

ELECTRON IRRADIATION OF WATER ICE ON DUST RESULTS IN ANOMALOUS OXYGEN ISOTOPE EXCHANGE Gerardo Dominguez¹, Lauren Tafra¹, Josh Lucas¹, Michelle Salem¹, Ming-Chang Liu², Kevin McKeegan², ¹Physics Department, California State University, San Marcos, CA USA ² Earth and Space Sciences Department, UCLA, Los Angeles, USA (gdominguez@csusm.edu)

Introduction: Understanding why the planets and planetary materials in general are enriched in the heavier isotopes of oxygen (¹⁷O, ¹⁸O) compared to the Sun is a primary and unsolved problem in cosmochemistry [1, 2]. Models that have been proposed to explain the observed anomalous distribution of oxygen isotopes generally fall into four classes: (1) nucleosynthetic origins due to supernova injection of ¹⁶O into the early solar system (2) photo-dissociation of gas-phase CO in protoplanetary disk and/or parent molecular cloud (a.k.a. self-shielding) (3) distinct isotopic compositions of interstellar dust compared to gas-phase oxygen [3] and (4) symmetry dependent mass-independent isotopic fractionations similar to the formation of ozone ($O_2 + O + M \rightarrow O_3 + M$) in the gas-phase [4]. One variant of this class is the hypothesis that the reaction pathways that lead to the formation of water on cold dust grains in molecular clouds may have imparted oxygen-bearing dust grains with enrichments in ¹⁷O and ¹⁸O compared to the bulk molecular cloud composition [5]. All of these models require a mechanism that creates, maintains, and transfers ¹⁷O, ¹⁸O enrichments to the planets, comets, volatile ices and asteroids of the solar system.

While the nucleosynthetic origins model has long been discounted, self-shielding of CO appears to be the most favored model despite the very specific conditions required for oxygen isotopic anomaly generation and mixing timescales. The hypothesis that the interstellar dust grain population that formed the planets had a distinct isotopic composition from the bulk of the solar system oxygen reservoir is intriguing. However, this model does not explain how a dust grain population was able to resist physical processes that in theory should promote isotopic mixing between the solid oxygen and volatile oxygen reservoirs in the parent molecular cloud. One of these processes, it turns out, is cosmic-ray irradiation.

Cosmic-rays, even in dense molecular clouds, are known to induce chemical evolution even in the absence of UV-light. Motivated by this, we performed a series of experiments to better understand how the secondary electrons generated by cosmic-rays induce isotope exchange between oxygen bearing water ice and interstellar dust at 10K.

Water Ice Irradiation Experiments: To perform electron irradiation experiments described here, we used the Isotope Characterization Experiment (ICE) at CSU San Marcos. This apparatus consists of: (1) a 12-inch diameter Ultra-High-Vacuum chamber (UHV) (2) a HV vacuum

line equipped with a septum that allows volatile gases, including water, to be introduced into the UHV chamber (3) a cavity ringdown (CRD) water isotope analyzer and (4) a sample holder designed to accommodate 10 mm in diameter disks at the center of the UHV chamber (5) A Kimball Physics electron gun ($E = 2\text{eV} - 5\text{keV}$, $I = 0\text{ nA} - 500\text{ }\mu\text{A}$) for the delivery of energetic electrons directly onto samples. To produce water-ice covered quartz (SiO_2) and sapphire (Al_2O_3) samples, we first pumped out the UHV chamber to pressures less than 1×10^{-8} Torr. We prepared water ice samples by injecting 5-10 μL of the GISP ($\delta^{18}O = -24.78 \pm 0.09\text{‰}$) or VSMOW ($\delta^{18}O = 0\text{‰}$) water standard into the $\sim 180\text{ cc}$ vacuum line followed by controlled deposition of this water onto the cold metal-oxide surface using a stainless steel needle valve. Once the pressure stabilized below $\sim 2 \times 10^{-8}$ Torr, the electron irradiation was initiated. Electron flux was monitored periodically using a Faraday cup, picoAmmeter, and data acquisition software written in Matlab. Once electron irradiation was complete, the He compressor was stopped and the surface was brought up to room temperature while simultaneously pumping using a Shimadzu mag-lev Turbo pump (TMP-303LM). Because we wanted to minimize water-liquid interactions, we did not collect the residual H_2O after these experiments. Pressures less than $\sim 3 \times 10^{-8}$ Torr were maintained throughout the electron bombardment, minimizing the potential for any gas-phase chemistry. One sample, $SiO_2 - 7$, was pre-irradiated and then exposed to VSMOW standard.

SIMS Analysis: The results we report here were irradiated in late spring-early summer of 2018 and the oxygen isotopic composition of the surfaces of these substrates was determined using the UCLA IMS-1290 ion microprobe. The samples were raster-sputtered ($50\text{ }\mu\text{m}$ by $50\text{ }\mu\text{m}$) with a 3 nA Cs^+ primary ion beam. Secondary ion intensities were measured in multi-collection mode under mass resolution ($M/\Delta M$) of 6,000, with ¹⁶O, ¹⁷O and ¹⁸O being collected with L'2 (Faraday cup, $10^{10}\text{ }\Omega$), axial electron multiplier (EM) and H1 (Faraday cup, $10^{11}\text{ }\Omega$), respectively. A $35\text{ }\mu\text{m}$ by $35\text{ }\mu\text{m}$ field aperture was used to ensure that only signals from the center of a crater were collected. No pre-sputtering was applied prior to data acquisition. Non-irradiated quartz and sapphire were used as standards to characterize instrumental mass fractionation.

Results: SIMS analysis of Al_2O_3 and SiO_2 surfaces reveals the following:

- Isotope exchange between volatile water ice and

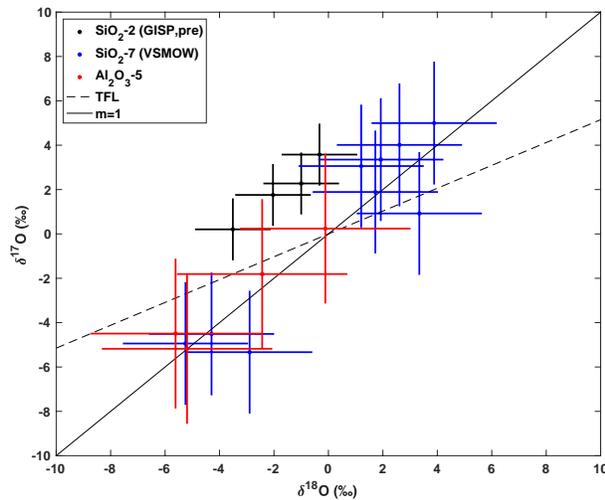


Figure 1: Delta-Delta plot of oxygen isotopic composition of irradiated surfaces as measured by SIMS and corresponding 2σ uncertainties. Composition is reported relative to the corresponding un-altered surfaces. Lines with slopes equal to the terrestrial fractionation line (TFL, $\delta^{17}\text{O}/\delta^{18}\text{O} \approx 0.515$) and a $\delta^{17}\text{O}/\delta^{18}\text{O} = 1$ trend are shown for reference. $\Delta^{17}\text{O}$ determinations for Al_2O_3 and quartz have estimated uncertainties of $\approx \pm 0.65\text{‰}$ and $\approx \pm 0.35\text{‰}$. These uncertainties were determined by adding the standard error of the cycle to cycle variation in δ values and their spot to spot variation standard error in quadrature.

solid refractory oxygen-bearing surfaces can occur as a result of electron irradiation in astrophysical conditions

- Isotope exchange is anomalous, producing fractionations with slopes ranging from 0.96-1.11 on a triple isotope plot, regardless of whether the substrate was Al_2O_3 or SiO_2

Discussion and Analysis: Cosmic rays in molecular clouds provide an obvious source of energy for breaking chemical bonds found within dust grains, thereby enabling isotope exchange to occur between dust grains and volatile ices found on their surfaces. While typical galactic cosmic rays consist of protons, the interaction of ionized energetic particles with materials is expected to produce a cascade of secondary electrons, in a manner that is analogous to our experiments with 5 keV electrons (as revealed by Monte-Carlo simulations). Thus, while our experiments do not involve the interaction of energetic protons, we believe that our experiments capture the essence of the cosmic-ray induced dissociation of metal-oxide bonds (e.g. Si-O, Al-O, etc) and radical chemistry that is expected to ensue that would couple the volatile and refractory isotopic reservoirs.

As our experiments reveal, energetic electrons ($E = 5$ keV) are capable of stimulating isotope exchange between volatile and refractory oxygen bearing reservoirs in molecular cloud environments with temperatures as low as 10 K. Our observations that this processing produces so-called mass-independent fractionation is somewhat surprising and the detailed physical mechanism(s) underlying the anomalous oxygen isotopic fractionation patterns we report are not clear. However, the observation that this type of mass-independent fractionation can occur in molecular cloud conditions as a result of non-equilibrium chemistry on dust grains surfaces is consistent with the prediction by [5] for the origins of the anomalous enrichment in ^{17}O and ^{18}O seen in solar system planetary materials. Energetic processing of volatile ice covered surfaces is expected to occur in molecular clouds and/or protoplanetary disks. The ubiquity of the process suggests that our observations have broad astrophysical implications, particularly astrophysical observations with oxygen isotopic resolution. That this process produces isotopic reservoirs with the $\delta^{17}\text{O}/\delta^{18}\text{O} \approx 1$ is intriguing and suggests a likely connection to the CCAM line [1]. Because the isotopic anomaly mechanism we describe here occurs on the dust grains themselves, this process would likely produce and sustain distinct oxygen reservoirs in the early solar system. The dependence of the overall isotopic shift as a function of electron fluence suggests that over time, cosmic rays and perhaps other sources of energetic particle radiation, may have produced the anomalous enrichments in ^{17}O and ^{18}O that characterize the planets. Work in progress is aimed at determining the efficiency of the isotope exchange mechanism described here to evaluate the timescales for isotopic mixing in astrophysical and protoplanetary environments.

References

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