹Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA; ram@caltech.edu.

Introduction: The unusual "mass-independent" oxygen isotope effect in stratospheric ozone [1] and in calcium aluminum enriched inclusions (CAIs) in chondritic meteorites [2] has aroused much interest. This effect, in which the ¹⁷O and ¹⁸O show equal fractionation, poses interesting challenges to experimentalists, theorists, and their interaction.

The stratospheric formation of ozone involves $O + O_2 \leftrightarrow O_3^*$, followed by $O_3^* + M \rightarrow O_3 + M$, where O_3^* is vibrationally excited and M is a third body. A non-RRKM explanation (non-statistical distribution of vibrational states) has been proposed for the O_3 phenomenon [3]: At the usual isotopic compositions only the ¹⁷O and ¹⁸O can form isotopically asymmetric ozone molecules, and for dynamical reasons they live longer than the symmetric isotopomers [3]. So, collisional stabilization of isotopically asymmetric ¹⁷O and ¹⁸O ozones occurs preferentially relative to symmetric ozones, yielding the mass-independent enhancement. (References to the statistical (RRKM, Rice, Ramsperger, Kassel, Marcus) theory of unimolecular reactions and bimolecular recombinations are found in [3], in which the present non-RRKM effect is also discussed.)

The CAIs, the earliest processed solids in the solar system, were formed instead some 4.56 billion years ago. CAIs, such as $(MgO)(Al_2O_3)_3$ and $(MgO)_2SiO_2$, are believed to have formed at 1500-2000 K and 10^{-3} to 10^{-4} atm.

Proposed mechanism and Discussion:

A possible chemical mechanism for CAI formation [4] involves the surface analogue of the O_3 phenomenon, with surface reactions leading to the vibrationally excited adsorbed species $XO_2^*(ads)$, as in $XO(ads) + O(ads) \leftrightarrow XO_2^*(ads)$, where $X = Si, Al, \dots$. Calculations and other data show that this $O(ads)$ would form principally from $H_2O + surface \rightarrow H_2 + O(ads)$, rather than from $O + surface \rightarrow O(ads)$ [4]. The surface of a growing grain has an entropic effect of many orders of magnitude on the position of the monoxide-dioxide equilibrium relative to the gas phase equilibrium by acting as a concentrator. A gas phase non-RRKM effect for ozone cannot apply to gas phase precursors of CAIs for two reasons, the rarity of the 3-body collisions at low pressures of M, and the H_2 and H attack dioxides. So a surface reaction is required instead for the desired fractionation.

If a surface non-RRKM effect exists, it would yield $XO_2^*(ads)$ that is mass-independently rich in ¹⁷O and

¹⁸O, and $O(ads)$ and $XO(ads)$ that are mass-independently poor in ¹⁷O and ¹⁸O. The ¹⁶O-depleted $XO_2^*(ads)$ is then lost to the gas phase, directly or after vibrational energy loss to the grain. It leaves the solid by evaporation or upon attack by a gas phase reductant. These $XO_2^*(ads)$ have a ballpark estimated natural lifetime toward dissociation of 500 fs at 2000 K. The other species, $O(ads)$ and $XO(ads)$, are ¹⁶O-enriched and react with $Ca(ads)$ and other adsorbed metal atoms or metallic oxides to form ¹⁶O-enriched CAIs. There is a competition between the loss of $XO_2^*(ads)$ (or $XO_2(ads)$) to the gas phase versus the incorporation of the XO , O , Ca , Mg and other species into the lattice to form the CAIs. ($X=Si, Al, \dots$)

One feature of this chemical mechanism for the oxygen isotope anomaly is that only one oxygen isotope reservoir is required in the solar nebula. It also does not require a sequestering of intermediate products which could undergo isotopic exchange, hence undoing the original isotopic fractionations.

While there are many indirect experimental tests of the mechanism proposed for isotope effects in ozone formation [3], direct tests, such as pump-dump laser excitation of O_3 and a search for non-single exponential dissociation decay of O_3^* , are so far absent. The more difficult study of the existence of a non-RRKM effect on a solid phase (or melt) would be desirable using a source of SiO and of H_2O (or O), and other atoms such as Ca and Al .

The study of the rate of dissociation of a mineral is easier than of its rate of formation by condensation from its components from the gas phase. The interesting question of whether a chemical mechanism for the CAIs isotope effect could also lead to a mass-independent fractionation in the dissociation of a mineral will be discussed. It would require two dissociation modes, one leading from $XO_2^*(ads)$ and the other from $O(ads) + XO(ads)$ in the assumed $XO(ads) + O(ads) \leftrightarrow XO_2^*(ads)$ pre-equilibrium. Each mode would have its own isotopic composition, and a separate trapping of each set of products would be needed to avoid their subsequent mixing $XO_2^*(ads)$. The difference in adsorbed O_3^* and XO_2^* is also discussed. Mass-independent fractionation poses new challenges in both gas phase and surface studies.

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THE FORMATION AND PROCESSING OF INTERSTELLAR OXYGEN-RICH DUST.

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Introduction: By means of spectroscopic observations in the infrared it is possible to study the mineralogical composition and grain properties of dust grains in interstellar and circumstellar environments. In particular the spectrographs mounted on space telescopes such as the Infrared Space Observatory [1,2] and the Spitzer Space Telescope [3,4] have enabled us to study the composition and dust properties in great detail. In this talk, I will provide an overview of what is known about the formation and evolution of oxygen-rich dust species.

The life cycle of dust: Oxygen-rich dust is formed in the outflow of evolved stars, which have exhausted hydrogen core burning. The main dust factories are the so-called Asymptotic Giant Branch stars, which have developed a dense stellar wind in which the conditions are suitable for the formation of dust. This environment is relatively sheltered from energetic radiation, and the newly formed dust shows an amazing variety of properties and compositions, including a relatively high degree of crystallinity [5,6]. In the

interstellar medium, the main depletion sink of oxygen in the interstellar medium is in the form of amorphous silicates, e.g. [8]. In this talk, I will discuss the differences between the circumstellar and interstellar environments, and give an overview of the processes that drive the evolution of the oxygen-rich dust properties.

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OXYGEN ISOTOPIC INSIGHTS INTO ORIGINS AND HISTORIES OF COMETARY MATERIALS. S. Messenger and L. P. Keller, NASA Johnson Space Center, Astromaterials Research & Exploration Science Division, Robert M Walker Laboratory for Space Science, Houston TX 77058.

Introduction: Originating from the coldest and most quiescent portions of the solar system, comets are likely to be the least processed remnants of the solar nebula. Though once considered to be unprocessed assemblages of interstellar materials, a minor population of crystalline silicates is apparent in some cometary spectra, suggesting that they contain materials processed at high temperatures [1].

Chondritic porous (CP) interplanetary dust particles (IDPs) bear similarities to cometary dust, including their fine grain sizes, fragile microstructures, high abundances of volatile elements and carbon, and anhydrous mineralogy. Infrared spectra of CP IDPs are also a remarkably good match to comets [2]. CP IDPs have been dynamically linked with comets from their high atmospheric entry velocities inferred from thermal release measurements of solar wind He [3].

Here we summarize constraints on the origins of cometary grains derived from oxygen isotopic measurements of submicrometer grains in CP IDPs, acquired with the Washington University NanoSIMS 50 ion microprobe.

Presolar Grains: Circumstellar silicates and oxides have been found in both meteorites and IDPs [e.g. 4-6]. These grains have highly non-solar isotopic compositions, with $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios varying by more than 2 orders of magnitude. Most grains apparently derive from red giant and asymptotic giant branch stars, with a minor (~1 %) population from supernovae [7]. Of the few presolar silicates whose mineralogy has been definitively identified by TEM, 4 are amorphous silicates including GEMS grains, and 2 are olivine grains. The mineralogy of presolar silicates is distinctly different from interstellar silicates, that appear to be dominated by amorphous grains.

Silicate stardust grains ARE more abundant in some CP IDPs (450 – 5,500 ppm; 4,8) than in meteorites (<180 ppm; 5,6). Nonetheless, these IDPs are clearly dominated (>99 %) by grains with O isotopic compositions that are so far indistinguishable (within ~50%) from solar.

Isotopically Solar Crystalline Grains: Crystalline oxides and Mg-rich silicates are common components of CP IDPs. The mineralogy and microstructure of these grains are consistent with condensation from a high T (>1,300 K) gas. Most (>95 %) such grains studied so far have solar O isotopic compositions. It is very likely that most such grains originated in the solar system itself because (1) most oxides and silicates

formed around evolved stars have distinctly non-solar O isotopic compositions and (2) crystalline silicates are extremely rare in the interstellar medium (<0.2% of interstellar silicates; 9). These grains probably formed in the inner, warmer regions of the solar nebula, and were transported to the Kuiper belt by turbulence or perhaps the X-wind [10,11].

Isotopically Solar Amorphous Silicates: Amorphous silicates are a major component of CP IDPs, including GEMS grains [12] and other glassy grains. GEMS grains are proposed to have been produced by extensive, gradual sputtering and re-condensation of materials in the ISM [12], a process that would tend to homogenize their chemical and isotopic compositions. Alternatively, these grains may have been late-stage nebular condensates [13], also naturally leaving the grains with solar isotopic compositions.

Because circumstellar silicates tend to have strongly non-solar O isotopic compositions, many interstellar grains will retain distinct isotopic compositions despite extensive mixing with isotopically solar interstellar gas. Among the 1,000 submicrometer grains measured in IDPs so far, less than 1% differ from solar O isotopic composition by more than 50 ‰. If these grains originally had O isotopic compositions similar to circumstellar oxides, their present O isotopic compositions indicate that most of them must have been *thoroughly* homogenized, containing less than 5% of the original stellar condensate. Higher precision O isotopic measurements will be required to identify the expected partially homogenized interstellar silicates that should be marked by moderately anomalous (50 – 100 ‰) isotopic compositions.

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NUCLEOSYNTHESIS AND GALACTIC CHEMICAL EVOLUTION OF THE ISOTOPES OF OXYGEN.

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Introduction: The stable isotopes of oxygen are important diagnostics of stellar nucleosynthesis and Galactic chemical evolution. This is primarily due to the fact that ^{16}O is a principal product of stellar evolution and is therefore very abundant in the Galaxy. It is also due to the fact that ^{16}O is a primary isotope while ^{17}O and ^{18}O are secondary isotopes.

Nucleosynthesis: ^{16}O is primarily produced at the end of helium burning in stars. ^{12}C produced by the triple-alpha reaction captures another ^4He to produce ^{16}O . This means that the interplay of the triple-alpha reaction and $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ determines the ratio of ^{12}C to ^{16}O in the star after helium burning, which, in turn, governs the subsequent stellar evolution (e.g., [1]). Experimental determination of the $^{12}\text{C}(\alpha,\gamma)^{16}\text{O}$ reaction rate is difficult and is the subject of intense study (e.g., [2]). ^{16}O abundance is increased further during neon burning. Because ^{16}O can be produced by stars initially composed only of hydrogen, it is a primary isotope. It is worth noting that ^{16}O is, in fact, one of the dominant products of massive stars. For example, one may consider a model of a star 25 times the mass of the Sun [3]. This model began with about 0.23 solar masses of ^{16}O but ejected 3.24 solar masses of that isotope.

By contrast, ^{17}O and ^{18}O are secondary isotopes, which means their production requires pre-existing seed nuclei. ^{17}O is dominantly produced by CNO burning of hydrogen into helium and is thus a prevalent isotope in hydrogen burning shells in stars. ^{18}O is primarily made when abundant ^{14}N , left over from CNO burning, captures ^4He . This means ^{18}O is abundant in helium-rich zones in stars. Because ^{16}O and ^{18}O production requires helium burning while ^{17}O only requires hydrogen burning, low-mass stars may contribute more significantly to the synthesis of ^{17}O than to ^{16}O or ^{18}O .

Galactic Chemical Evolution: Since ^{16}O is a primary isotope, it was produced in the first generation of stars. Observations of very metal-poor stars show the rise of oxygen with metallicity in the early Galaxy (e.g., [4]). The primary nature of the nucleosynthesis of ^{16}O means that this rise is roughly linear in time. By contrast, the secondary nucleosynthesis of ^{17}O and ^{18}O means that the abundance of these isotopes in the Galaxy will rise roughly quadratically with time in a chemical evolution model (e.g., [5]). Such evolution is evident in Figure 1, which shows the evolution of the mass fraction of the oxygen isotopes in the interstellar

medium from a standard Galactic chemical evolution model. The figure was generated with the Clemson University online Galactic Chemical Evolution code available at the web site

http://nucleo.ces.clemson.edu/home/online_tools

Interested readers are invited to explore the details of stellar yields and Galactic chemical evolution of the oxygen isotopes with this tool.

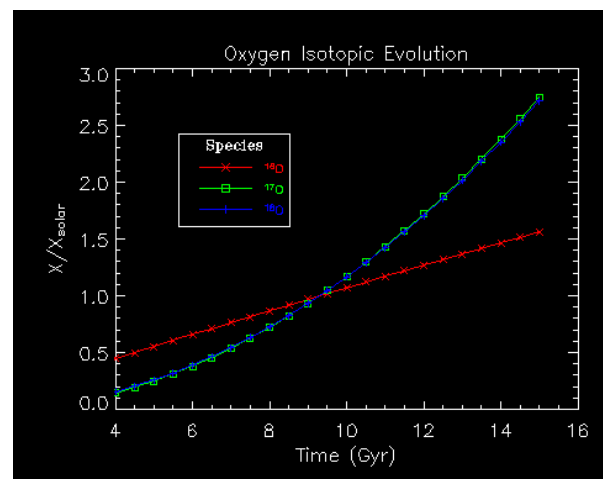


Figure 1: Chemical evolution of the mass fractions of the oxygen isotopes relative to their solar values in the interstellar medium in a standard chemical evolution model. The ^{16}O mass fraction rises linearly with time because it is a primary isotope. ^{17}O and ^{18}O rise quadratically with time because they are secondary isotopes. This figure was generated with the Clemson University online Galactic Chemical Evolution code.

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Presolar O-Rich Dust Grains In The Solar System. L. R. Nittler¹, ¹Carnegie Institution of Washington, Washington DC, 20015, USA, email: lrn@dtm.ciw.edu.

The bulk solar system composition represents a mixture of materials that were formed or processed through countless numbers of individual stars in the billions of years of presolar galactic history. Although most of the pre-existing dust grains were vaporized and their atoms homogenized with the solar nebula gas during early stages of solar system formation, a small fraction of presolar dust survived in the matrix of primitive meteorites and in interplanetary dust particles (IDPs). These grains are recognized as presolar stardust on the basis of highly unusual isotopic compositions, compared to other materials found in the Solar System. These isotopic compositions reflect the stellar gases from which they condensed and provide information about a wide array of astrophysical processes [1-3]. This talk will review the subset of known presolar grains that are O-rich, including both silicate and oxide phases.

O isotopic ratios for the known presolar O-rich grains are shown in the Figure. More than 600 presolar oxide grains (including Al_2O_3 , $(\text{Mg,Fe})(\text{Al,Cr})_2\text{O}_4$, CaAl_2O_9 , TiO_2 , and FeCr_2O_4) and more than 60 presolar silicate grains (including olivine, pyroxene and glass) have now been reported from meteorites and IDPs [4-10]. In addition to O isotopes, Mg isotopes have been measured in many grains, Ti and/or Ca isotopes in a few oxides and Si isotopes in a few silicates.

The observed isotopic signatures point to a diversity of stellar sources. The majority of grains are enriched in ^{17}O and depleted in ^{18}O , relative to Solar – a signature of H burning by the CNO cycle. Most of these grains are believed to have formed in low-mass asymptotic giant branch (AGB) stars, in agreement with astronomical estimates that AGB stars dominate the production of O rich stardust in the Galaxy [11]. The large ^{18}O depletions and high inferred $^{26}\text{Al}/^{27}\text{Al}$ ratios of a fraction of ^{17}O -rich grains ($^{18}\text{O}/^{16}\text{O} < 10^{-3}$) point to non-standard mixing in their parent stars [12]. A supernova origin is likely for a few grains, including the grains with the lowest $^{17}\text{O}/^{16}\text{O}$ and/or highest $^{18}\text{O}/^{16}\text{O}$ ratios [6, 13, 14]. The rarity of such grains indicates that supernovae did not dominate the production of O-rich dust in the interstellar medium from which the Sun formed.

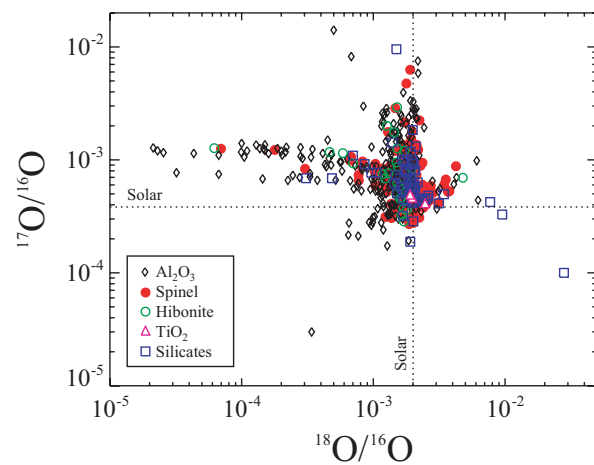
The mineralogy and microstructures of presolar grains provide information about stellar dust formation processes and help to interpret infrared spectra of dusty stars. For example, presolar Al_2O_3 is found both in the crystalline corundum structure and in an amor-

phous form [15], consistent with infrared evidence that both forms are present in some O-rich AGB stars. Both crystalline and amorphous grains have been found among the presolar silicates. However, both the ratio of crystalline to amorphous grains and the iron contents appear to be higher in the meteoritic grains compared to astronomical observations of circumstellar and interstellar silicates. The data are limited, however, and silicates are likely to be more sensitive to parent body effects than more resistant phases like Al_2O_3 .

Note that the average composition of the presolar grains is enriched in ^{17}O and depleted in ^{18}O , relative to the bulk Solar System. Since the grains probably represent a reasonably representative sample of stellar sources of O-rich dust, this indicates that most of the O in the Solar System originally was expelled from stars (primarily supernovae) in gaseous form.

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The Interstellar Heritage of Cometary Composition

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It is a generally held belief that comets represent objects that contain significant amounts of material that experienced relatively little alteration during cometary formation in the solar nebula, and that these materials subsequently suffered very little parent body alteration afterwards. If this is the case, then comets should represent a reservoir of unaltered, or only slightly altered, interstellar materials. Comparison of the volatile icy components of dense molecular clouds with the composition of cometary ices as inferred from remote observations of the gas phase species in cometary comae are consistent with this possibility; the same molecular species are seen to dominate in both. Thus, the oxygen inventory of cometary volatiles may have a very direct relationship to the oxygen contents of interstellar volatiles, with the main carriers being molecules like H₂O, CO, CO₂, and CH₃OH. Deuterium and ¹⁵N isotopic studies of IDPs suggest a similar relationship may also exist for some organic materials, although the oxygen contents of these materials are less well defined. The talk will explore some of the abundance and isotopic implications that are implied by a close genetic relationship of cometary and interstellar volatiles. The inter-relationship of interstellar and cometary O carriers in more refractory phases may be more complex, since interstellar silicates are thought to be dominated by amorphous silicates, while cometary silicates appear to contain both amorphous and crystalline silicates.

VALENCE OF Ti AND V IN FASSAITE: A RECORDER OF OXYGEN FUGACITY DURING CRYSTALLIZATION OF COARSE-GRAINED REFRACTORY INCLUSIONS. S. B. Simon¹, S. R. Sutton^{1,2}, and L. Grossman^{1,3}. ¹Dept. Geophysical Sci., 5734 S. Ellis Ave.; ²Consortium for Advanced Radiation Sources; ³Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@midway.uchicago.edu).

Introduction. Fassaite (Ti-, Al-rich clinopyroxene [1]) is a major phase in Type B (pyroxene-rich), coarse-grained refractory inclusions, which are found in CV3 carbonaceous chondrites. Both Ti and V are compatible in this phase during fractional crystallization of inclusion melts, and both have two valence states that are stable at the oxygen fugacity of the solar nebula, ~ 7 log units below the iron-wüstite buffer. This makes fassaite a potential recorder of f_{O_2} that can tell us whether inclusions crystallized in a solar gas. The Ti^{3+}/Ti^{4+} ratio of fassaite can be calculated from electron probe (EMP) analyses assuming stoichiometry [2] and it can be measured directly by X-ray absorption near edge structure (XANES) spectroscopy. Measurement of V^{2+}/V^{3+} ratios in fassaite requires XANES.

Typically V_2O_3 , Sc_2O_3 and total Ti oxides ($TiO_2 + Ti_2O_3$) decrease from core to rim in Type B fassaite [3]. The Ti^{3+}/Ti^{4+} ratio commonly decreases from core to rim in fassaite in Type B1 (having a melilite-rich mantle) inclusions but not in fassaite in Type B2 (no mantle) inclusions. Also, Type B1 fassaites commonly exhibit sharp increases, or “spikes”, in their Ti and V contents and their Ti^{3+}/Ti^{4+} ratios but not in Sc or rare earth element contents [4], which seems to rule out a simple change in crystallization assemblage, such as incoming of anorthite, as the cause of the spikes. As the only affected elements are the two with multiple valence states, a redox change is suggested. To investigate this feature we have measured the Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios in fassaite in a Type B1 and a Type B2 inclusion from Allende.

Methods. Major element zoning and Ti oxidation state were documented by EMP, and abundances and valence states of Ti and V were determined by XANES. As in [5], with a 5 μm X-ray beam, XANES spectra were measured over the V K pre-edge peak (~ 5468 eV) from 5450 to 5500, with additional normalization measurements at 5600 eV. Analogous measurements were made over the Ti K pre-edge peak, at 4969 eV. By comparing the spectra to those for pure oxidation state standards, we determined oxidation states for each analysis spot, reported as values between 3 and 4 for Ti and between 2 and 3 for V.

Results. EMP and XANES traverses were conducted across two spikes in TS34 (B1) and across

two grains in TS21 (B2). XANES results agree with EMP data, which show sharp increases in Ti (e. g., in one grain in TS34, from 3.57 to 5.10 wt%) and V (0.03 to 0.12 wt%) oxide contents and in Ti^{3+}/Ti^{4+} at the spike. In that grain, the Ti oxidation state drops from a pre-spike value of 3.54 ± 0.05 (i.e., $Ti^{3+} \approx Ti^{4+}$) to 3.14 ± 0.11 ($Ti^{3+} \gg Ti^{4+}$). Surprisingly, across the same spike, we did not detect a change in V valence, with measurements of 2.51 ± 0.03 pre-spike and 2.49 ± 0.08 at the spike. In Type B2 inclusions, fassaite Ti^{3+}/Ti^{4+} ratios are within the range of those of Type B1 fassaites, and the V valence in two B2 fassaite crystals we analyzed averages 2.40 ± 0.09 and 2.52 ± 0.09 , within error of the results for the two B1 grains, 2.39 ± 0.08 and 2.42 ± 0.10 . These results are clear evidence for the presence of V^{2+} in both Type B1s and B2s, with $V^{2+} \approx V^{3+}$.

Discussion. The measured Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios are consistent with crystallization from a liquid in equilibrium with a gas of solar composition. Fassaite favors Ti^{3+} over Ti^{4+} [2] so fractional crystallization can cause the Ti^{3+}/Ti^{4+} ratio to decrease from core to rim in a crystal, but only if the residual liquid is isolated from the nebular gas and prevented from reequilibrating. This seems to have occurred in the B1s but not in the B2s. Many late B1 liquids had low Ti^{3+}/Ti^{4+} but were exposed to the nebular gas before completion of crystallization, causing reequilibration and sharp increases in Ti^{3+}/Ti^{4+} of crystallizing pyroxene. The V^{2+}/V^{3+} ratio of the residual liquid should have behaved similarly, in which case the spikes in V contents would imply that V^{2+} is more compatible in fassaite than V^{3+} . This scenario is feasible, as V^{2+} can enter the pyroxene M1 or M2 site and does not require a coupled substitution for charge balance, but experiments are needed for confirmation. If $D_{V^{2+}} > D_{V^{3+}}$, it is unclear why a change in the V oxidation state at the concentration spike was not detected. One possibility is that the V valence in the fassaite reequilibrated by subsolidus charge transfer with relatively abundant Ti.

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OXYGEN IN THE DIFFUSE INTERSTELLAR MEDIUM. Theodore P. Snow and Adam G. Jensen, University of Colorado (CASA - University of Colorado, 389 UCB, Boulder, CO 80309-0389; tsnow@casa.colorado.edu).

Oxygen is observed in the interstellar medium in lines of sight sufficient optically thin to allow measurements of ultraviolet absorption lines of the neutral atom, O I, which is the dominant ionization stage in diffuse and dense clouds. Starting with the *Copernicus* satellite in the 1970s, there is now an extensive archive of O I measurements, for clouds with visual dust extinctions ranging from 0 to 5 magnitudes. The *Cosmic Origins Spectrograph*, to be installed aboard the Hubble Space Telescope in 2007, will extend this range to $A_v = 10$ magnitudes or more.

In this paper we describe the observations of UV O I lines and summarize the

results to date. We address the gas-phase abundance of oxygen in the diffuse ISM and its dependence on local physical conditions; the question of the standard oxygen abundance to be used in assessing the depletion of oxygen from the gas onto dust grains; and the constraints on the oxygen content of the dust. We will discuss the question of whether the fraction of oxygen stored in interstellar dust increases with increasing cloud density, and whether enhanced depletion onto dust might occur during the early stages of star formation. We conclude with a summary of the important remaining issues regarding interstellar oxygen and its relationship to oxygen in the solar system.

Oxygen and Other Volatiles in Jupiter: Insights into the Early Solar System.

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Workshop on Oxygen in the Earliest Solar System. 19–22 September 2005, Gatlinburg TN.

Introduction

Water is the primary oxygen-bearing species in Jupiter's atmosphere, but its bulk abundance in the planet has probably not yet been measured. Oxygen and the other volatiles were brought to Jupiter's atmosphere via planetesimal accretion, so these elements provide insight into the properties of the planetesimal diet consumed by the young Jupiter.

Measurements of Jupiter's volatiles

The Galileo Probe Mass Spectrometer (GPMS) provided the deepest available measurement of the water mixing ratio in Jupiter [1,2]. Water mixing ratios are shown in Fig. 1 for the 10–12 bar and 17–21 bar ranges. For a hypothetical well-mixed Jupiter atmosphere with a solar abundance of H₂O, the cloud base would be near 5 bar, and a uniform mixing ratio would be expected below that level. However, the probe descended into a 5- μ m hotspot and measured volatile abundances depleted by local meteorological effects. The condensable gases (NH₃, H₂S, and H₂O) were seen to increase with depth, and it is impossible to determine based on the available data whether the deep H₂O mixing ratio was sampled. Examples of attempts to infer the deep oxygen abundance by a wave propagation model [3], CO measurements [4], or infrared spectroscopic water retrievals [5] have not been conclusive.

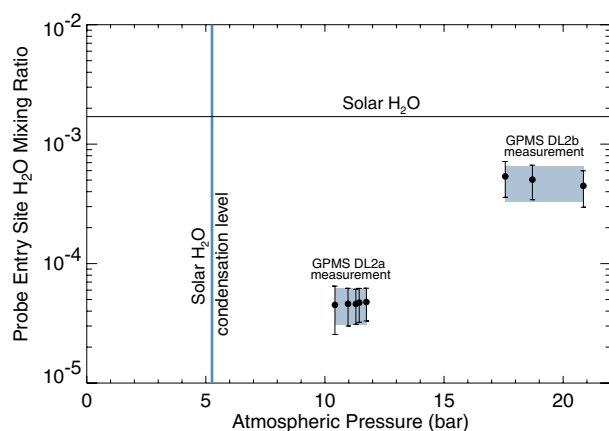


Figure 1. The GPMS measurements of water near 11 and 20 bar [2] in the probe entry site.

The GPMS measurements of CH₄, NH₃, and H₂S (Fig. 2) were successful at determining bulk abundances of these species in Jupiter's atmosphere, and the CH₄ and NH₃ results are in good agreement with independent

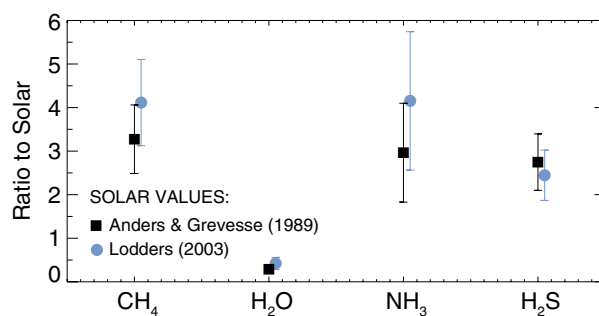


Figure 2. Ratios of GPMS measurements of volatile gases [2] to protosolar abundances [6,7].

spectroscopic determinations [8,9,10], while the H₂S mixing ratio was uniquely measured by the GPMS.

Implications for giant planet formation

The enriched volatiles (Fig. 2) and noble gases in Jupiter were delivered by accreted planetesimals, with candidate compositions such as amorphous ice formed at $T \leq 30$ K [11], crystalline ice with volatiles trapped in clathrates [12,13], and “tarry” carbonaceous material [14]. Both icy planetesimal scenarios require large water enrichments, whereas Lodders [14] cannot place any constraints on water or nitrogen abundances, so an accurate determination of Jupiter's oxygen abundance is needed to distinguish between candidate planetesimal compositions.

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H₂O TRANSPORT AND Δ¹⁷O IN THE SOLAR NEBULA. E.D. Young¹, ¹Department of Earth and Space Sciences and Institute of Geophysics and Planetary Physics, University of California Los Angeles, 2676 Geology Building, Los Angeles, CA 90095 (eyoung@ess.ucla.edu).

Introduction: Recent theoretical studies suggest that the inner solar nebula became enriched in H₂O with time by inward transport and sublimation of water ice [1]. At least two proposed means for producing non-mass dependent oxygen isotope effects (Δ¹⁷O ≠ 0) in the nebula, photolysis of CO at disk surfaces accompanied by shielding of FUV light by CO and H₂ [2, 3] and a grain surface-mediated chemical η effect [4], suggest a direct link between [H₂O] and Δ¹⁷O. The link provides testable predictions.

Oxygen fugacity: A rise in the number density of H₂O in the vapor phase should have resulted in a general correlation between the fugacity of oxygen (calculated fO₂ is a proxy for [O]) and Δ¹⁷O in inner solar system materials. To the extent that CAIs, generally the most ¹⁶O-rich objects in the solar system, are also among the most reduced rocks [5], the prediction appears to be born out by the data. The [O] associated with changing Δ¹⁷O has clear implications for the η effect [4] as well as for the purported links with [H₂O] [2].

Total gas Δ¹⁷O: In order to constrain the original isotopic composition of the inner solar system gas one needs an estimate of the fraction of oxygen that was bound as rock-forming dust relative to the fraction of oxygen that was in the gas. The relevant steady-state mass-balance equation is

$$\begin{aligned} \delta_{\text{gas}}^f - \delta_{\text{gas}}^o &= \frac{x_{\text{rx}}}{1 - x_{\text{rx}}} (\delta_{\text{rx}}^o - \delta_{\text{rx}}^f) \\ &= F (\delta_{\text{rx}}^o - \delta_{\text{rx}}^f) \end{aligned} \quad (1)$$

where ^o refers to the initial condition, ^f refers to the final condition, δ is the oxygen isotope ratio of interest in per mil, x_{rx} is the fraction of oxygen bound to rock-forming elements, and x_{gas} is the oxygen fraction in the gas phase. With revised solar abundances F = 0.36. Taking δ_{rx}^o = -50 ‰ for both δ¹⁷O and δ¹⁸O [6], and assuming the oxygen isotopic compositions of Earth, Moon, Mars, and Vesta (HEDs) are representative of the vast majority of rocky material in the solar system (Δ¹⁷O ≤ |0.3| ‰), the minimum initial gas Δ¹⁷O is +8.6 ‰, as shown previously [7]; the minimum value for total gas Δ¹⁷O of ~ 9 ‰ is a robust result.

Water Δ¹⁷O: The calculation can be extended to provide a constraint on the isotopic composition of H₂O. Thermodynamics and kinetics conspire to assure

that the most stable oxygen-bearing species in the nebula was CO so that the nominal nebular H₂O/CO was 0.5. The oxygen mass-balance expression for the gas composed of CO and H₂O is then

$$\delta_{\text{gas}} = f_{\text{H}_2\text{O}} \delta_{\text{H}_2\text{O}}^o + (1 - f_{\text{H}_2\text{O}}) \delta_{\text{CO}}^o \quad (2)$$

where f_{H₂O} refers to the mixing ratio (oxygen fraction) for water and δ_{gas} is the oxygen isotopic composition of the gas in bulk (allowing for isotopic exchange between CO and H₂O at high T). The water Δ¹⁷O value implied by equation (2) is +41 ‰ (for δ_{CO}^o = -24 ‰). This is a maximum based on the solar f_{H₂O}.

Transport: H₂O/CO in the inner solar nebula should have risen above the baseline value of 0.5 by virtue of transport of H₂O ices inwards through the snowline. A simple equation that captures the essence of this process is

$$\Delta^{17}(t) \sim \Delta_{t=0}^{17} \exp(-kt) + \frac{J}{k} (1 - \exp(-kt)) \quad (3)$$

where k is the rate coefficient for net loss of ¹⁷O and ¹⁸O to condensed phases and J is the rate of advective addition of ¹⁷O and ¹⁸O. Δ¹⁷O will reach steady state according to (4) on a time scale 4τ = 4/k. Estimates of k suggest τ on the order of years. To the extent that J is significant [1], we should expect that Δ¹⁷O of H₂O was ≤ 41 ‰. We should expect further that changes in Δ¹⁷O with time in the inner nebula resulted from variations in J.

Conclusion: High Δ¹⁷O of nebular H₂O is a robust constraint on models for the oxygen isotopic evolution of the solar protoplanetary disk. Reaction networks are being constructed to test models for variable Δ¹⁷O against the water Δ¹⁷O and correlations with fO₂ implied by the meteorite data. Preservation of the slope-1 line in δ¹⁷O vs. δ¹⁸O space suggests that oxygen isotope exchange at high temperature was an important part of the nebular reaction network.

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OXYGEN ISOTOPIC CHARACTERISTICS OF REFRACTORY INCLUSIONS. H. Yurimoto¹, S. Itoh¹ and A. N. Krot², ¹Division of Earth & Planetary Sciences, Hokkaido University, Sapporo 060-0810, Japan (yuri@ep.sci.hokudai.ac.jp), ²Hawai'i Institute of Geophysics & Planetology, University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA.

Introduction: Refractory inclusions, which consist of Ca-Al-rich inclusions (CAIs) and amoeboid olivine aggregates (AOAs), have compositions corresponding to high temperature condensates from the solar composition gas [1]. Study of refractory inclusions started from CV3 chondrites, especially in Allende meteorite. Because the oldest age in the solar system has been determined in CAIs [2] and Al-Mg systematics suggest that this age also applied to other refractory inclusions [3,4,5], refractory inclusions should be key materials to study of origin of the solar system. In 1973, oxygen isotopic anomalies of ¹⁶O-enrichment relative to the Earth have been discovered in refractory inclusions, indicating at least two oxygen isotopic reservoirs existed in the solar nebula [6]. Because oxygen is the third most abundant element in the solar system and the most abundant element of solid planets, study of the oxygen isotopic reservoirs is essential to understand material evolution in the solar system. Here we review oxygen isotopic characteristics among refractory inclusions and discuss possible situations of oxygen isotopic reservoirs in the solar nebula.

Classification of refractory inclusions: The CAIs are petrographically classified by mineral sizes and the texture. The CAIs whose minerals and textures are enough to be easily studied (>~50μm in size) with an optical microscope are named coarse-grained, and those that are too fine-grained to do so are named fine-grained [7]. Although the boundary between these two categories is not sharp, these nomenclatures are widely used. Coarse-grained inclusions are common in CV chondrites but are rare in other chondrite group. On the other hand, fine-grained CAIs are commonly distributed in all chondrite groups. Mineral sizes in AOAs are equivalent to those in fine-grained CAIs and the mineral assemblages continuously changes from fine-grained CAIs to AOAs. AOAs are also commonly distributed in all chondrite groups with higher abundance than fine-grained CAIs. Aqueous alteration in chondrite parent bodies easily affects fine-grained CAIs and AOAs, and disturbs their textures and mineral assemblages [8]. In this study our discussion focus to primary minerals prior to the aqueous alteration.

Oxygen isotopes of fine-grained CAIs and AOAs are uniformly enriched in ¹⁶O (~5% excesses)

for many chondrite groups [8,9,10,11,12]. The exception is only observed in CB, CR and CH chondrites. Oxygen isotopic compositions of fine-grained CAIs in CB chondrites are uniformly depleted in ¹⁶O [13]. Those in CH and CR chondrites distribute from ¹⁶O-rich to ¹⁶O-poor, but individual inclusion has uniform value [14,15]. These characteristics indicate that most fine-grained CAIs and AOAs formed in ¹⁶O-rich nebular environment but some was in ¹⁶O-poor environment. Evidence of uniform oxygen isotopic composition for each inclusion suggests that they had simple thermal histories.

Coarse-grained CAIs were crystallized from Ca-Al-rich liquid droplets. Oxygen isotopes of coarse-grained CAIs heterogeneously distributes among minerals. The minerals at early- and late-crystallization stages are enriched in ¹⁶O (~5% excesses), whereas those at intermediate crystallization stages are depleted in ¹⁶O [16]. The heterogeneous oxygen isotopic characteristics indicate complex thermal history and different oxygen isotopic environments for the formation. Recent isotope point-analyses and isotope imaging for micro-area reveal that the ¹⁶O-poor minerals formed at later heating stage in ¹⁶O-poor nebular environment [16,17,18] and close genetic relation between CAI-rim and fine-grained inclusions [19].

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