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The nature and origin of ancient oxygen isotopic heterogeneities in Mars' crust

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Abstract

Dynamical simulations of planet formation have started to successfully combine cosmochemical tracers such as nucleosynthetic anomalies of measured samples with proposed accretion reservoirs to reveal new information about early solar system processes. As sampled terrestrial planets have over-abundances in the highly siderophile elements (HSEs), it is possible that Earth and Mars experienced significant mass augmentations (~1 wt. %) in one or more Late Veneer (LV) colossal impacts. Additional evidence for LVs may be traceable by isotopic signatures in the crust and upper mantle of the planets; this would be especially true for Mars which has much more sluggish geodynamics than Earth, and may therefor better preserve primordial isotopic heterogeneities. To investigate for a record of Mars' late accretion, I measured the multiple O-isotopic compositions (¹⁶O, ¹⁷O, ¹⁸O; expressed in conventional Δ^{17} O-notation) in fragments of the martian meteorite, NWA7034. Analysis shows that discrete domains in this ancient martian regolith breccia record anomalous $\Delta^{17}O_{VSMOW}$ values compared to the Shergottite-Nakhlite-Chassigny-ALH84001 baseline composition of $\Delta^{17}O_{VSMOW} = 0.3\%$. To account for Δ^{17} O values in NWA7034 as high as +1‰, I propose that a minimum admixture of approximately 22 wt.% LL-Ordinary Chondrite (OC). If Mars' LV was delivered by an object approximately the mass of Ceres (9×10^{20} kg; ~1000 km diameter) but with an OC composition, this places the martian LV at odds with Earth, which was affected by an Enstatite Chondrite-type mass augmentation in its late accretion history after the Moonforming event. I attribute this difference in outcomes to Mars' proximity to the asteroid belt.

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Introduction

The formation of Mars and its history of late accretion is a long-standing problem that is slowly being resolved by coupling planetary dynamical simulations with cosmochemical data (Brasser and Mojzsis, 2017). For example, Mars' anomalously small mass for its location from the Sun is difficult to reconcile with various classical planetaryaccretion scenarios (Chambers, 2004). Several mechanisms have been proposed to overcome this dilemma, the most successful of which is the "Grand Tack" (**Figure 1**) wherein gas-driven migration of growing Jupiter truncates the disk of planetesimals, thus stunting Mars' growth (Walsh et al., 2012). Subsequent to its formation, Mars as well as the whole of the solar system, experienced an epoch of late accretion by the left-overs of the planet formation process (Brasser et al., 2016).

To understand this history of late accretion, cosmochemists turn to the elemental abundances of highly siderophile elements (HSEs) in Mars' mantle, as they have done for Earth and Moon (Brasser and Mojzsis, 2017). These strongly "metal-loving" elements serve as a signature of late accretionary mass augmentations to the rocky planets and the Moon because the HSEs are expected to have strongly partitioned into metallic cores during planetary differentiation (Stevenson, 1982; Bottke et al., 2010). The expected result of late accretion is that Late Veneer-type additions to the rocky planets would be expressed as anomalously high HSE abundances in silicate mantles (Chou, 1978; Walker, 2009). Estimates are that a Late Veneer contributed an additional 0.8 wt. % to Mars before ca. 4.49 Ga (Brasser and Mojzsis, 2017). It has been further proposed that such a supplement can be accounted for by a Vesta-to-Ceres-sized object striking Mars that concurrently gave rise to its hemispheric dichotomy and moons, Phobos and Deimos (Canup and Salmon, 2018). Compared to Earth, Mars has a mundane geodynamical history that would only weakly erase isotopic heterogeneities introduced by late accretion events such as a Late Veneer. Samples from earliest Mars might be expected to preserve anomalous values of cosmochemical tracers such as O-isotopes and nucleosynthetic anomalies (e.g. ε^{50} Ti, ε^{62} Ni) in light of the very long mixing time of the martian mantle.

Any progress in refining the details of such an impact, including size and origin of the impactor, would provide useful insight into Mars' early history and the dynamical environment of the first ca. 100 Myr of the solar system.

In addition to the dynamical scenarios cited above, the Mars' ancient geomorphology is poorly understood. Previous work suggests that Mars has a long history of heterogeneous crust with multiple silicate reservoirs (Bellucci et al., 2015). As such, isotopic heterogeneities in major elements such as oxygen amongst various martian meteorites might be evident. Of the 100+ identified Martian meteorites, all but two fall within the discrete categories of Shergotty, Nakhla or Chassigny – dubbed SNCs – with the exception of the regolith breccia NWA7034 and its pairings (Agee et al. 2013; Humayun et al., 2013), and the ca. 4 Ga (Mittlefehldt, 1994) orthopyroxenite ALH 84001. Only the clan of samples belonging to NWA7034 and its pairings show a strong deviation towards enrichment in the minor O-isotope (¹⁷O) compared to all other martian meteorite samples. Here, I show that high spatial resolution in situ analyses for the multiple ¹⁶⁻¹⁷⁻¹⁸O isotopic system in different mineralogical and petrological components within martian meteorite NWA7034 (Figure 2), provides robust boundary conditions for such a late veneer as well as a postulated early magma ocean on Mars. Further, I predict that, from its Δ^{17} O value, NWA7034 is remnant of the primitive Martian crust (Figure 3). Finally, based on mixing calculations, I show that the most likely explanation for my measured Δ^{17} O values is a late accretion admixture of type L-OC meteorite that I use to calculate anticipated nucleosynthetic anomalies in Ti, Ni, Cr and Mo isotopes.



Figure 1: From Raymond, S., 2018, this model depicts the general events which modified the configuration of the solar system as we know it today. Ca 2-3 Myr after t=0, Jupiter and Saturn's planetary cores migrate inward. About 1 Myr later, the giant planets reverse direction and migrate back outward, mixing planetesimals (asteroids) and creating dynamical chaos. The present day solar system is depicted at the bottom. We hypothesize that Mars as a planetary embryo would have migrated inward as Jupiter did, and then not back outward due to its Keplerian orbit about the Sun.



Figure 2: From the University of New Mexico, NWA7034 main meteorite mass. Fusion crust and are face shown with interior breccia visible in face.

Background

NWA7034

The meteorite NWA7034 discovered in Morocco in 2011 is a polymict basaltic breccia of martian origin (Agee et al., 2013). It is the best match so far from the collection of martian meteorites to the overall chemical composition of the martian crust as observed by our fleet of landers and orbiters. The meteorite exhibits a fine-grained matrix of alkali basaltic composition which closely resembles the composition of material identified at Gusev crater by the Mars Exploration rovers (Agee et al., 2013 and Humayan et al., 2013). As a polymict regolith breccia, NWA7034 contains at least six distinct igneous components surrounded by matrix material (Agee et al., 2013; Humayun et al., 2013; Udry et al., 2014; Gattacceca et al., 2014; Santos et al., 2015; Nyquist et al., 2016). Previous petrographic analyses identify the following clasts to exist within the various components: felsic clasts, clast-laden impact melt rock (CLIMR), melt spherules, matrix melt. The felsic clasts showcase mineral assemblages including alkali feldspar, plagioclase, pyroxene, apatite, ilmenite, trace amounts of zircon and are sometimes referred to as 'monzonitic clasts'. These monzonitic clasts also have elevated concentrations of HSEs and exsolved textures indicative of melting of the Martian protocrust (Humayan et al., 2013; Udry et al., 2014; Bellucci et al., 2015; Nemchin et al., 2015; Wittman et al., 2015; Lorand et al., 2018)

Furthermore, the bulk Δ^{17} O value of NWA7034 and its pairings is distinctly different than that of the contemporary martian meteorite inventory that is used to compute Mars' bulk oxygen isotopic composition. The value of NWA7034 (bulk) is Δ^{17} O = 0.58 ± 0.05‰ (Agee et al., 2013) (**Figure 4**), a nearly .28 per mil enrichment. Considering the regional Δ^{17} O values described in the next section this anomalous enrichment in ¹⁷O - unique to NWA7034 and its pairings – may be explicable by contamination of Mars' crust by ordinary chondrite.

Previous geochronological work on NWA7533, a pairing to NWA7034, found zircon ages upwards of 4428 ± 25 Ma with evidence for a thermal resetting event at 1712 ± 85 Ma (Nemchin et al., 2014 and Cassata et al., 2018) (**Figure 5**). These zircon ages directly establish the antiquity of some preserved elements of the martian crust since approximately 150 Myr after solar system formation. Also, U-Pb geochronology yields ages that are younger, approximately 1.3 Ga (Bellucci et al., 2015 and McCubbin et al., 2016).

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Finally, it is noteworthy that the heat-released water Δ^{17} O value for NWA-034 is broadly similar to that established for the average Martian crust, Δ^{17} O= 0.330 ± 0.011‰ (Agee, 2013) (**Figure 5**). These findings seem to suggest that the igneous minerals in NWA-7034 document multiple oxygen reservoirs in the Martian crust from pre-Noachian (before 4000 Ma) times.

Mass Fractionation

Physical or chemical processes which act to separate isotopes is known as fractionation. Some isotopic variations in meteorites cannot be related to terrestrial, radiogenic, or cosmogenic effects and are instead of nucleosynthetic origin. These heterogeneities exist because the protoplanetary disk was enriched with producs of stellar nucleosynthesis that were not fully homogenized when the solar system formed (Dauphas and Shauble, 2016). These 'patches' can be used to describe the genetic relationship between planetary bodies and identify primitive configurations that would otherwise appear physically invisible in the solar system as we know it. Most isotopic variations are generally mass-dependent fractionation, caused by typical geologic processes, whereas relative variation in isotopic ratios scale with the difference in mass of the isotopes involved (e.g., δ 17 O \approx 0.52 δ 18 O). Alternatively, nucleosynthetic processes and/or photodissociation of some elements, specifically oxygen, results in mass independent fractionation, providing a one-to-one ratio, or δ 17 O \approx δ 18 O, where the slope is conserved.

Significance of $\Delta^{17}O$

The minor isotope of stable oxygen, ¹⁷O, can be related to the covariance by mass of the major isotopes, ¹⁸O and ¹⁶O (Equation 1) and expressed using delta-notation such that $\Delta^{17}O = \delta^{17}O_{VSMOW} - 0.52 \delta^{18}O_{VSMOW}$, where δ denotes deviations in parts-per-thousand (%) to isotopic ratios normalized to a terrestrial standard.

$$\delta^{17,18}0 = \frac{({}^{17,18}O/{}^{16}O_{sample}) - ({}^{17,18}O/{}^{16}O)_{standard}}{({}^{17,18}O/{}^{16}O)_{standard}} * 10^{3}(\%)$$

Equation 1: standard-delta notation, describes deviations in parts-per-thousand (per mil, $\%_0$) of an isotope (17,18 O) relative to the more abundant standard (16 O).

This Δ^{17} O relationship permits the discrimination between primordial nebular heterogeneities inherited during planet formation and mass-dependent fractionation induced by planetary processes and is widely used as a reliable isotopic fingerprint for different meteorite parent bodies relative to the Earth standard (Clayton and Mayeda, 1976) (**Figure 6**). The globally-used standard as of 1995 is the Vienna Standard Mean of Ocean Water, where 18 O/ 16 O = 2005.20 ±0.43 ppm and 17 O/ 16 O = 379.9 ±1.6 ppm (Hornberger, 1995).

Nucleosynthetic deviations in Δ^{17} O are prevalent in the solar system (Figure 6) because of condensation sequences in the protoplanetary disk. Below silicate condensation temperature, but above condensation temperature of ices, about 25% of oxygen was likely incorporated into solid phases. Thus, oxygen isotopes *in solids* put forth insight to the range of oxygen compositions in the solar nebula. In general, a sub-group of meteorites - termed enstatite chondrites - are considered to have been one of the dominant sources of Earth's accretion (e.g. Dauphas, 2017); the enstatite chondrites have in Δ^{17} O values that are close to terrestrial values, at about 0%. Meanwhile, Carbonaceous chondrites exhibit a vast range of Δ ¹⁷O values, some depleted while others enriched in ¹⁷O. Another common group of chondritic meteorites dubbed the ordinary chondrites are of the most enriched objects in the solar system in ¹⁷O resulting in Δ^{17} O values that range from +0.6 to +1.2‰. Martian meteorites: Shergottites, Chassignites and Nahklites (or SNCs) are also enriched in ¹⁷O relative to Earth, such that bulk Martian soil averages Δ^{17} O=0.3 ‰. These compositional patterns may be indicative of 'feeding zones', a regional gravitational bias of material accreting to a nearby mass. Supposing the enstatite chondrites dominated the inner terrestrial region, followed by the ordinary chondrites would result in these predicted and observed Δ^{17} O fluctuations (Brasser and Mojzsis, 2017).

Scanning Electron Microscopy

To obtain a better visual understanding of the complexity and heterogeneity of NWA-7034, scanning electron microscopy (SEM) is the first step. This technique is widely useful in that it can reveal information about a sample regarding external morphology, chemical composition, crystalline structure and orientation without severely destroying/distorting the sample surface. Common tools in petrographic analyses, SEMs

are used to generate two-dimensional mappings, colored by composition of a sample surface with nanometer resolution. In this application, we use the Tescan Mira3 SEM at the Colorado School of Mines in Golden, CO. The accompanying imaging software is Quantax EDS for SEM by Bruker.

Fundamentally, an SEM accelerates electrons that interact with the sample (as it is coated in an electrically-conductive film, carbon in this case) and return various reflective and refractive signals in the shape of a teardrop (**Figure 7**). The principle signals returned are backscattered electrons, characteristic X-rays, visible light and heat. The most valuable returns in the case of meteoritic mapping are the characteristic X-rays and backscattered electrons.

Backscattered electrons are used to generate an image of the sample surface; such image is interpreted as heavier elements appear brighter and lighter elements darker. The characteristic X-rays are especially useful. Each element in a mineral that is excited by the electron beam produces these X-rays. Since the interaction with the beam cause discrete atomic energy transitions, these yield a difference in energy levels specific to an element, later translated to mineral composition and location.

Secondary Ion Mass Spectrometry

The primary tool to obtain the diminutive mass differences between ¹⁶O and ¹⁸O is secondary ion mass spectrometry (SIMS). There are three different analyzers for SIMS: sector, quadrupole and time-of-flight. Quadrupole mass analyzers (used in our analyses) are necessary to separate the secondary ions by their mass-to-charge ratio. For low atomic number elements, such as oxygen, large radius, double focusing SIMS is required for the necessary micron resolution. All analyses represented here were acquired using the Cameca Sims 1290 high-resolution ion microprobe at the National Ion Microprobe Center at UCLA.

Ion microprobes generate a beam of positive or negative ions which are focused on a sample surface; positive ion beams are generally Cs and negative beams 0. The interaction between the ion beam and sample surface results in the ionization of materials on the surface. The secondary ions produced (of mostly of the opposite charge as the initial beam) travel across a constant high electrostatic potential and are focused by an extraction lens

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and then analyzed by the mass spectrometer, all within a high vacuum environment. As an ion beam passes through a magnetic field, ions are acted on by a force at right angles to both the direction and the motion of the ion and to the direction of the magnetic field (Equation 2). Thus, the secondary ions are separated into individual beams by passing through the magnetic sector. Sorting such ion beams by mass is necessary to determine the ratio of 16 O to 18 O.

$$\frac{m}{q} = \frac{B^2}{2V} \times r^2$$

Equation 2: magnitude of magnetic field required to deflect ions of various mass-tocharge ratio. m/q: Mass to charge ratio (Kg and C); B: strength of magnetic field (Wb/m²); V: ion accelerating voltage (V); r: radius of curvature of magnetic field (m).



Figure 3: Plot illustrating the abundance of Δ^{17} O for the known Martian meteorites and NWA7034. It appears that all samples prior to ca. 4 Ga are less enriched in the minor isotope. We predict that the Δ^{17} O for NWA7034 is remnant of the primitive Martian crust.



Figure 4: From Humayan et al., 2013, plotted here is the correlation between δ ¹⁸O and δ ¹⁷O for the standard Martian meteorites (SNCs) and samples of NWA7034. The terrestrial fractionation line (TLF) is plotted for reference. The slope of these relationships is Δ ¹⁷O : Mars = 0.3 per mil, Avg NWA7034 = 0.58 per mil.



Figure 5: From Cassata et al., 2018, a linear timeline of events recorded within NWA7034. The oldest zircons date to 4.428Ga with a thermal event recorded at 1.712 Ga. The whole-rock average age of this rock (and its pairings) is 2.2 Ga (Nemchin et al., 2014).



Figure 5: From Nemchin et al., 2015, this plot shows the relationship of δ ¹⁸O and δ ¹⁷O for four zircon samples in NWA7034. The Mars fractionation line (MFL) and TFL are also plotted for reference. The noteworthy component of this plot is the water composition data points, which fall right on the MFL, evidence that NWA7034's enrichment in ¹⁷O could not be explained by water in the primitive Martian atmosphere.





Methods

Scanning electron microscopy

Four sample fragments of NWA-7034 were analyzed using a Tescan MIRA3 scanning electron microscope at Colorado School of Mines. Considering previous petrographic work, we selected to focus on two general clast types: melt and lithic. Regarding the melt clasts, we collected measurements on two kinds: impact melt and fine-grained clast-laden impact melt rock (CLIMR). It has been said that the CLIMR material resembles the chemical composition of wind-blown dust on Mars and can provide clues to the original igneous processes which formed the primary Martian crust (Humayan et al., 2013) while impact melt should contain the bulk rock composition of the impactor and yield information on progression of ¹⁷O over time. In terms of lithic clasts, we identify and measure isotopic values within alkali feldspars (potassium-rich and albite), perthite and antiperthite, plagioclase, and pyroxenes (primarily augite). Perthitic feldspar describes the texture of exsolution of sodic alkali feldspar from potassium feldspar; these textures appear as striations, or lamellae, within the clasts. See the ternary plots in **Figure 8** for an illustrative understanding of these lithic mineral abundances in NWA7034.

The accompanying imaging software used with this SEM is Quantax EDS for SEM by Bruker and was used to create the necessary petrological maps of characteristic x-ray and the backscattered secondary electron images. Each map was then customized using Adobe Illustrator to highlight our targets of interest as well as create a visual aid for navigating at 50-micron resolution in the SIMS (see **Figure 9** for a collection of the clast maps compiled and used). These samples and standards were also reimaged using the techniques and instruments described above following the SIMS analysis using a view field of 20-40 microns, allowing for the resulting ion beam pits to be analyzed.

Secondary ion mass spectrometry

In situ oxygen isotope ratios ${}^{18}\text{O}/{}^{16}\text{O}$ and ${}^{17}\text{O}/{}^{16}\text{O}$ were obtained using the CAMECA Sims 1290 high-resolution ion microprobe at the National Ion Microprobe Center at UCLA. We prepared six mounts using an epoxy resin, consisting of: one standards-only mount, two mounts with two unknowns (NWA7034-458-1 + NWA7034-534, and NWA7034-362 +

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NWA7034-372) and one of each standard, and three mounts with one unknown and one of each standard (NWA7034-A, NWA7034-B, NWA7034-C,); the standards used were perthite and adularia. Each mount was permitted to bake, cure and degas for one week followed by grinding, polishing and deposition of a thin (~100 nm) gold coating on the clean surface. A Cs⁺ (cesium) primary beam with an aperture of 400 microns and accelerating voltage of 10 keV was used in static multi-collection mode into faraday cups. We opted to use a presputter time of 60s to allow for mixing of the upper layers of the sample, implant atoms from the primary ion beam onto the surface and allow for the secondary ions to be ejected from the sample surface (as described by Texas A&M Materials Characterization Facility).

In total, we probed 145 unknown and 137 standard sites from three of the six prepared mounts. Correction factors for ratio computation were not applied using the Cameca software and were accounted for after data collection manually. Degassing of one sample, NWA7034-A, resulted in flooding and charging the sample surface, distorting the sample surface and eliminating the secondary ion signal entirely; this mount was removed, and the data is not included in this work. Additionally, we experienced some instrumental issues with low count rates and thus, data points with count rates below 2.5E9 were discarded.

Instrument drift and fractionation correction

Low-frequency noise inherent to the operation of the instrument is known as "drift". This effect is corrected by subtracting the slope of a linear fit amongst count rates per sample per day (**Figure 10**). Another effect to correct for, known as instrument mass fractionation (IMF), or sometimes as "matrix effects", is a result of near-surface variations in the ionization of sputtered atoms. We corrected for IMF by determining the difference between the measured value and true value (obtained from laser fluorination techniques at the University of New Mexico by colleague, Zach Sharp). We then compute δ ^(18, 17) corrected

using Equation 3

$$\delta_{\text{true(sample)}} = \left[\frac{\left(\delta_{\text{raw(sample)}} + 1000 \right) \left(\delta_{\text{true(std)}} + 1000 \right)}{\left(\delta_{\text{raw(std)}} + 1000 \right)} \right] - 1000 \quad \text{(below)}.$$

Equation 3: to compute the corrected delta-value for the two oxygen isotopes, 17, 18. Standards used were perthite and adularia and true values for these were obtained from the University of New Mexico.

Qualitative analysis

Extensive qualitative assessment was done for each probe location on the five meteorite fragments using the follow-up SEM ion beam pit images. Data points were then sorted into three categories of good, mediocre, and bad regarding physical appearance of the pit: **Figure 11** provides a visual reference for this process. In the end, 38 good data points were selected which exhibited little-to-no nearby cracking or crumbling with a regular ovular pit-shape and erosion steps and a flat bottom. We identify 26 images showcasing some cracking, but maintain a regular shape and depth were identified as slightly flawed or mediocre data and the remaining 81 probe locations feature extensive cracking, irregular pit shape and depths, and chossy texture. It is worth noting that these data are the result of repeating this process twice, but by the same observer.



Figure 7: From the University of Glasgow, this illustration depicts the fundamental processes occurring at the sample surface in scanning electron microscopy (SEM). An SEM accelerates electrons that interact with the sample (as it is coated in an electrically-conductive film, carbon in this case) and return various reflective and refractive signals in the shape of a teardrop.



Composition of pyroxenes in NWA 7034 by clast type

Figure 8: From Kelly, N., 2018, Lithic mineral abundances in NWA7034. Top: Pyroxene ternary plot for NWA7034 (fragments 534, A and B). Bottom: Feldspar ternary plot for NWA7034.

Composition of feldspars in NWA7034







Figure 10: From Kelly, N., 2018, data-reduction process to correct for and eliminate instrumental drift. Count rate deviation is plotted on the y-axis and the number of samples which have been probed on the x-axis. The slope of linear fit amongst these data provides the value which the data will be corrected by. This process was repeated for all standards and then applied to the unknown samples which correspond.



Figure 11: A visual example of the qualitative data-reduction process. Here are four examples of the various pit-appearances from the ion beam. A: perthite standard pit, used as reference to compare and grade the unknown pits, features a flat bottom, oval shape, and steps on one end. B: An example of a 'good' data point, pit is ovular, flat-bottomed and looks like the standard. C: An example of a 'mediocre' pit, the shape is consistent, but there is nearby cracking that may interfere with the sputtered secondary electrons, the back end of the pit also exhibits a chossy (crumbly) texture. D: An example of a 'bad' data point, the pit is faint-to-nearly-unrecognizable, there is a massive fracture and nearby cracking.

Results

Qualitative analyses yield 38 'good' data points which make up the dataset presented in Table 1 and any plot below representing data from this project. The average ¹⁷O value for these data is 0.57 ±.05‰ and the 26 mediocre and 81 bad data points result in $\Delta^{17}O = 0.581 \pm .06\%$, and 0.586 ±.06‰, respectively. The average error for ($\delta^{17}O$, $\delta^{18}O$) of the good, mediocre and bad data for comparison are (.103, .187), (.13, .216), and (.129, .203) each per mil.

The average of all samples in our single-mineral approach should match the bulkrock measurements, and indeed these results are consistent with previous bulk-rock analyses (Agee et al., 2013; Humayan et al., 2013; Nemchin et al., 2015; Santos et al. 2015). The average of all 145 data points, unfiltered, is $\Delta^{17}O = 0.57 \pm .06\%$. Furthermore, the dataset presented here expands the previous work by up to 8 per mil. The filtered data exhibit a range of 3.64 < $\delta^{18}O$ < 14.33 and 2.36 < $\delta^{17}O$ < 8.28 (**Figure 12**) where such ranges are an extension of approximately 4-8‰ regarding $\delta^{18}O$ and approximately 2-4‰ regarding $\delta^{17}O$.

Individual clast analyses indicate significant variation in Δ^{17} O. From the filtereddata, I have identified 22 clasts which have been categorized by composition and plotted as such in **Figure 13**. There is an abundance of potassium feldspar (Kfs) and Perthite within the samples, but less plagioclase and minimal pyroxene. See Table 1 below for an outline of these clasts by composition and their corresponding Δ^{17} O values. **Figure 14** depicts the relationship between the unknowns and known meteorites relative to the terrestrial and Martian fractionation lines (TFL, MFL).

The histogram in **Figure 15** shows the distribution of Δ^{17} O enrichment amongst the individual clasts. The two most-populous bins are of Δ^{17} O=.4-.5 and Δ^{17} O=.8-.9. 60% of the material in NWA7034 appears to fall within the bounds of Martian material (as classified by the SNCs) with an average of about 0.37 per mil while about 40% is distinctly different material, averaging approximately 0.95 per mil. Supposing such mixing, this is consistent with the hypothesis of an ordinary chondritic contamination, specifically type L-OC as the average of the sub-group is about 1.033 per mil.

Analysis	Clast Comp	D170 (per mil)	Error
372-F1-2	Kfs (Mantle)	0.65	0.21
372-F8-3	Kfs+Albite	0.333	0.18
372-F9-1	Kfs+Albite	0.498	0.11
372-C8-3	Plag melt	0.474	0.12
458-1-F2-1	CLIMR	1.16	0.13
458-1-F2-2	CLIMR	0.107	0.17
458-1-F2-3	CLIMR	0.281	0.19
458-1-F2-4	CLIMR	0.897	0.24
458-1-F3-3	Perthite	0.369	0.16
458-1-F4-1	Perthite	0.469	0.17
458-1-F6-1	CLIMR	0.494	0.25
458-1-F8-2	Perthite+Plag	0.465	0.23
458-1-C4-1	Impact melt	0.847	0.14
458-1-C4-2	Impact melt	1.488	0.26
458-1-C4-3	Impact melt	0.862	0.23
458-1-C4-4	Impact melt	1.047	0.26
534-F1-1	Perthite	0.828	0.26
534-F1-2	Perthite	0.795	0.14
534-F1-3	Perthite	0.866	0.23
534-F2-1	Perthite	1.142	0.18
534-F4-2	CLIMR	0.866	0.23
534-F12-1	Kfs+Plag	1.197	0.27
534-F12-2	Kfs+Plag	0.39	0.37
534-F10-1	Kfs+Plag	0.746	0.16
534-F14-1	Antiperthite	0.298	0.26
362-F1-3	Plag	0.705	0.23
362-F4-1	Perthite	0.09	0.15
362-F4-2	Perthite	0.215	0.23
362-F4-3	Perthite	0.366	0.21
362-F6-1	Kfs	0.826	0.17
362-F14-2	Kfs	0.183	0.19
362-F14-3	Kfs	0.221	0.15
362-F7-1	Kfs+Albite	0.608	0.21
362-F7-2	Kfs+Albite	-0.154	0.19
362-F8-1	Kfs	0.397	0.12
362-C2-1	Pyroxene	0.372	0.18
362-C2-2	Pyroxene	0.142	0.16
362-F8-2	Kfs	0.129	0.13

Table 1: all filtered unknowns organized by analysis, clast composition as described in methods, and corresponding Δ^{17} O (per mil) as well as computed standard deviation.



Figure 12: All corrected, 'good' data, henceforth called 'filtered unknowns' plotted with TFL and MFL for reference. These data clearly exhibit an enrichment in ¹⁷O (mass-independent fractionation), but also appear to have mass-dependent fractionation. Notably, these data expand on previous work by 4-8‰ regarding δ^{18} O and approximately 2-4‰ regarding δ^{17} O. The average of these data is 0.57 ±.05‰ , which is consistent with previous work (Agee et al., 2013; Humayan et al., 2013; Santos et al., 2015; Nemchin et al., 2015).



Figure 13: Filtered unknowns plotted by clast composition. For reference: ∆: impact melt , o: CLIMR, —: perthite, antiperthite, x: plagioclase, □: Kfs, albite, §: pyroxene. TFL and MFL plotted as reference. There is an obvious clustering of Martian-like material and then clasts which exhibit a different origin. Consistent with our hypothesis, the impact melt clast (should exhibit bulk average material composition of the bolide) are very enriched in ¹⁷O, and cluster together. Similarly, the felsic, lithic materials tend to be Mars-like, indicative of contemporary crust material. Some perthite and plagioclase lie above the MFL and may be remnant of the primitive Martian crust.

Figure 14: Filtered unknowns plotted by clast composition with known meteorite groups H, L and LL ordinary chondrites (OC) and group CI carbonaceous chondrites (CI).

Top: δ ¹⁸O and δ ¹⁷O plot, it appears that the green line, OC-L transects most of the unknown data points. This may be indicative of a contamination by a type L OC. Bottom: δ ¹⁸O and Δ ¹⁷O, there is an obvious grouping near the MFL and another grouping that is laterally (Δ ¹⁷O) similar to the type L OC.







Figure 15: Histogram of all filtered unknowns. Bin gradient represents correlation of the unknown Δ_{17} O value to the known meteorite groups. Gradience was determined using the Clayton and Mayeda 1976 database and includes SNCs, CC-CI, OC-L, LL and H. The far left values may be attributed to other CC material, typically depleted in Δ_{17} O, or enstatite chondrite material (EC) typically around 0 per mil.

Conclusions and Discussion

The results from this study indicate that Earth/Moon, and likely Venus, accreted material dominantly from EC, whereas Mars was largely supplied by OC. This regional discontinuity was predicted by Warren et al., 2011 and further investigated by Brasser and Mojzsis, 2017 (**Figure 16**). As the hypothesis of this project outlined, NWA7034 reveals the isotopic signatures to uphold a late veneer accretion by an ordinary chondrite. It seems, from the filtered data, that a type-L ordinary chondrite (**Figure 14**), likely of a size between 500 and 1000km (Canup and Salmon, 2018) impacted Mars. As Mars lacks plate tectonics and efficient plate-recycling mechanisms (or has yet to provide evidence for such), this material will not be effectively mixed and distributed globally –resulting in a non-homogenous composition of the crust. This evidence for a heterogeneous crust compliments the concept of multiple oxygen reservoirs on Mars, just as multiple silicate reservoirs have been described (Bellucci et al., 2015). Further, the likelihood of a protracted global magma ocean is unlikely considering these heterogeneities.

Additionally, these data may provide evidence for Mars having formed further from its current distance from the Sun. Presently situated around 1.5 AU, to accrete material to Mars, the small red planet must have first developed closer to the asteroid belt, potentially nearing 2 AU (also illustrated in **Figure 17**). Such a scenario is compatible with the outcome of the Grand Tack model (Walsh et al., 2011, Brasser and Mojzsis, 2017) (**Figure 1**) as well as the concept of Mars being a 'planetary embryo' rather than full-size planet (having not experienced oligarchic growth). We are presently unable to describe the accretion signatures in NWA7034 as a result of feeding zone accretion in planetary formation or a later impact by an OC. In order to understand such formation scenarios, it is critical that we obtain Pb/Pb ages for the clasts outline in **Table 1**. The predicted outcome of such analysis is that the clasts which plot enriched in both δ^{18} O and δ^{17} O (e.g. 458-C4 as impact melt and 534-F1 as lithic material) also plot as the oldest components within NWA7034 (**Figure 3**) which would indicate that the rock contains both primitive martian crust and remnants of the bolide. **Figure 17** illustrates a potential pre-migration chemical and isotopic configuration based on these ¹⁷O data and hypothesized corresponding ages.

The advantage and importance of this work when compared to other studies is that single-mineral measurements expose variations within the rock on a clast-by-clast basis.

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This rigorous process is necessary when analyzing a rock containing at least six separate igneous components (Agee et al., 2013; Humayun et al., 2013; Udry et al., 2014; Gattacceca et al., 2014; Santos et al., 2015; Nyquist et al., 2016). As expected, we observe immense variation amongst the lithographic components with a minimum of $\Delta^{17}O = -0.154\pm.19$ and maximum of $\Delta^{17}O = 1.49\pm0.26$ (**Figure 13**). It seems that the components that resemble contemporary Mars are dominantly potassium feldspar (Kfs) and CLIMR whereas the others (anti-perthite, impact melt, and perthite) seem to be of a different origin. It should be noted, though, that perthite appears within the contemporary Martian values as well. Further investigation is necessary and planned to obtain Pb/Pb ages of these components to determine correlation between oxygen and age, as well as which material is primitive martian crust, contemporary martian crust, or bolide components.

The investigation of nucleosynthetic isotopic anomalies is a powerful tool for planetary science. These conclusions are evidence that discrete isotopic analyses reveal signatures of the primitive solar system that are invisible to us now. The current configuration of the planets has proven to be difficult to reproduce, but with the progress in dynamics, specifically the Grand Tack model coupled with the precision and chemical parameters outlined by ¹⁷O and ¹⁸O, we are privy to a window into the first tens of millions of years of the solar system. Yet, further work must be done.

I intend to continue the analyses presented here on the mediocre and bad-labeled datasets to determine if pit-shape is indeed correlated with an increased IMF or error in hopes to further expand the coverage and precision of the oxygen dataset for NWA7034. I also would like to investigate in depth the variation in Δ^{17} O within clasts that should be of the same composition. Exsolved clasts like perthite or clasts with inclusions of other minerals may be the source of this variation.

The precision acquired in this project is not readily available whole-sale for all meteoritic groups, including the SNCs. An update to the preexisting database is required to fully reconcile the various dynamical models and is the logical next step. My experience with building the NWA7034 dataset in new ways (using the isotopic, geochronological and petrographic relationships) will be added to existing isotopic database of O-, Si-, V-, Nd-, Cr-, Ti-, Ru-, Mo- and other nuclides I have compiled from the literature. Such a compilation for

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the key isotopic systems for the various meteorite groups offers a one-stop-shop for cosmochemical information relevant to dynamical and geological processes.

Further, I intend to test NWA7034 for nucleosynthetic isotope tracers as mentioned above in collaboration with colleagues Dr. Audrey Bouvier (soon to be at Bavarian Geological Institute, Bayreuth, DE) and Dr. Mario Fischer-Gödde (University of Cologne, DE). These colleagues have already pledged to work with me to obtain the abundances of ⁵⁰Ti, ⁶⁴Ni, and ⁵⁴Cr in sub-samples of NWA7034 earmarked for analysis based on O-isotopes and relative to Earth standards, Mars and the various meteorites classes for which data already exist. Measurements of these relationships are necessary to support the observed ¹⁷O deviations as nucleosynthetic/photochemical rather than by secondary alteration from Mars' atmosphere.

Following this study and the further work described above, future work would include the reintroduction of dynamical simulations via collaboration with Dr. Ramon Brasser (Earth-Life Science Institute, JP), to compare the simulated-solar system formation outcomes with our observed isotopic relationships. The Grand Tack Model is able to reproduce Mars' size and location via giant planet migration, but does the model also reproduce the accretion reservoirs, or feeding zones, indicated by isotopic deviations amongst Earth, the Moon, NWA7034 and the SNCs? At the present time, we do not know.



Figure 16: From Brasser, Mojzsis, 2017, top: scatter plot of the average percentage contribution of enstatite (orange) and ordinary chondrite (green) to the bulk compositions of Venus, Earth and Mars. Data are plotted as a function of the distance where the disc changes its composition from one meteorite class to another. This model was used to illustrate the pre-migration potential isotopic configuration depicted in **Figure 17.** Bot: Pie chart of the composition of the terrestrial planets for the successful simulation results depicted in the top image. Note that the successful case has a composition for Mars that is strikingly different than that of the other three planets.



Figure 17: A potential illustration of the primitive solar system, before ca 4 Myr after t=0, prior to the chaos and mixing of giant-planet migration. The gradient was emplaced using the outcomes of Brasser, Mojzsis' 2017 models as well as the Δ^{17} O values confirmed and discovered in this study.

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F		
362-F1-3	Plag	
362-F4-1	Perthite	
362-F4-2	Perthite	
362-F4-3	Perthite	
362-F6-1	Kfs	
362-F14-2	Kfs	
362-F14-3	Kfs	
362-F7-1	Kfs+Albite	
362-F7-2	Kfs+Albite	
362-F8-1	Kfs	
362-C2-1	Pyroxene	
362-C2-2	Pyroxene	
362-F8-2	Kfs	
A.2Ion probe locations for cla	st number NWA7034-372	
372-F1-2	Kfs (Mantle)	
372-F8-3	Kfs+Albite	
372-F9-1	Kfs+Albite	
372-C8-3	Plag melt	
A.3Ion probe locations for cla	st number NWA7034-458-1	
458-1-F2-1	CLIMR	
458-1-F2-2	CLIMR	
458-1-F2-3	CLIMR	
458-1-F2-4	CLIMR	
458-1-F3-3	Perthite	
458-1-F4-1	Perthite	
458-1-F6-1	CLIMR	
458-1-F8-2	Perthite+Plag	
458-1-C4-1	Impact melt	
458-1-C4-2	Impact melt	
458-1-C4-3	Impact melt	
458-1-C4-4	Impact melt	
A.4Ion probe locations for cla	st number NWA7034-534	
534-F1-1	Perthite	
534-F1-2	Perthite	
534-F1-3	Perthite	
534-F2-1	Perthite	
534-F4-2	CLIMR	
534-F12-1	Kfs+Plag	
534-F12-2	Kfs+Plag	
534-F10-1	Kfs+Plag	
534-F14-1	Antiperthite	

Appendix A A.1Ion probe locations for clast number NWA7034-362























