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EXTREME OXYGEN ISOTOPE RATIOS IN SILICA-RICH GRAINS FROM CARBONACEOUS CHONDRITES : A MULTI-APPROACH STUDY.

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Introduction: Extreme isotopic variations (up to several orders of magnitude) in minute meteoritic grains are usually attributed to stellar nucleosynthesis before the birth of the solar systeme [e.g. 1]. Micrometer-sized silica-rich grains with ^{17}O and ^{18}O excesses up to a factor 200 were recently discovered emebedded in the refractory organics of the Murchison meteorite [2]. These grains were found to account for almost 1 ppm of the host meteorite, as much as all other presolar oxide grains (with the exception of silicates) [3-5]. Contrary to typical presolar grains, oxygen in these silica-rich grains was found to be a mixing between only two reservoirs : an extreme anomalous oxygen reservoir and a solar or close to solar reservoir. Similar extreme compositions were observed in an unusual post-asymptotic-giant-branch star [6] but conventional AGB star nucleosynthesis models fail to explain these observations. Because all grains must have come from a single source, assuming they are presolar require that the young Sun encountered an unusual post-AGB star. By contrast nucleosynthesis upon irradiation of the circumsolar gas by particles with characteristics of impulsive flares produce the expected composition. In order to establish whether these grains are presolar and come from a single unusual star or if they were formed in the vicinity of the young Sun by the selective trapping of an irradiated gas, we investigated several tracers: (1) D/H with C/H ratios and $^{15}N/^{14}N$ with C/N ratios were mapped by IMS 1270 ion probe to search for large isotopic anomalies, (2) an ion probe depth profile for O isotopes was done to investigate possible heterogeneities at the 10-20 nm scale, (3) a sample of insoluble organic matter from Orgueil was studied and finally (4) we started a mineralogical study of the grains by transmission electron mircoscopy.

Results: *O isotopcs mapping in the insoluble organic matter from Orgueil*. No anomalous silica-rich grains were found in Orgueil. With the extraction yield and the mapped area, the abundance of these grains was found to be less than ~50 ppb, at least a factor of 10 less than in Murchison.

O isotopes depth profiling. Depth profiling over complete erosion of two grains reveal the absence of sharp isotopic contrast indicative of subgrains or isotopic heterogeneities. By contrast both grains show a smooth profile with lower isotopic ratios at the beginning of the analysis and at the end. The final decrease can easily be attributed to the erosion of the grains and the rapid increase at the beginning suggests that a significant amount of contamination was removed.

Nitrogen isotopic mapping. No significant isotopic anomaly was found (within a factor 2). The low ion yields and the similarity with the surrounding organics suggests that these elements are dominated by contamination from the meteoritic IOM. If present isotopic anomalies must be small and at low concentrations.

Hydrogen isotopes. Again H isotopes were found to be similar to the surrounding organic material but C/H ratios in the grains were lower by a factor 10 indicative of an hydrated component in the grains. Whether this component is truly indigenous or results from terrestrial hydration still remains to be determined.

TEM mineralogy. Two residual grains were sectioned using a Focused Ion Beam and examined by TEM. Preliminary results indicates that these grains are amorphous silica. A more extensive study is required to better understand their formation.

Conclusions: More detailed results will be presented at the meeting, but these preliminary observations suggests that, as already observed for Si and Mg [2,7], the silica-rich grains lack exotic isotopic compositions of H and N that would have traced either a presolar origin or an irradiation process. Together with the non-detection of the grains in Orgueil, a meteorite rich in presolar grains but depleted in high temperature solar system components (chondrules, Ca-Al-rich inclusions), this suggests that the selective trapping of an anomalous O reservoir by condensation in the early solar system is the most likely origin for the O isotopic anomalies.

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FIRST EVIDENCE FOR CO-EXISTING ^{16}O-POOR AND ^{16}O-RICH GASES IN THE EARLY SOLAR NEBULA INFERRED FROM A COMPOUND CA-AL-RICH INCLUSION FROM EFREMOVKA.

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Introduction: Compact igneous Ca-Al-rich inclusions (CAIs) in CV chondrites show an oxygen isotope dichotomy: spinel and pyroxene are enriched in ^{16}O, whereas melilite and anorthite are usually not ^{16}O [1]. Recently it was proposed that the ^{16}O-rich composition was the initial composition of the nebular gas [2,3]. However, the origin of the dichotomy is still not well understood. Several mechanisms have been studied involving a late O isotopic exchange with a ^{16}O-poor reservoir during (1) partial melting events [4], (2) solid-state diffusion [5], or (3) parent-body alteration [6] but no single model succeeded in explaining all, observations. Because they have recorded different CAI-forming events, compound inclusions are of great interest and might help in deciphering the origin of these O isotopic variations. E49 is a compound CAI from the reduced CV3 chondrite Efremovka that has previously been studied for mineralogy, petrology, Rare Earth Elements (REE) and Mg isotopes [7]. Both mineralogy and REE patterns indicate that E49 is made of two different lithological units, hereafter called the host and the xenolith, respectively. The host is a fragment of a compact type A inclusion, rimmed by a complete Wark-Lovering sequence (WLR), and consists almost exclusively of melilite, with minor isolated spinel and perovskite grains. The xenolith is mostly composed of spinel and Al-Ti-rich pyroxene, with some melilite and minor anorthite. Fractionated REE patterns in melilite from the host and the xenolith indicate crystallisation from a melt. Melilite from both the host and the xenolith shows ^{26}Mg excesses attributable to the decay of ^{26}Al. The data fall on a single isochron, with an initial ^{26}Al/^{27}Al of 4.1×10^{-5} [7], indicating formation early in the history of the solar system. Oxygen isotopes were measured with the IMS 1270 ion microprobe at CRPG, Nancy, in the two inclusions and the WLR, with an emphasis on melilite.

Results: As typically observed in igneous CAIs, spinel and pyroxene are systematically enriched in ^{16}O (Δ^{17}O < -19 ‰) with one exception in pyroxene. Melilite in the xenolith is rich in ^{16}O with minor variations (Δ^{17}O < -15‰) and has an intermediate composition in the WLR (Δ^{17}O ~ -12‰). In contrast, the oxygen isotopic composition of melilite in the host covers a large range between the ^{16}O-rich spinel and the terrestrial mass fractionation line (-18‰ <

Δ^{17}O < +3‰). These variations are correlated with the location within the inclusion. Immediately below the WLR, melilite is ^{16}O-rich, but the ^{16}O-excess decreases progressively toward the center of the inclusion. This variation is correlated with the Åk content of the melilite : ^{16}O-rich melilite below the WLR is nearly pure gehlenite (down to $Åk_1$) and ^{16}O-poor inner melilite is typically $Åk_{20-30}$. This concentric chemical zonation is typically that observed in melilite from type B1 inclusions [8] and is opposite to that expected from isotopic exchange in a ^{16}O-poor reservoir after CAI crystallisation. This suggests that oxygen isotope exchange took place during crystallisation of melilite from a melt droplet. Two mechanisms can be proposed. (1) The CAI liquid was initially ^{16}O-rich and exchanged O in a ^{16}O-poor reservoir during fractional crystallisation that started from the exterior such as in type B1 CAI mantle [8]. This hypothesis requires diffusion of O from the gas through the compact layer of already crystallised melilite, possibly along melt-wetted grain-boundaries. (2) The host CAI was molten (or partially molten) in a ^{16}O-poor gas but its outer portion later underwent exchange of oxygen in a ^{16}O-rich reservoir. Both hypotheses require rapid transport in nebular regions with different oxygen isotopic compositions. The ^{16}O-rich xenolith was injected into the host melt either in the ^{16}O-poor or ^{16}O-rich reservoir before the onset of fractional crystallization that resulted in the chemical zoning of the host CAI.

Conclusion: Melilite in E49 formed when ^{26}Al was alive. Assuming an initial ^{26}Al/^{27}Al $= 7 \times 10^{-5}$ [9], both a CAI-like ^{16}O-rich and a planetary-like ^{16}O-poor nebular regions were co-existing 5×10^5 years after the birth of our solar system. Oxygen isotopic changes in the protosolar nebula must thus have taken place in less than half a million years.

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THE REVISED SOLAR ABUNDANCE OF OXYGEN. Carlos Allende Prieto and David L. Lambert, University of Texas, Austin, TX, 78712. callende,dll@astro.as.utexas.edu.

Introduction: Measurements of chemical abundances in the solar photosphere are regularly revised, but tend to change very slowly, in particular for light elements. These changes are usually related to improvements in the available observational material, or the modeling. A few years back, it became apparent that the [OI] line at 630.0 nm, one of the primary indicators of the solar oxygen abundance, was significantly affected by an overlapping Ni I transition. This realization was possible by the use of new 3-D hydrodynamical model atmospheres. Classical 1-D hydrostatic models predict perfectly symmetric line profiles centered at rest wavelengths. Observed line profiles, in turn, are asymmetric and blue-shifted due to convective motions (solar granulation). State-of-the-art solar hydrodynamical models reproduce the observed line profiles with exquisite detail. The observed [OI] feature was suspiciously symmetric and not as blue-shifted as expected, revealing the presence of a contaminating transition.

The forbidden line: The [OI] at 630.0 nm connects the lowest states of the OI atom ($2p\ ^3P$ and $2p\ ^1D$), separated by ~ 2 eV. These levels are thermalized in the solar photosphere and the lines form very close to Local Thermodynamic Equilibrium (LTE) conditions. Line formation calculations in a 3-D hydrodynamical model atmosphere led to a derived abundance 18 % lower than determined from classical static models. A larger correction (see Fig. 1), was due to a blending Ni I feature, further reducing the final abundance estimate by 30 % to $\log N(O)/N(H) + 12 = 8.69 \pm 0.05$ (Allende Prieto, Lambert & Asplund 2001).

Permitted atomic and molecular transitions: An extension of the analysis based on 3-D model atmospheres to a second forbidden line, permitted O I transitions, and OH molecular lines confirmed the result from the [OI] line at 630.0 nm. Permitted O I lines are formed far from LTE, and therefore detailed 3-D non-LTE calculations are necessary. 3-D effects are significant for molecular species in the presence of convection at solar temperatures, as they tend to concentrate in the cool intergranular lanes. Considering all the indicators, the derived mean value is $\log N(O)/N(H) + 12 = 8.66 \pm 0.05$ (Asplund et al. 2004). Further support for the revised value was obtained from center-to-limb observations of the OI triplet at 777 nm (Allende Prieto, Asplund & Fabiani Bendicho 2004).

Then, carbon: A slightly smaller correction to the carbon abundance, albeit for somewhat different reasons, was first discovered from an analysis of the [CI] line at 872.7 nm (Allende Prieto, Lambert & Asplund 2002), and later confirmed by a study of C I, CH, and C_2 transitions (Asplund et al. 2005). Compared to previously adopted values, the photospheric abundance was reduced by ~ 30 % to $\log N(O)/N(H) + 12 = 8.39 \pm 0.05$.

Implications: The revised abundances change the overall solar metallicity (mass fraction of elements heavier than helium) from $Z = 0.017$ to $Z = 0.013$. The new oxygen abundance is in good agreement with measurements in the local interstellar medium for realistic gas-to-dust ratios and the abundances derived for nearby B-type stars, solving a long-standing conundrum. In addition, the reduced Z, has introduced significant problems with helioseismic measurements (Bahcall, Serenelli & Basu 2005). The solution may lie on the opacity calculations for the temperatures relevant at the base of the convection zone (Badnell et al. 2005), or an unexpected value for the Ne abundance in the solar envelope (Antia & Basu 2005). Errors in the surface solar chemical composition dominate the uncertainties in the predicted solar neutrino fluxes (Bahcall & Serenelli 2005).
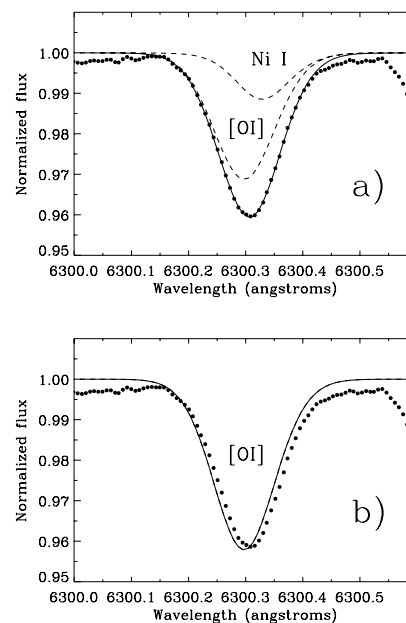

Figure 1: (a) Comparison between the observed (filled circles) and synthetic (solid line) profiles after the χ^2 minimization. The individual calculations of the oxygen and nickel lines are also shown as dashed lines. (b) Best fit, assuming the observed feature is entirely produced by the oxygen forbidden line.

OXYGEN ISOTOPES IN THE VOLATILE MATERIAL OF COMETS

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The material of comets represents the most pristine material to be found in the solar system. Studying the composition of this material can help to understand the history of the solar system formation and can connect the present day composition of the solar system with the composition of the molecular cloud from which it emerged. Isotopic ratios are one of the most important clues for the chemical and physical processing of the material since its formation.

In the talk we will review the measurements of the oxygen isotopic ratio in the volatile material of comets. We will discuss the possible fractionation processes in the formation of the molecules. Because most measurements have been and will also in the future be made in the coma of comets it is important also to know possible fractionation processes in the nucleus, during sublimation and in the coma.

Rosetta on its way to 67P/Churyumov-Gerasimenko will be the first spacecraft which can analyze oxygen isotopes in situ in different molecules (e.g. CO, CO2) on a cometary surface [1]. It will also measure deuterium, oxygen isotopes, and other isotopes in different molecules of the cometary coma [2]. The capabilities of the corresponding instruments will be discussed.

For the correct interpretation of the data we will need relevant laboratory measurements of reaction rates and processes. A list of such measurements will be presented

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High Energy Radiation Fields Impinging the Surfaces of Protoplanetary Disks

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In recent years there has been new information gleaned on the shape and strength of the far-ultraviolet (FUV) radiation field that characterizes the early stages of proto-stellar evolution.   I will present these new observations and examine the nature of this field and show that there is clear evidence for a dominant flux in hydrogen Lyman alpha that induces molecular hydrogen fluorescence and an additional source of FUV continuum that may be induced by stellar X-rays. Energetic radiation and an evolving dust opacity (due to coagulation and sedimentation) are key determinants of the disk chemical evolution.   I will show how these various factors influence the chemistry, with a focus on water, a key oxygen bearing species.

STATUS OF OXYGEN ISOTOPE MEASUREMENTS FROM GENESIS SOLAR WIND SAMPLES. D. S. Burnett and the Genesis Science Team, Division of Geological and Planetary Sciences, 100-23, California Institute of Technology, Pasadena, CA 91125 (burnett@gps.caltech.edu).

Background The Genesis Discovery Mission exposed pure materials to the solar wind at the L1 Lagrangian Point for 27 months from December 2001 through March 2004 [1]. In mission planning, we identified 19 prioritized "measurement objectives", i.e., specific studies related to various aspects of solar abundances. The first 6 of these were isotopic studies and the highest priority was assigned to the measurement of the oxygen isotopic composition.

In addition to passive collectors, LANL science team members designed an ion telescope ("Concentrator"), which focused the solar wind by about a factor of 20 onto a 6 cm diameter "target" [2,3]. The Concentrator was built essentially entirely to support oxygen isotopic analysis because of the ubiquity of oxygen as a contaminant in potential collector materials, and as background in potential analytical schemes.

A parachute deployment failure caused the crash of the Sample Return Capsule upon return to Earth. This has caused damage and contamination of the collector materials. However, we have recovered sufficient quantities of materials to meet our science objectives. We have not yet demonstrated that we can adequately decontaminate the samples for all analyses, but a wide variety of promising approaches are being tested. We are cautiously optimistic that we can accomplish most of our measurement objectives.

Materials for Oxygen Isotopic Analysis. The Concentrator target is divided into four 3 cm radius quadrants. Two of the quadrants are epitaxially grown single crystal SiC (CREE, Inc). One quadrant is polycrystalline CVD diamond made from 99% isotopically pure ^{13}C (Raytheon, Inc.). The final quadrant is an amorphous diamond-like carbon layer on silicon prepared by T. Friedmann (Sandia Labs). All three materials have been shown to be sufficiently pure. Among the passive collectors, float zone silicon is sufficiently pure for oxygen isotope analysis.

Status. The Concentrator target was recovered intact after the crash with 3 of the 4 targets in place. The Sandia quadrant was broken into several pieces, but these have been recovered. Visual inspection indicates no major surface damage.

Analysis Plans. A Genesis Allocation Committee is in place (A. M. Davis, Chair) and sample request guidelines are available (judith.h.allton@jsc.nasa.gov). Samples are available to all qualified analysts.

A major advantage of sample return missions is that important measurements can be replicated using different analytical approaches. In this spirit, the Project has supported 3 analytical approaches and selected appropriate materials: (a) high energy SIMS analysis (K. D. McKeegan, UCLA); (b) laser ablation of the ^{13}C CVD diamond with analysis by static source gas mass spectrometry as CO (I. Franchi, Open U.); and (c) laser fluorination with analysis as O_2 (M. H. Thiemens, UCSD).

Precision. The required precision for oxygen isotopic analysis was initially set as $\pm$ 1 ‰, 2 σ for both ^{17}O and ^{18}O. Eventually, a measurement to at least this precision is highly desirable. However, since important differentiation between present models for the origins of oxygen isotopic variations in planetary materials can be made with lower precision than this, the Allocation Committee is prepared to support a request for an initial measurement with lower precision than 1 ‰.

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OXYGEN ISOTOPES OF SECONDARY PHASES IN UNEQUILIBRATED CHONDRITES: IMPLICATION FOR THE FLUIDS/ICES IN THE NEBULA AND ASTEROIDS. B.-G. Choi[1], M. Cosarinsky[2] and J. T. Wasson[2], [1] Earth Science Education, Seoul National University, Seoul 151-748 KOREA (bchoi@snu.ac.kr), [2] Earth and Space Sciences, University of California, Los Angeles, CA90095-1567, USA.

Chondrites are mixtures of materials that formed at many different times, places and conditions in the solar nebula and asteroids. Thus the O isotope heterogeneity recorded in them must be interpreted as a result of such events. The O isotopes of high-temperature solar nebular gas are recorded in refractory phases in chondrites, such as pristine CAIs and chondrules. However, many of them, even in the most primitive chondrites, experienced various degrees of alteration in the nebula or, more significantly, in their parent bodies. Therefore, the secondary signature must be extracted to sort out the primary oxygen. The secondary oxygen can be measured or estimated from secondary and altered phases. In addition, the compositions of such oxygen give the information on the nature of the fluid present in chondritic asteroids and of low-temperature nebular gas that condensed either as OH in hydrous silicates or ice in inner or outer solar system, respectively.

The $\Delta^{17}O$ values of hydroxyl in phyllosilicates [1,2], calcites [3] and magnetite [4-9] from unequilibrated chondrites are shown in Fig. 1, along with those of matrix and whole rocks [10,11].
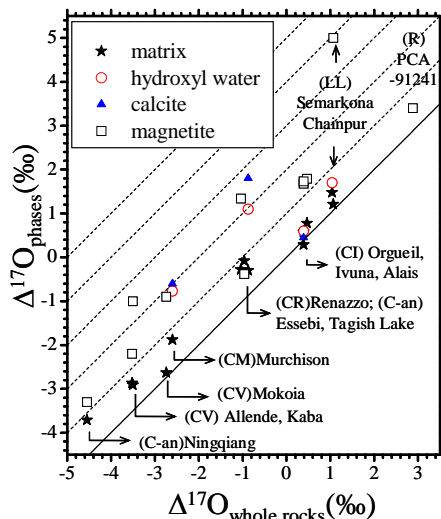
Fig. 1. A correlation diagram of the average $\Delta^{17}O$ values of secondary phases *vs.* their host chondrites. The solid line is for $\Delta^{17}O_{phases} = \Delta^{17}O_{whole\ rock}$ and the dashed lines for $\Delta^{17}O_{phases} = \Delta^{17}O_{whole\ rock} + 1, +2, +3, +4, +5$.

Some anhydrous silicates in chondrites seem to have been affected by aqueous alteration. The $\Delta^{17}O$ of melilite is about -4‰ in most carbonaceous chondrite CAIs. Efforts to account for this by exchange with the nebular gas have not been successful. It was shown that melilite in unaltered carbonaceous chondrites has

$\Delta^{17}O$ <-20‰ and suggested that melilite in altered chondrites exchanged by asteroidal alteration [12]. In CVs olivines of matrix and accretionary rims show continuous mixing between primary ^{16}O-rich and secondary ^{16}O-poor oxygen. This progressive variation correlates with FeO content [13]. In contrast, altered products, mostly Ca- and Fe-rich silicates, define a mass fractionation line with a $\Delta^{17}O$ of -3 to -2 ‰ [14].

The O isotopes of asteroidal water can be estimated by measuring OH in phyllosilicates. The $\Delta^{17}O$ values of water released by pyrolysis are up to 2‰ higher than whole rocks. It should be noted that this hydroxyl water is probably not the original water that altered chondrites, instead it is secondary after isotopic exchange with other phases during alteration.

The $\Delta^{17}O$ values of calcite are also up to 2 or 3 ‰ higher than those of whole rocks. In CMs, carbonates show variable $\Delta^{17}O$, which correlate with degree of alteration, possibly means different water/rock ratios.

In unequilibrated chondrites magnetite has the highest $\Delta^{17}O$ values, with large variations in both $\delta^{18}O$ and $\Delta^{17}O$ even in a single chondrite. Along with petrological characteristics, this imply that magnetite formed by reaction between O-free phases and fluid in closed systems. The larger the O isotopic variations and differences between magnetite and whole rocks are, the smaller the O isotopic exchange between fluid and rocks prior to magnetite formation.

In summary, (1) the $\Delta^{17}O$ values of secondary and altered phases are always larger than those of whole rocks and 'primary phases', (2) in most unequilibrated chondrites, magnetite has the highest $\Delta^{17}O$ followed by calcite and hydroxyl water. (3) The $\Delta^{17}O$ values of initial water for carbonaceous and ordinary chondrite parent asteroids were > 2 and > 7‰, respectively, and became progressively smaller during aqueous alteration, and (4) during the condensation of water the $\Delta^{17}O$ values of the nebular gas were larger than 7‰.

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ASTROPHYSICAL MODELING OF THE DISTRIBUTION OF WATER IN PROTOPLANETARY DISKS: IMPLICATIONS FOR NEBULAR REDOX CONDITIONS AND OXYGEN ISOTOPES.

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Introduction: Protoplanetary disks are evolving objects. Observations show that mass is transferred through these objects and accreted by the central star at rates up to 10^{-6} solar masses per year and decreasing over time [1]. This evolution is observed to last up to ~10 million years in some systems and results in the disks cooling and becoming less massive over time. Superimposed on this evolution will be the transport of solids and gaseous molecules by advection, diffusion, and gas drag migration. These processes will combine to change the physical and chemical structure of the disks over their lifetimes. It is in this context that we must understand how early solar system solids were processed.

Absolute and relative chronologies of chondrules and refractory inclusions in primitive chondrites provide important constraints on the duration of thermal processing of solids in our protoplanetary disk. Pb-Pb [2,3] and Al-Mg isotopic studies [5] show that CAI formation started 4567.2±0.7 Myr ago and may have lasted < 0.5 Myr; chondrule formation may have started shortly after CAIs and lasted for ~3 Myr. Although chondrules in CB chondrites formed 4562.7±0.6 Myr ago, they appear to have formed by a collision between planetary embryos after dust in the protoplanetary disk largely dissipated [6]. Based on these observations, we infer that our protoplanetary disk may have lasted ≤ 3-5 Myr.

The mineralogy and O-isotopic compositions of CAIs, AOAs, and chondrules recorded redox conditions and O-isotopic compositions of the inner solar nebula. CAIs and AOAs appear to have formed in an ^{16}O-rich nebular gas under relatively reduced conditions. In contrast, most chondrules originated in the presence of ^{16}O-por nebular gas under oxidizing conditions (chondrules in enstatite chondrites are the only exception) [e.g., 6,7]. We will discuss a physical model that can explain this meteoritic record in a way that is consistent with astronomical observations.

Model: We have recently developed a model to track how the distribution of water changes in an evolving protoplanetary disk [8]. The disk evolution is calculated using the α-viscosity model where the viscosity is assumed to be due to turbulence in the disk. This allows us to calculate how the surface density and temperature structure change over the disk lifetime.

As the disk evolves, we also track how the water distribution changes as the vapor and solids are subjected to transport, vaporization, condensation, accretion, and collisional destruction. We consider four distinct dynamic groups of nebular materials: vapor, dust, migrators, and planetesimals. Vapor and dust will be transported by diffusion, which carries them either inward or outward along concentration gradients. Migrators correspond to the meter-sized rubble in the disk that is rapidly carried inward (~1 AU/century) by gas drag. Planetesimals are larger objects (>1 km) which are massive enough to be unaffected by the gas in the disk and are immobile in our simulations.

Results: In the early stages of disk evolution, water transport is dominated by the coagulation of dust particles into meter-sized rubble that then rapidly moves inwards due to gas drag. This results in more water being carried inward across the snow line than can be removed by the advection of the disk and diffusion of water vapor. Thus the inner disk immediately inside the snow line becomes enhanced in water vapor. This inward flux continues as the water vapor is redistributed in the inner disk, resulting in a uniform enhancement of water vapor inside of the snow line, with the maximum enhancement reaching ~10×solar. These inward migrating bodies may be enriched with heavy oxygen isotopes, causing the inner disk to become increasingly ^{16}O poor over time, which is consistent with O-isotopic evolution of the inner solar nebula recorded by chondrules and refractory inclusions [6, 8-11].

Over time the influx of icy bodies from the outer disk diminishes for two reasons. The first is that as migrators form and are carried inwards over time, the outer disk becomes depleted in dust and is no longer able to readily create these fast moving objects. The second reason is that as planetesimals grow in the outer disk, it becomes more likely that the migrators would be swept up and accreted rather than surviving their transport to the inner disk. Because vapor is not being supplied to the inner disk at such a rapid rate, diffusion becomes the dominant transport mechanism. Vapor is thus carried outward where it condenses and the resulting solids are then locked up in the planetesimals in the outer disk. The concentration of vapor in the inner disk then decreases over time.

Discussion: The evolution of protoplanetary disks naturally leads to fluctuating oxidation conditions inside the snow line. The environment that forms inside the snow line is intimately tied to processes (both physical and chemical) that occur in the outer disk. We will discuss how this evolution can explain the observations of the oxidation state and O-isotopic compositions of materials in primitive meteorites.

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HISTORICAL PERSPECTIVE — THE UNIQUE ROLE OF OXYGEN IN THE EARLIEST SOLAR SYSTEM. Robert N. Clayton, Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (r-clayton@uchicago.edu).

The modern era of oxygen isotope cosmochemistry began in 1969, the year of the fall of the Allende carbonaceous chondrite, and of the first lunar sample return. The "fingerprint" or provenance applications were not known at that time, and the emphasis was on thermometry, identifying the igneous origins of differentiated achondrites and lunar rocks, the conditions of metamorphism of ordinary chondrites, and the low-temperature aqueous alteration of CI and CM chondrites. Complications arose in the attempt to use $^{18}O/^{16}O$ ratios in Allende CAIs to estimate their condensation temperature. The entire nature of the subject changed in 1973 with the accidental discovery of variations in $^{17}O/^{16}O$ that did not follow the expected mass-dependent fractionation law. It was quickly recognized that the array on a three-isotope graph represented some sort of two-component mixing line, with end-members differing primarily in their abundance of ^{16}O. The nature and origins of these reservoirs was an unsolved question for the next thirty years, in part because there were two alternative reasonable interpretations: (1) an inherited isotopic heterogeneity of the solar nebula, of nucleosynthetic origin, and (2) an isotopic heterogeneity produced *within* the nebula by a non-mass-dependent chemical reaction. A third mechanism, based on isotope-selective photolysis of carbon monoxide, was discussed in the context of molecular clouds in the astronomical literature since 1972 [1, 2], but was largely ignored by the meteoritical community. Photochemical shielding in O_2 was considered as a possible solar nebular process [3, 4], but was abandoned [5] when it was shown that the non-mass-dependent fractionation in ozone formation does not require photolysis of O_2.

Several elements (H, C, N, O, and noble gases) are strongly depleted in solid planetary bodies, so that their isotopic compositions in those bodies need not be representative of the overall solar nebula, now represented by the Sun. The solar isotopic compositions of most of these elements are unknown, but should soon be revealed through laboratory analyses of the Genesis solar wind samples. Without knowledge of the solar composition, it has been difficult to interpret isotopic analyses of these elements in meteorites and planets. One advantage of the photochemical shielding model is that it makes a specific prediction of the solar oxygen isotope composition,

and is therefore falsifiable. The same is not true for alternative models.

Three alternative versions of the self-shielding model have been proposed, differing in the astrophysical setting, which leads to large differences in gas densities, temperatures, and time-scales. All of these models predict that the mean oxygen isotopic composition of the solar nebula, and hence the present-day composition of the Sun, is quite different from that of the Earth and other inner solar system solid bodies, and is probably close to that seen in the ^{16}O-rich end of the CAI mixing line, at $\delta^{17}O = \delta^{18}O \approx$ $-50‰$. The models of Yurimoto and Kuramoto [6] and Lyons and Young [7] use photolysis of CO at low densities and low temperatures to form ^{16}O-depleted atomic oxygen, which reacts with hydrogen to form water ice, [6] in the parent molecular cloud or [7] in the outer reaches of the solar nebula. This ^{16}O-poor water reservoir subsequently reacts with solar-composition solids, in a separate process, to generate the slope-1 mixing line seen in meteorites. Time-scales for production of the ^{16}O-poor water reservoir, using ambient starlight as the source of ultraviolet radiation, are on the order of 10^5 years [6, 7]. The third model [8, 9] envisions the photochemical isotope effect and the formation of chondrules and CAIs as parts of the same process, occurring very near the growing Sun, on time-scales of seconds to days. These conditions are met in the X-wind models of Shu and others [10]. The advantage of the X-wind setting is that it unites the chemical and isotopic aspects of oxygen in the earliest solar system.

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EXPERIMENTAL CONSTRAINTS ON HIGH TEMPERATURE OXYGEN ISOTOPIC EXCHANGE AND ON MASS DEPENDENT ISOTOPIC FRACTIONATION AND REDOX CONDITIONS DURING EVAPORATION.

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Introduction: Calcium-, aluminum-rich inclusions (CAIs) in primitive meteorites provide a record of thermal and chemical processing in the early solar system. Here we review experimental measurements of self-diffusion of oxygen in minerals and of the isotopic and redox effects of high temperature evaporation.

Diffusion of Oxygen: After the discovery of ^{16}O excesses in CAIs [1], Clayton and coworkers investigated the effect in more detail by analyzing mineral separates from a number of individual CAIs [2]. In addition to defining the now well-known slope-0.95 CCAM (carbonaceous chondrite anhydrous material) line on the three-isotope oxygen plot, they made a remarkable discovery: regardless of which CAI was analyzed, different minerals cluster at different positions along the CCAM line. It is convenient at this point to introduce the quantity $\Delta^{17}O$, which provides a measure of deviation from the terrestrial mass fractionation line and is defined as $\delta^{17}O - 0.52 \times \delta^{18}O$. Spinel is quite ^{16}O-rich, with $\Delta^{17}O = -20$ ‰ and fassaitic pyroxene is nearly as ^{16}O-rich, with $\Delta^{17}O = -15$ to -20 ‰. In contrast, melilite and anorthite lie close to the terrestrial fractionation line, with $\Delta^{17}O = -6$ to -2 ‰. This result was quite striking, as crystallization of a CAI from a melt is expected to yield minerals that all have the same $\Delta^{17}O$ value. A number of explanations were proposed, among them that all minerals initially crystallized with $\Delta^{17}O \approx -20$ ‰ and were then later exchanged with another reservoir with $\Delta^{17}O \approx 0$ ‰. This required that melilite have a much faster diffusion rate for oxygen than pyroxene and spinel, but no measurements of relevant diffusion rates were available at the time.

The first reliable measurements of self-diffusion of oxygen in melilite came in 1989 [3], with the use of an ion microprobe to measure diffusion profiles in single crystals of åkermanite and gehlenite from diffusion experiments. Diffusion rates for åkermanite are about ten times faster than for gehlenite along the same crystallographic direction and in åkermanite, diffusion is about ten times faster along the *a*-axis than along the *c*-axis. The most useful set of oxygen self-diffusion coefficients were obtained by ion microprobe depth profiling in natural diopsidic pyroxenes, natural anorthite, synthetic spinel and synthetic åkermanite [4]. Models with isothermal heating or linear cooling showed that if the observed grain sizes are used for the diffusion dimensions, the observed data in CAIs were not reproduced; a better match was obtained by making the domain sizes of anorthite, pyroxene and spinel the same [4]. Partial melting and solidification provided the best fit for melilite, anorthite and spinel, but this model predicted that pyroxene would have the same isotopic composition as melilite. The failure of these simple models led to the conclusion

that processes other than diffusion and partial melting must play a role in oxygen isotopic exchange [4].

Diffusive exchange remains a possibility, as the order of increasing diffusion coefficients and $\Delta^{17}O$ in CAI minerals are: spinel, pyroxene, anorthite, melilite.

Oxygen Isotopic Effects of Evaporation: A class of CAIs with oxygen isotopic compositions off the CCAM line, the FUN (for their Fractionation and Unidentified Nuclear isotopic effects) inclusions were discovered in 1977 [5]. It seems that these CAIs may have begun with the same oxygen isotopic composition as normal CAIs, on the CCAM line with $\Delta^{17}O = -20$ ‰. They were then mass fractionated along a line parallel to the terrestrial fractionation line and subsequently partially exchanged oxygen with the same reservoir as the normal CAIs. The idea that the large isotopic fractionation effects in oxygen could be produced by high temperature evaporation was confirmed experimentally in vacuum evaporation of Mg_2SiO_4 melts [6]. Oxygen isotopes followed the predicted Rayleigh behavior for fractionation by the kinetic isotope effect, but the fractionation factor was somewhat smaller than predicted. Subsequent vacuum evaporation experiments on melts of initially chondritic composition showed similar effects [7].

Redox Effects of Evaporation: Evaporation is a kinetic process, so that equilibrium terms such as oxygen fugacity are not applicable. Nonetheless, evaporation residues can have interesting redox effects. Vacuum evaporation of rare-earth-doped chondritic melts [7] or of bulk Allende meteorite [8] produced large negative cerium anomalies in residues, suggesting highly oxidizing conditions. These anomalies are not observed in vacuum experiments run in much more reducing conditions, in low-pressure hydrogen [9]. There can also be indicators of both oxidizing and reducing conditions in the same experiment. Vacuum evaporation of REE-doped stoichiometric perovskite produced negative cerium anomalies, indicating oxidizing conditions [10], but the residue quenches to perovskite plus a titanium oxide in which about half of the titanium is trivalent and half tetravalent, indicating reducing conditions [11].

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Astronomical and Spectroscopic Perspective of Comets: Direct Detection of Oxygen-bearing Parent Volatiles at Infrared Wavelengths

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The near infrared ($\lambda \sim 2.5 - 5.0$ µm) is ideal for the study of molecules housed as ices in the nuclei of comets ("parent" volatiles), as this spectral region contains a multitude of ro-vibrational bands. Over the past decade, it has become possible to conduct direct ground-based measurements of important constituent molecules using modern long-slit array spectrometers. These instruments (NIRSPEC at Keck 2 10-m telescope and CSHELL at the NASA-IRTF 3-m telescope, both located atop Mauna Kea, HI) provide high spectral resolving power ($\lambda/\Delta\lambda \sim 2 - 3 \times 10^4$) and small pixels, thereby permitting line-by-line study of the spatial distribution of emission intensities along the slit.

Since 1996, our group has routinely measured up to ten parent molecules in comets, using CSHELL and NIRSPEC. Included are carbon monoxide (CO) and methyl alcohol (CH_3OH) in all eleven Oort cloud comets observed, and formaldehyde (H_2CO) in six of these (C/1999 H1 Lee, C/2001 LINEAR A2, C/2001 LINEAR WM1, C/2002 C1 Ikeya-Zhang, C/2002 LINEAR T7, and C/2004 Q2 Machholz). In each comet observed, we also have simultaneous direct measurements of H_2O, the most abundant ice in comets, through non-resonant fluorescent emission and/or prompt emission from OH, which we use as a proxy for the parent H_2O.

Measuring the abundances of the chemically-linked molecules CO, H_2CO, and CH_3OH in comets can provide a test of the efficiency of conversion of CO, for example through surface hydrogen addition on the icy mantles of pre-cometary grains, or by radiation processing in the dense cloud core. The conversion efficiency is expected to depend on local H-atom densities, and laboratory measurements suggest a strong dependence on temperature between ~10 and 25 K as well. Therefore, its measurement can provide information on conditions to which the grains were exposed prior to their incorporation into the nucleus.

Accurate abundance measurements require knowledge of the excitation state of molecules in the coma (i.e., knowledge of the rotational temperature, T_{rot}). We will present comparisons between modeled and observed emission intensities. These comparisons are based on two complementary approaches: (1) A correlation analysis between the observed emission spectrum containing lines spanning a range in rotational energy and the modeled spectrum convolved to the resolution of the data. The best-fit value of T_{rot} corresponds to the maximum correlation coefficient. (2) A Boltzmann (excitation) analysis, where the ratio of observed to predicted line strengths is plotted against rotational energy for states giving rise to each line. At the best-fit T_{rot}, this ratio is independent of energy (i.e., the least-squares slope is zero).

Having accurate abundances for H_2O, CO, H_2CO, and CH_3OH permits robust mixing ratios (abundances relative to H_2O) in the nucleus to be determined. Based on these, conversion efficiencies for CO will be presented for several comets in our database, and comparisons will be made with laboratory measurements.

EVOLUTION OF OXYGEN ISOTOPIC COMPOSITION AND C/O RATIO AT LATE STAGE OF PROTO-PLANETARY ACCRETION DISK. T. Fukui and K. Kuramoto, *Hokkaido University, Sapporo 060-0810, Japan, (ftakashi@ep.sci.hokudai.ac.jp)*.

Introduction: It is well known that chondrites have following chemical/isotopic features: (i) Their constituents show mass-independent fractionation of oxygen isotopic composition. In particular, CAIs have ^{16}O-rich composition, and chondrules have ^{16}O-poor one. (ii) Redox state of chondritic groups is different from each other. In addition, more reduced group tends to have higher Si/Mg ratio. This relation is well explained by inhomogeneous addition of reduced material SiC [1]. However, reduced environment (C/O > 0.95) is required for SiC formation [2]. These features imply that isotopic and chemical compositions of proto-planetary disk considerably changed with time and location. In this study, we simulate the chemical and isotopic evolution of a proto-planetary disk.

Mechanisms which control composition of disk: In a proto-planetary accretion disk, dust particles migrate inward faster than gas due to gas drag. Their migration velocities strongly depend on the mass accretion rate and the velocity ratio of dust to gas (v_{dust}/v_{gas}) increases with the decay of accretion. Volatile components in dust particles evaporate when ambient temperature exceeds their frost point. The difference in migration velocity between dust and gas causes enrichment of dust evaporants in gas phase. In this way, the composition of inner disk deviates from the original (solar) one.

Icy and organic materials play important role in changing isotopic and redox condition in the inner disk. In molecular cloud, H_2O ice is expected to be ^{16}O-poor and CO gas to be ^{16}O-rich [3]. H_2O enrichment caused by the above process would change O isotopic composition of inner disk in ^{16}O-poor direction. In a similar way, evolution of C/O ratio would change by the enrichment of H_2O ice and organic evaporants.

We perform numerical calculation to estimate the effect of these processes quantitatively and examine how the oxygen isotopic composition and C/O ratio could evolve in a proto-planetary accretion disk.

Numerical model: The concentrations of dust evaporants are described by advective-diffusive equations

$$\frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} - \frac{1}{\Sigma r}\frac{\partial}{\partial r}\left(\Sigma r D \frac{\partial c_i}{\partial r}\right) = \frac{S_i}{\Sigma}, \qquad (1)$$

where c_i is the concentration of dust species i in the disk with the gas accretion velocity v_r, the surface density Σ and the diffusion coefficient D. S_i is the source of species i due to evaporation. Our reference model assumes steady temperature and surface density profiles same as the "minimum mass" solar nebula model [4]. In this model, H_2O ice and organic material evaporate at 3, 0.3 AU from the disk center, respectively. Under these conditions, we perform numerical calculations for the case that mass accretion rate decreases from 10^{-8} to $10^{-9} M_\odot$/yr, which are typical for the late stage of proto-planetary accretion disk [5].

Results & Discussion: As the accretion rate decreases H_2O and C-bearing vapor begin to concentrate from their evaporation fronts respectively and are transported inward by gas accretion (Fig. 1A). This is caused by the increase in v_{dust}/v_{gas} with the decay of disk accretion. The H_2O enrichment in gas phase makes O isotopic composition of the disk center gradually ^{16}O-poor (Fig. 1B). Increase in $\delta^{17,18}O$ (+70 ‰) caused by these processes is large enough to explain that of meteorites (+50 ‰) relative to ^{16}O-rich CAI. C/O ratio of the disk also changes with the enrichment of H_2O and C-bearing vapor (Fig. 1C). If these evaporants are mixed in their original relative fraction, the C/O ratio will be almost kept at the solar proportion. However, water vapor which evaporate at 3 AU takes some time to be transported to the disk center. This time lag nearly equals the regidence time of inner disk given by $M_D/\dot{M}_D \sim 4 \times 10^6$ yr. When the time scale of the accretion decay is much shorter than the regidence time, the C/O ratio of the disk center will considerably change. The condition required for SiC formation would be satisfied during 1/3 of the residence time. Thus sufficient amount of SiC would be formed and possibly affect the redox state of the inner disk if they are returned to disk by some sort of material circulation.
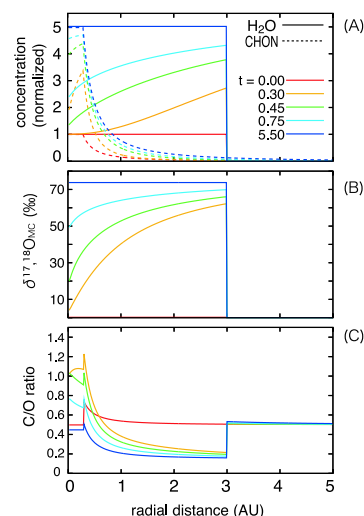
Figure 1: (A) Concentration profiles of H_2O and C-bearing vapor in gas phase. The concentrations are normalized by which achieved for unfractionated solar nebula. Time is scaled by residence time of the inner disk. In this case, we assumed accretion rate instantaneously decreases. The lower panels show the time variation of O isotopic composition (B) and C/O ratio (C). In this case, $\delta^{17,18}O$ of H_2O ice and CO gas are +100‰, −230‰, respectively. For the original mixture of gas and dust, C/O ratio is taken to be 0.5, a half of C is partitioned to CO gas and another half to be organic materials. O is partitioned into silicate, H_2O and CO to be 1:3.5:1.5.

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REDOX CONDITIONS DURING NEBULAR CONDENSATION. L. Grossman, Dept. of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637. yosi@midway.uchicago.edu.

Theory: In thermodynamic calculations of molecular equilibria in high-temperature cosmic gases, $CO_{(g)}$ is so stable that it consumes the entirety of whichever of C or O is the lower in abundance, leaving the excess of the more abundant element to form other molecules and condensates. The best estimate of the solar C/O ratio is 0.50 [1,2], yielding oxide and silicate condensates, and of the H/O ratio is 2041 [3], yielding a very reduced system. Virtually all oxygen in excess of that in $CO_{(g)}$ and condensates reacts with hydrogen to form $H_2O_{(g)}$, and virtually all of the remaining hydrogen forms $H_{2(g)}$. During condensation of a solar gas at 10^{-3} b, the P_{H_2O}/P_{H_2} ratio falls gradually from 4.27×10^{-4} at 2000K to 3.95×10^{-4} at 1417K, then more steeply to 2.66×10^{-4} at 1300K, and levels off, reaching 2.52×10^{-4} at 900K [4], yielding $\log f_{O_2}$ from IW-6.8 (1500K) to IW-7.1.

Refractory Inclusions: Near-spherical white inclusions (CAIs), up to 1 cm in diameter, are found in CV3 chondrites at the ~5% level. Type As contain ~80% melilite and 20% spinel, with accessory clinopyroxene (cpx) and perovskite, while Type Bs contain ~40% melilite, 30% cpx, 20% spinel and 10% anorthite. Type B1s have a monomineralic melilite mantle, B2s do not. The mineralogy of CAIs indicates that their precursors are high-temperature solid condensates from the solar nebula [5], and their major element chemical and isotopic compositions indicate that they underwent later melting and partial evaporation [6]. The cpx, called "fassaite", contains 25% CaO, 10-22% Al_2O_3 and 1-20% TiO_2^{tot} (all Ti calculated as TiO_2). When $TiO_2^{tot} \geq 4$ wt%, chemical formulae calculated from EMP data on the basis of 6 oxygen anions and 1.00 Ca ion show Ti^{3+}/Ti^{tot} is 0.2 to 0.8, agreeing with optical [7] and XANES [8] spectral identification of Ti^{3+}. The assemblage spinel+melilite+fassaite, the latter of the same composition as that in CAIs, was crystallized from liquids having the compositions of CAIs under controlled f_{O_2} at 1500K [9], near the CAI solidus. From compositions of the synthetic phases and a non-ideal solution model for fassaite, equilibrium constants were determined for 2 reactions involving spinel, melilite and fassaite in which $O_{2(g)}$ converts Ti^{3+} into Ti^{4+}. From these and analyses of coexisting CAI phases, it was found that the $\log f_{O_2}$ at which the fassaite crystallized was -19.5±0.8 at 1500K, and that this applies to all 3 CAI types. This translates to IW-8.1±0.8, ≥0.5 log unit below that of a solar gas.

Ti^{3+}-bearing fassaite is the only oxygen barometer that says that anything in chondrites formed in a gas that was near-solar in composition. This argues against CAI formation by repeated evaporation and condensation due to solar flares in a reconnection region close to the protosun, as one prediction of this is that CAIs would have formed from a very dust-enriched, and thus very oxidizing, gas [10]. Depletions of W and Mo relative to other refractory siderophiles in whole CAIs suggest they may contain trace components formed at higher f_{O_2} [11], and the presence in CAI rims of both pyroxene with low Ti^{3+}/Ti^{tot} [12] and Fe^{3+}-bearing andradite [5] implies that CAIs were affected by later events under much more oxidizing conditions. One idea is that such redox variability accompanied secondary exchange of ^{17}O and ^{18}O in disequilibrium reactions using atomic oxygen made by CO photolysis [13].

Fayalite in Chondritic Olivine: Solar gas is so reducing that metallic NiFe and pure forsterite co-condense at high T. FeO is eventually stabilized as fayalite, but only at such low T that slow Fe-Mg interdiffusion in olivine prevents 1μ grains from reaching x_{Fa}=0.001, even for 10^6-yr nebular cooling times [4], far short of the apparent minimum x_{Fa} of the precursors of chondrules in UOCs, ~0.15. Models involving enhancement of O/H and O/C ratios by vaporization of regions enriched in dust relative to gas, formed by reasonable degrees of vertical settling [14] or radial transport [15] of dust, yield too low an f_{O_2} to overcome this major obstacle to understanding the oxidation state of chondrites.

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OXYGEN ISOTOPES OF INDIVIDUAL MINERALS IN THE PINK ANGEL. Yunbin Guan[1], Weibiao Hsu[2], Takayuki Ushikubo[1], Laurie A. Leshin[1,3], [1]Dept. of Geological Sciences, Arizona State University, Tempe, AZ 85287, USA. (yunbin.guan@asu.edu), [2]Laboratory for Astrochemistry and Planetary Sciences, Purple Mountain Observatory, Nanjing, 210008, China. (wbxu@pmo.ac.cn), [3]Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287, USA. (laurie.leshin@asu.edu).

The Allende Pink Angel is a unique inclusion that was first described in [1]. It has a large pinkish interior (core) (90% of the total mass) surrounded completely by a whitish rim of ~400 μm wide. The interior is composed of a fine-grained, porous aggregate of Fe-rich spinel (60%), sodalite (30%), and grossular (5%). The rim is a compact assemblage of fine-grained spinel, anorthite, and diopside. We are carrying out correlated investigations of oxygen isotopes and of short-lived radionuclides in the Pink Angel. In this report, we present preliminary oxygen isotopic data for individual minerals in the Pink Angel.

In situ oxygen isotope analyses were carried out with the Cameca IMS 6f ion microprobe at Arizona State University. A total of 14 spots in one of the polished thin sections of the Pink Angel were measured and the results are plotted in Fig. 1. All the data plot along the carbonaceous chondrite anhydrous minerals (CCAM) line. Four spinel grains, one from the core and three from the rim, show "typical" ^{16}O-enrichments with δ^{18}O and δ^{17}O values at -44‰ to -50‰, similar to spinel from other Allende calcium-aluminum-rich inclusions (CAIs). Two diopside grains in the rim contain intermediate ^{16}O-excesses, plotting along the CCAM line at δ-values of -37‰ and -39‰.

One anorthite grain in the core has oxygen isotopes of about -15‰ for both δ^{18}O and δ^{17}O. However, two anorthite spots from the rim are less ^{16}O-enriched, with δ^{18}O = ~ -6‰ and δ^{17}O = ~ -9‰. Measurements of two sodalite grains, overlapping to small amounts of spinel and diopside, yielded oxygen isotopes of about -15‰, undistinguishable from the core anorthite. Sodalites of similar oxygen isotopic compositions with a larger variation range were also observed in a Ningqiang CAI [2]. The anorthite and sodalite in the Pink Angel are less depleted in ^{16}O than their counterparts in Allende CAIs [*e.g.*, 3]. The oxygen isotopic compositions of two grossular grains in the core are slightly heavier than those of sodalite and anorthite in the core, but similar to those of the two rim anorthites. One hedenburgite in the rim also plots on the CCAM line and is most ^{16}O-depleted among the phases measured, with δ^{18}O = 5‰ and δ^{17}O = -0.4‰.

The oxygen isotopes of sodalite, grossular, and even hedenburgite, which are believed to be alteration products of primary CAI minerals, all plot intriguingly along the CCAM line, probably produced by the same isotopic exchange between ^{16}O-rich solids and ^{16}O-poor nebular gas (or some other ^{16}O-poor components) as suggested for the isotopic heterogeneity among primary CAI minerals. Therefore, the alteration of the Pink Angel and the Ningqiang CAI [2] could have taken place in a nebular setting. Interestingly, sodalites from both inclusions contain ^{36}S excesses from *in situ* decay of the short-lived radionuclide ^{36}Cl [4, and unpublished data].

The Pink Angel thin sections used in this study are graciously provided by G. J. Wasserburg.

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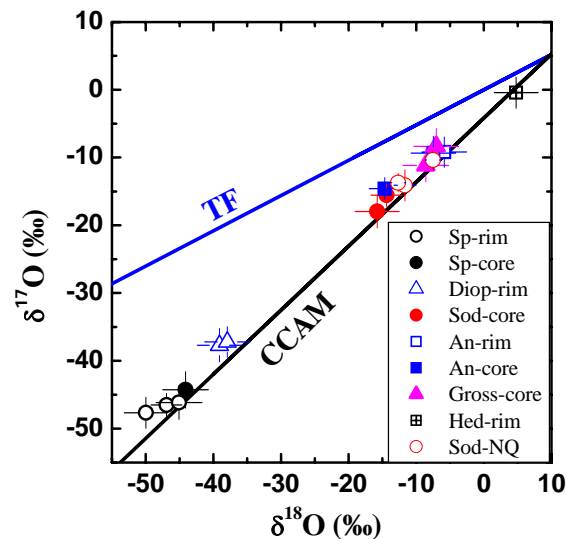
Fig. 1 Oxygen isotopes of individual minerals in the Pink Angel. Abbreviations: Sp – spinel; Diop – diopside; Sod – sodalite; An – anorthite; Gross – grossular; Hed – hedenburgite, TF – terrestrial fractionation line; CCAM – carbonaceous chondrite anhydrous minerals line; "core" and "rim" indicate that the minerals are from the core and rim of the Pink Angel, respectively. Sod-NQ represents data for sodalite in a Ningqiang CAI [2]. Error bars are 2σ.

OXYGEN ISOTOPE COMPOSITION OF SOLAR WIND IMPLANTED IN LUNAR SOILS: A ^{16}O-RICH PROTOSOLAR NEBULA.

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The discovery of strong [16]O enrichments in Ca-Al-rich inclusions from carbonaceous chondrites [1] was followed in the last 30 years by a systematic search for non mass-dependant oxygen isotopic anomalies in all available solar system rocks [*e.g.*, 2]. The picture which emerged from these studies is that most of the chondritic and achondritic meteorites as well as Earth and Mars have variable bulk oxygen isotopic compositions which cannot be derived one from others by 'normal' chemical and physical processes obeying mass dependent fractionation laws. The mass dependence of rate constants and equilibrium constants of most chemical/physical processes dictates that the abundance ratios of the three stable oxygen isotopes in all solar system objects should be related by a law which can be described by the approximated equation $\delta^{17}O = 0.52 \times \delta^{18}O$ (the terrestrial fractionation line). The fact that the oxygen isotopic composition of most meteorites are distributed on both sides of this line has been interpreted as reflecting either (i) the presence in the solar accretion disk of grains and gas which differed in their relative [16]O contents because of different nucleosynthetic origins and which were mixed in various proportions [1,2] or (ii) the occurrence in the early solar system of peculiar reactions in the gas phase which would not obey the mass fractionation laws [3-5].

Central to this issue is the O isotopic composition of the protosolar gas from which all early solar system solids derive. This composition is not known but is likely preserved in the outer layers of the Sun. Using the successful technique we have previously applied for identification of the solar composition of N [6] and C [7] from lunar samples, we have attempted to determine the O isotopic composition of the Sun [8].

We have analyzed so far ~40 metallic grains collected from the Apollo 17 soil sample 79035. Most of the metallic grains were enveloped with oxide layers whose thicknesses were 100-500 nm. The O concentrations of this layer were as high as ~30 wt%, which are enough to totally mask the solar wind component whose concentration is expected to be ~1 wt% at most, as derived from our previous estimate of solar wind C concentration among grains from the same sample [7]. The $\Delta^{17}O$ values ($\equiv \delta^{17}O - 0.52 \times \delta^{18}O$) of the oxide layers for most of the grains were ~0 ‰, suggesting a terrestrial origin of these oxides [8]. However, a small fraction of metallic grains (~10%) exhibited a surface correlated O component with a significantly positive $\Delta^{17}O$ value, up to +8.3 ± 2.2 ‰ (1σ). Detection of such [16]O depleted component among lunar grains is compatible with the result of Ireland *et al.* [9] who observed among metallic grains from lunar soil 10084, an O component with a $\Delta^{17}O$ value of about +27 ‰, although $\delta^{18}O$ values are largely different: our samples showed negative values (-10 ‰ or lower), whereas their grains showed positive values up to +100 ‰. The high O concentration of our observed [16]O depleted component, up to 24 wt%, suggests a non-solar origin of this component. Although it is still premature to identify the nature of this component from the current data sets, we suspect contribution of planetary components with positive $\Delta^{17}O$ values [*e.g.*, 10] supplied to the Moon surface.

At depth in the grains (>500 nm), below the above mentioned oxide layers, we observed a tenuous (<1 wt%) but clearly visible component which is strongly enriched in [16]O. This component is attributable to the implanted solar energetic particles [8]. We conclude that the solar gas, compared to the terrestrial composition, is enriched in ^{16}O, by at least 20 ‰ in $\Delta^{17}O$. Our conclusion suggests that O in Earth, Mars, Moon and meteorites, which is in bulk depleted in ^{16}O, must have originated from precursors which were produced by 'specific reaction pathways', as recently proposed [*e.g.* 3-5,11-13], and was thus strongly isotopically fractionated in a non-mass dependant way from the protosolar nebular gas.

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