Introduction: We have measured Sr, Zr, Mo, and Ba isotopes in presolar silicon carbide (SiC) grains with the Chicago Instrument for Laser Ionization (CHILI) [1, 2]. These elements are particularly important for understanding the s-process during stellar nucleosynthesis. Here, we focus on results from Mo isotopes analyzed in 18 SiC grains. Molybdenum has seven stable isotopes: two p-process isotopes (92Mo and 96Mo), three s- and r-process isotopes (95Mo, 97Mo, and 98Mo), one s-process-only isotope (99Mo), and one r-process-only isotope (100Mo).

Samples and Analytical Procedures: Thirty-one randomly selected SiC grains from the Murchison (CM2) KJG (1.5–3 µm) size separate [3] were analyzed in this study. CHILI uses resonance ionization mass spectrometry (RIMS) to measure isotopic abundances from a cloud of atoms liberated from a sample by a desorption laser and selectively ionized with a set of lasers tuned to element-specific electronic transitions. CHILI is equipped with six tunable Ti:sapphire lasers, which allow simultaneous analysis of three elements with independent two-photon resonance ionization schemes. Fifteen grains were analyzed for Sr, Zr, and Ba isotopes, and 18 grains, including two from the first round, were analyzed for Sr, Mo, and Ba.

Results: Traces of Sr and Ba were found in all 31 SiC grains, and Zr and Mo were detected in all grains analyzed for these elements. Some of the Sr, Zr, and Ba analyses suffered from very low count rates, and, in a few cases, we observed some mass interferences from nonresonantly ionized molecules. However, Mo was detected in all 18 grains analyzed and seems to be free of any mass interference. For five of the 31 grains, all measured isotope ratios are consistent with terrestrial ratios within 2σ for 18 grains analyzed and seems to be free of any mass interference. For five of the 31 grains, all measured isotope ratios are consistent with terrestrial ratios within 2σ for all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ for all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ for all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ for all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ for all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ. For all other grains, the measured isotope ratios are consistent with terrestrial ratios within 2σ.

Discussion: The large variation in MSWD values provides information about the variability of conditions (neutron density and particle density) during s-process nucleosynthesis in the grains’ parent stars. MSWD values close to one for δ9Mo vs. δ92Mo and δ96Mo vs. δ92Mo suggest little relative variation in s-process production rates for 96Mo, 99Mo, and 98Mo. Branching in the s-process path at 95Zr would bypass 96Mo leading to relative 99Mo and 98Mo enrichments, which can therefore be excluded for our 18 grains. Large MSWD values for δ94Mo vs. δ92Mo, δ95Mo vs. δ92Mo, and δ96Mo vs. δ92Mo suggest variable conditions in the production of 96Mo, 95Mo, and 100Mo relative to 96Mo. This could be explained by slightly varying conditions under which these grains formed affecting branching points at 97Zr, 98Zr, and 98Mo, of which all but 98Zr show significant temperature dependence.

Conclusions: Because of their increased precision, the variability of the new Mo isotope data is no longer dominated by statistical uncertainties from counting statistics but reflects true variability of conditions in stellar environments during s-process nucleosynthesis.

ATOM PROBE TOMOGRAPHY OF LUNAR REGOLITH ILMENITE GRAIN SURFACES

J. Greer1,2, S. S. Rout1, D. Isheim3, D. N. Seidman3, P. R. Heck1,2, 1Chicago Center for Cosmochemistry, Dept. of the Geophysical Sciences, Univ. of Chicago, Chicago IL, USA (*E-mail: jennika@uchicago.edu). 
2Robert A. Pritzker Center for Meteoritics and Polar Studies, The Field Museum, Chicago, IL, USA. 3Northwestern Univ. Center for Atom-Probe Tomography, Dept. of Materials Science & Engineering, Northwestern Univ., Evanston, IL, USA. 4Inst. für Geochemie und Petrologie, ETH Zürich, Zürich, Switzerland.

Introduction: The surfaces of airless bodies, such as the moon and asteroids, are subject to space weathering, which alters their mineralogy. Space weathering is predominantly caused by micrometeorite bombardment, irradiation by solar wind, and galactic cosmic rays [1]. Products of space weathering include amorphization resulting in agglutinate glass, submicroscopic or nanophase metallic iron (SMFe and npFe0), re-deposition rims, or vesicles filled with implanted solar wind [2]. Ilmenite from lunar soil (FeTiO3) is particularly well studied as it is retentive to the products of space weathering, including noble gases [3]. Recent studies of space weathering products on lunar samples have used TEM to demonstrate that these noble gases can be present in vesicles and planar defects [4]. In atom probe tomography (APT), atoms are field-evaporated from the surface and detected by a position-sensitive time-of-flight mass spectrometer, allowing both the compositions and the distributions of atoms imaged in 3-D with sub-nm to nm spatial resolution [5]. APT has previously been used to study simulated space weathering products (npFe0 produced by hydrogen implantation) in olivine [6].

Methods: Ilmenite grains in the size range 75-150 μm were extracted from Apollo 17 sample number 71501 at ETH Zurich. The sample was ion-beam-sputter coated with Ni to protect the mineral surface from Ga+ ion irradiation during focused-ion beam (FIB) based sample preparation. Several APT tips were prepared from this grain using the TESCAN LYRA3 FIB-SEM at the Univ. of Chicago. Ridges of this grain were annularly milled to produce nanotips that were then lifted out [7] and mounted on flat-top Si micro tips by Pt deposition. The nanotips were then sharpened by ion-milling to tip apex radii of ~30 nm. The nanotips were analyzed with a LEAP 4000X Si tomograph at the NUCAPT facility of Northwestern Univ.

Results and Discussion: Three out of four nanotips were successfully analyzed. Two of the nanotips (B and C) sampled the top surface of ilmenite at different depths with space weathering products. Nanotip D sampled the ilmenite at about 50 nm below the surface. Besides Fe, Ti, and O, the major elements of ilmenite, traces of Mg, Si, Al, Ca, Mn, and Cr were detected. These elements are a large component of bulk lunar soil [8]. Nanotip C (Figure 1) contains the most dramatic representation of space weathering products and compositional zoning. Both nanotips contain npFe0; in nanotip B, small Fe clusters (~3 to 10 nm diameter) are present throughout the nanotip, with the particles becoming less frequent towards the bottom. In nanotip C, there is small amount of npFe0 in the very top of the nanotip (not displayed in Figure 1), above the Ti-depleted zone, and near the bottom of the nanotip. The middle of nanotip C is dominated by a large (>30 nm diameter) Fe particle (SMFe) of almost pure Fe, surrounded by a rim of TiO. Nanotip C also contains a void space (~15 nm in diameter), which we interpret as a vesicle. No noble gases were detected in this vesicle, likely because they were simply lost during FIB-milling. Noble gases in extraterrestrial samples present as a product of space weathering have yet to be detected by APT because no one has tried to date.

In summary, we have demonstrated that APT can be successfully used to analyze natural samples to characterize products of space-weathering compositionally and texturally at near-atomic resolution.

Meteoritic Constraints on the Origins of our Solar System

Vikram V. Dwarkadas¹, Nicolas Dauphas², Bradley. S. Meyer³, Peter H. Boyajian¹, Michael Bojazi¹, ¹Dept. of Astronomy and Astrophysics, University of Chicago, 5640 S Ellis Ave, ERC 569, Chicago, IL 60637 (vikram@oddjob.uchicago.edu), ²Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, University of Chicago, ³Dept. of Physics and Astronomy, Clemson University, Clemson, SC

Introduction: The abundance of $^{26}$Al ($t_{1/2}=0.7$ Myr) as inferred in meteorites is ~17 times larger than the average ISM abundance at solar system birth from gamma-ray astronomy [1,2,3,6], which is too high [4,5,6] to be accounted for by long-term Galactic chemical evolution [4,7,8] or early solar system particle irradiation [9,10].

This led to suggestions starting 40 years ago [11] that a nearby supernova (SN) explosion triggered the collapse of a molecular cloud and the formation of the solar system. $^{26}$Al was created via stellar and SN nucleosynthesis, and injected into the protostellar cloud by the shock wave. This suggestion has been followed up by several authors [7,12,13]. If correct, one would expect this to be accompanied by a high abundance of $^{60}$Fe ($t_{1/2}=2.6$ Myr) which is produced in SN explosions. Recent work instead found that the $^{60}$Fe/$^{56}$Fe ratio at solar system formation is about an order of magnitude lower that the average ISM value, inconsistent with direct injection from a nearby SN [6,14].

Any potential model of solar system formation thus needs to explain both high $^{26}$Al/$^{27}$Al and low $^{60}$Fe/$^{56}$Fe ratios. The distribution of $^{26}$Al in the Galaxy closely traces the distribution of very massive stars, making Wolf-Rayet (W-R) stars and core-collapse SNe the primary candidates for $^{26}$Al production [20]. The former are stars with initial mass $\geq 25$, which have lost their H and possibly He envelopes. Many authors have suggested that stellar winds from massive stars, could be the source of $^{26}$Al in the early solar system [5,14,15,16,17,18].

Using a combination of semi-analytic calculations, astronomical observations, and numerical modeling, in this presentation we advance the idea that our solar system was formed by triggered star formation in the dense shell of a Wolf-Rayet wind bubble, which can simultaneously explain both the high $^{26}$Al and low $^{60}$Fe abundance.

$^{26}$Al Yields from massive stars: A single massive star above 50 $M_{\odot}$ generally provides sufficient $^{26}$Al to account for the early solar system budget. In some scenarios lower mass W-R stars may suffice. The $^{60}$Fe yield from the wind is negligible - $^{60}$Fe in the proto-solar nebula arises from the swept-up material.

Wolf-Rayet Bubbles: W-R stars are post-main-sequence, hot massive stars which have strong winds with terminal velocities of 1000-2000 km s$^{-1}$ [19]. The combined action of the supersonic winds and ionizing radiation results in the formation of photo-ionized wind-blow bubbles around the stars, consisting of a low-density interior surrounded by a high-density shell. Most of the volume is occupied by a low-density high-temperature plasma. Star formation has been seen at the boundaries of wind-bubbles around O, B and WR stars [20,21,22,23,24].

Injection of $^{26}$Al from the Wind to the Solar System: We suggest that $^{26}$Al condenses onto, and is injected mainly via dust grains (see also [25,26]). Dust forms close in to WC stars [27,28], with grains $\sim$ 1 $\mu$m in size [29]. The stopping distance of 1 $\mu$m size grains in bubbles is several parsecs, exceeding the bubble size. The grains can survive passage through the reverse shock and the low density shocked wind, and reach the outer dense shell. They would then be injected into the high density cores, penetrating depths of 1 to several hundred AU.

Finally, the massive star will explode as a SN of Type Ib/c. We have explored why the material ejected in the explosion, which contains both $^{26}$Al and $^{60}$Fe, may not be able to contaminate the early solar system.

THE RISE AND FALL OF IRON-60.

P. Boehnke, K. D. McKeegan, T. Stephenson, R. C. J. Steele, R. Trappitsch, A. M. Davis, M. J. Pellin, and M-C. Liu. Department of the Geophysical Sciences, The University of Chicago, and Chicago Center for Cosmochemistry, Chicago, IL, USA, Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA, USA, Institute for Geochemistry and Petrology, ETH, Zürich, Switzerland, Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA, USA, Enrico Fermi Institute, The University of Chicago, Chicago, IL, USA, Materials Science Division, Argonne National Laboratory, Argonne, IL, USA, (kdm@epss.ucla.edu)

Introduction: Iron-60 is a uniquely important short-lived radionuclide because it cannot be produced by particle irradiation, and thus, high initial $^{60}$Fe abundances inferred in early-formed Solar System objects must be attributed to injection from a stellar source. Estimates of the initial $^{60}$Fe/$^{56}$Fe ratio range over a factor of 60 from $1\times10^{-8}$ as determined by bulk measurements [1] to $6\times10^{-7}$ from in-situ measurements of high Fe/Ni phases [2,3]. The reasons for this significant discrepancy between high-precision bulk analyses and in-situ analyses of high Fe/Ni phases are not clear. It is possible that SIMS (secondary ion mass spectrometry) analyses are biased by unrecognized, low-level interferences on $^{60}$Ni. Resonance ionization mass spectrometry (RIMS) can be used to overcome these problems.

Methods: To investigate this, we used the UCLA IMS 1290 ion microprobe to analyze Orgueil carbonate grains that exhibit very high Fe/Ni ratios ($>10^5$) and are known from $^{53}$Mn-$^{54}$Cr systematics to have formed within ~5 Myr of CAIs [4]. The analyses were made at high mass resolving power (MRP>6000) to separate known molecular ion interferences. It is notable, however, that there is no accessible MRP that can resolve the isobars $^{56}$Fe and $^{60}$Ni from corresponding Ni isotopes. Because $^{61}$Ni is a very low abundance isotope, poor counting statistics preclude precise correction for mass fractionation, and therefore, SIMS analyses effectively rely on only one isotope ratio, $^{60}$Ni/$^{62}$Ni, as a measure of the potential abundance of radiogenic $^{60}$Ni.

To test the accuracy of the SIMS Ni isotope measurements, we analyzed the same carbonate grains with RIMS using CHILI, the CHICago Instrument for Laser Ionization [5]. CHILI was configured to ionize Ni resonantly using a four-color scheme. Iron was ionized nonresonantly by the Ni lasers. By not using a Fe RIMS scheme, the Fe sensitivity was diminished relative to the Ni sensitivity, which resulted in Fe and Ni signals being of roughly equal intensity during analysis of the high-Fe/Ni samples.

Results: Our preliminary SIMS investigations found two Orgueil breunnerite grains that show apparent $^{60}$Ni$^*$. Correlations with Fe/Ni are generally not well defined, but the data imply a relatively high $^{60}$Fe/$^{56}$Fe ratio, in the range of $10^{-7}$, at the time of carbonate formation.

The same grains with apparent $^{60}$Ni$^*$ were analyzed by CHILI. Because of the very high Fe/Ni ratios in the carbonates, Fe peaks are present in most mass spectra, although at low enough levels to permit accurate peak-stripping of $^{56}$Fe. This correction was smaller than 5% (of the total mass 58 peak), except in two analysis spots where it was 8 and 12%. The data obtained on the Orgueil carbonates reveal correlations between $^{56}$Ni/$^{58}$Ni and $^{60}$Ni/$^{62}$Ni that are strictly mass-dependent. The range in mass fractionation is very large, ~25 to 30‰/u favoring the light isotopes, whereas the range of mass fractionation effects in terrestrial siderite and San Carlos olivine standards is ~2.5 to +2.5‰/u. The large mass fractionation effects in Orgueil carbonates are made evident only by the ability to measure $^{56}$Ni with CHILI, even in phases with very high Fe/Ni ratios. In SIMS analyses, where mass fractionation of Ni isotopes cannot be independently determined with good precision, isotopically light Ni, with high $^{60}$Ni/$^{62}$Ni ratio, can be misinterpreted as addition of radiogenic $^{60}$Ni$^*$. Our RIMS measurements conclusively demonstrate the occurrence of mass-fractionated Ni in meteorite samples, which is large enough that elevated $^{60}$Ni/$^{62}$Ni ratios could be incorrectly attributed to $^{60}$Fe decay if this mass fractionation is not accurately accounted for. We are not yet able to place a limit on the early Solar System $^{60}$Fe/$^{56}$Fe ratio because we cannot reliably measure Fe/Ni ratios with the current RIMS analyses, but it is clear that no excess $^{60}$Ni$^*$ has been detected in old high-Fe/Ni carbonates from Orgueil.

CALCIUM AND TITANIUM ISOTOPE SYSTEMATICS IN REFRACTORY INCLUSIONS FROM CM, CO, AND CR CHONDrites.

L. Kööp,1,2* A. M. Davis1,2,3, A. N. Krot4, K. Nagashima5, S. B. Simon6. 1Department of the Geophysical Sciences, 2Chicago Center for Cosmochemistry, 3Enrico Fermi Institute, University of Chicago, Chicago, IL, 4HIGP/SEOST, University of Hawai‘i at Mānoa, Honolulu, HI, 5Institute of Meteoritics, University of New Mexico, Albuquerque, NM. *E-mail: koeoep@uchicago.edu

Introduction: Calcium-aluminum-rich inclusions (CAIs) are the oldest dated materials that formed in the Solar System [1]. They also preserve larger nucleosynthetic anomalies than later-formed Solar System objects [1,2]. Nucleosynthetic anomalies are commonly observed in coarse-grained igneous CAIs from CV chondrites [e.g., 2], in FUN CAIs (fractionated and unidentified nuclear effects) [3 and ref. therein], and in hibonite-rich CAIs from CM chondrites [4–7]. In contrast, the degree of nucleosynthetic variations in CAIs from other chondrite groups is not well constrained. Here we report on Ca and Ti isotopic compositions of 24 CAIs from CM, CO, and CR chondrites.

Methods: Calcium and titanium isotopic compositions were determined by secondary ion mass spectrometry using the Cameca ims-1280 at the University of Hawai‘i. The protocol was similar to that reported previously [6,7]. For Ca and Ti-rich phases (hibonite, Al,Ti-pyroxene), isotopic compositions of both elements were measured, but for Ti-poor phases (mellilite and sometimes grossite), only Ca isotopes were measured.

Samples: The CM CAIs were separated from Murchison (Field Museum specimens ME 2752 and ME 2644) and include SHIBs (spinel-hibonite-inclusions), a melilite-rich CAI (previously described in [7]); a mass-fractionated grossite-rich CAI, and two single hibonite crystals. The CO CAIs include two concentrically zoned objects (31-2 from DOM 08006 and 16-1 from DOM 08004) consisting of, from inside outward, hibonite, grossite, spinel, perovskite, melilite, clinopyroxene, enstatite, and forsterite [8,11]. The other CO CAIs studied are two hibonite-grossite-rich objects (56-1 from DOM 08006 and 26-1 from DOM 0804; reported in [8]) and the Sc-rich Orans CAI OSCAR [9]. The CR CAIs are from El Djouf 001 (MK #5), GRA 95229 (-17 #7), and Gao-Guineu (b) (FUN CAI #3). The meteorology, O and Al-Mg isotopic systematics of the CR CAIs have been previously reported in [10].

Results: CM CAIs: Of the 15 studied objects, only two have clearly resolved anomalies in 48Ca and/or 50Ti. These are a spinel-hibonite object (δ48Ca ~ 27‰, δ50Ti ~ −8‰), for which O and Al-Mg systematics are not yet known, and a single hibonite crystal (δ50Ti 4.3±2.6‰). Another single hibonite crystal is mass-dependently enriched in heavy Ca and Ti isotopes, but has no resolved nucleosynthetic anomalies.

CO CAIs: The two concentrically zoned CAIs have clearly resolved anomalies: 16-1 (δ48Ca ~ −27‰, δ50Ti ~ −30‰) and 31-2 (δ48Ca ~ 11‰, δ50Ti ~ 4‰). Hibonite, grossite, and Al,Ti-diopside were analyzed individually in both CAIs (melilite in 31-2 as well), which revealed no variations between different minerals within the same CAI. Anomalies were also found in the two hibonite-grossite-rich CAIs: 56-1 (δ48Ca ~ −10‰, δ50Ti ~ 0‰) and 26-1 (δ48Ca ~ −21‰, δ50Ti ~ −30‰). OSCAR has no resolved anomalies in 48Ca and 50Ti.

CR CAIs: No resolved anomalies were found in the 26Al-rich CAI GRA 95229-17 #7. The 26Al-poor CAI El Djouf 001 MK #5 has a large 48Ca excess (~20‰). The FUN CAI Gao-Guineu (b) #3 also has a large 48Ca excess (27‰).

Discussion and Conclusion: Our study of CAIs from three different chondrite types shows that large nucleosynthetic anomalies can be found in CAIs from all three chondrite groups, and are, therefore, not limited to CM hibonites. For a subset of the studied CAIs, Al-Mg systematics have been previously reported [7,8,10]. Combined with our new Ca and Ti isotope measurements, the data for CM, CO, and CR chondrite CAIs are generally consistent with the mutual exclusivity relationship between large nucleosynthetic anomalies and incorporation of considerable amounts of live 26Al. A possible exception may be FUN CAI Gao-Guineu (b) #3, which has a large 48Ca excess in spite of a possibly relatively high inferred 26Al/27Al ((2.0±1.7)×10−5 ) [10]).

The CO CAIs 31-2 and 56-1 have been interpreted as equilibrium condensates [11]. If true, the sizable nucleosynthetic anomalies in these two CAIs suggest that nucleosynthetic anomalies were preserved in the gas phase, likely due to large-scale nucleosynthetic heterogeneity in the early Solar System. The lack of isotopic variation between different phases would suggest that no significant dilution took place during condensation.

ISOTOPIC COMPOSITIONS OF STRONTIUM, MOLYBDENUM, AND BARIUM IN SINGLE PRESURGAR SILICON CARBIDE GRAINS OF TYPE AB FROM MURCHISON.

N. Liu1, T. Stephan2, P. Boehnke2, L. R. Nittler1, B. S. Meyer1, C. M. O’D. Alexander1, J. Wang1, R. Trappitsch2, M. J. Pellin2,3, A. M. Davis2, 1Dept. of Terrestrial Magnetism, Carnegie Institution for Science, Washington, DC 20015, USA, niu@carnegiescience.edu, 2The University of Chicago, Chicago, IL 60637, USA, 3Clemson University, Clemson, SC 29634, 4Argonne National Laboratory, Argonne, IL 60439, USA.

Introduction: AB grains are a group of presolar SiC grains that are characterized by low 12C/13C ratios (<10) with a wide range of 14N/15N ratios (~50 to 10,000). Proposed stellar sources include J-type carbon stars, born-again asymptotic giant branch (AGB) stars, novae, and Type II supernovae (SNe) [1,2,3]. A recent study of AB grains [4] showed systematic differences between 15N-rich AB (14N/15N< solar, AB1) and 14N-rich AB (14N/15N≥ solar, AB2) grains. In detail, AB1 grains show negatively correlated 26Al/27Al and 14N/15N ratios (N-Al correlation) with higher 30Si excesses (relative to AB2 grains), while AB2 grains do not show such a N-Al correlation.

Methods and Results: To better understand the sources of AB1 and AB2 grains, we analyzed 28 sub-µm- to µm-sized AB grains with a wide range of 14N/15N ratios (25 to ~6,000) for their Sr, Mo, and Ba isotopic compositions with CHILI [5]; 15 mainstream (MS) SiC grains were also measured during the same session. We obtained Mo isotope ratios in all 43 grains; correlated Sr and Ba isotope ratios were obtained in only a few cases, indicating lower efficiencies of the Sr and Ba resonance ionization schemes and/or lower Sr and Ba concentrations in the grains. We found anomalous isotopic compositions (>2σ different from solar values in at least one of the Sr, Mo, or Ba isotope ratios) in 9 of 16 AB1 (56%), 2 of 12 AB2 (17%), and all 15 MS (100%) grains. The isotopic anomalies are consistent with s-process isotopic signatures, in contrast to a previous study on AB grains, in which none of the AB grains had s-process signatures [6]. The different results could be explained by a higher degree of contamination in the previous study, as we used a focused ion beam to remove small grains adjacent to the grains of interest prior to the CHILI analysis to reduce potential contamination.

Discussions: A higher percentage of AB1 grains shows anomalous compositions compared to that of AB2 grains, providing further support for the two distinct subgroups. State-of-the-art model calculations and observations suggest that J-type carbon stars and born-again AGB stars are likely to be 15N-rich [2,7], and thus are potential stellar sources of AB1 grains. J-type carbon stars show no observable s-process elemental enhancements, while born-again AGB stars are expected to have similar or stronger s-process enhancements relative to AGB stars [2,7]. Although the normal compositions measured in some of the AB2 grains could be caused by surface contamination, the fact that a much higher fraction of AB2 grains had normal compositions than that of the MS grains from AGB stars on the same sample mounts suggests that J-type carbon stars are a dominant source for AB2 grains.

The N-Al correlation found in AB1 grains [4] strongly indicates that this subgroup came from SNe with H ingestion in the pre-SN phase that resulted in explosive H-burning in the He/C zone during the explosion [8]. The s-process Mo isotopic patterns observed in 56% of the AB1 grains, therefore, can be used to constrain the neutron-capture environment in SNe. Two regions in a SN are predicted to show s-process Mo isotope ratios [9]: the inner C/O zone as a result of neutron capture during the pre-SN phase, and a small region in the outer zone (He/C or He/N) with smaller anomalies as a result of neutron capture during the explosion. The C/O zone, however, is extremely O-rich and is unlikely to be a major contributor to the Mo budgets of the AB1 grains. In the outer zone, the explosive neutron-capture process produces a non-negligible amount of 94Nb that decays to 96Mo with a half-life of 20.3 kyr. To explain most of the AB1 grain data along the 1:1 line in the plot of δ94Mo versus δ96Mo, only <30% of Nb relative to Mo could have condensed into the grains. Interestingly, two of the grains fall off the 1:1 line with slightly enhanced 94Mo abundances, which could result from the in-situ decay of 96Nb. Since the Mo signatures in this region are produced by explosive nucleosynthesis, the predicted location and isotopic ratios depend on the explosive energy and the initial stellar mass adopted in the models. A new set of SN models is under development with a range of explosive energies, and we will compare the new models to AB1 grain data to provide constraints.

Conclusions: The comparison of the AB2 with the MS grains in this study clearly points to J-type carbon stars as a dominant source for AB2 grains. In contrast, a higher percentage of AB1 grains show anomalous isotopic compositions with s-process signatures that probably resulted from explosive neutron capture in the He/C or He/N zone of a SN, which is roughly consistent with the mixing of regions indicated by the N-Al correlation of AB1 grains [4].

THE LIFE AND DEATH OF IRON-60.


1 Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA 94550; 2 Department of the Geophysical Sciences, 3 Enrico Fermi Institute, The University of Chicago, and Chicago Center for Cosmochemistry, Chicago, IL 60637; 4 Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, DC 20015; 5 Hawai‘i Institute of Geophysics and Planetology, School of Ocean, Earth Science and Technology, University of Hawai‘i at Mānoa, Honolulu, HI 96822. (trappitsch1@llnl.gov)

Introduction: There is controversy over the initial abundance of $^{60}\text{Fe}/^{56}\text{Fe}$ in the early Solar System. While bulk analysis methods infer a low $^{60}\text{Fe}/^{56}\text{Fe}$ of $(1.01\pm0.27)\times10^{-8}$ [1], in-situ secondary ion mass spectrometry (SIMS) analyses inferred initial ratios of up $(3.8\pm0.8)\times10^{-7}$ [2] or $(7.8\pm3.7)\times10^{-7}$ [3]. While a low $^{60}\text{Fe}/^{56}\text{Fe}$ ratio is consistent with the estimated galactic background at the start of the Solar System, the high initial $^{60}\text{Fe}/^{56}\text{Fe}$ requires a supernova injection of live $^{60}\text{Fe}$ into the solar nebula. Using resonance ionization mass spectrometry (RIMS), we reanalyzed Semarkona (LL3.0) chondrule DAP1 [2], one of the samples with high inferred $^{60}\text{Fe}/^{56}\text{Fe}$, for its Ni isotopic composition.

Methods: Using the Chicago Instrument for Laser Ionization (CHILI) RIMS instrument at the University of Chicago [4], we analyzed a total of 29 spots on DAP1 for their Ni isotopes. Thirteen of these spots are on the surface of the sample, while the other 16 measurements were made inside the previously analyzed SIMS craters. While we could not determine the elemental Fe/Ni ratio in these samples using RIMS, previous SIMS measurements [2] determined this elemental ratio for the pits. Compared to the SIMS pits, which have diameters of ~20 µm, RIMS measurements were done using a 351 nm desorption laser with a spot size of ~1 µm [4]. We used four lasers to resonantly ionize Ni and one laser to nonresonantly ionize Fe isotopes, resulting in much higher sensitivity for Ni than for Fe. This way, all Ni isotopes could be measured, because we could correct $^{58}\text{Ni}$ for nonresonant $^{58}\text{Fe}$ contribution with high accuracy assuming a terrestrial $^{56}\text{Fe}/^{56}\text{Fe}$ ratio.

Results: There was a maximum contribution of <1% to the $^{58}\text{Ni}$ signal from nonresonantly ionized $^{56}\text{Fe}$. In addition, we collected off-resonance spectra, which showed that our Ni isotope measurements did not suffer from any other interference. On DAP1, the Ni isotopic measurements show a slight mass-dependent fractionation, varying from spot to spot. To remove the mass-dependent fractionation effects from the measurement and look for actual excesses in the $^{60}\text{Ni}/^{58}\text{Ni}$ ratios from $^{60}\text{Fe}$ decay, we internally normalized our measurements to the terrestrial $^{56}\text{Ni}/^{58}\text{Ni}$ ratio using an exponential mass fractionation law (see, e.g., [5]). Using the fractionation-corrected $^{60}\text{Ni}/^{58}\text{Ni}$ ratio, given as $\Delta^{60}\text{Ni}^{*}$ in ‰, and the elemental Fe/Ni ratio as determined by SIMS, we calculated an isochron with an initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio of $(4.2\pm7.6)\times10^{-5}$ (2σ, MSWD = 1.15) using an error-weighted regression [6]. This isochron is in good agreement with the low initial $^{60}\text{Fe}/^{56}\text{Fe}$ ratio by bulk methods [1]. The RIMS measurements were done on the same sample for which SIMS analysis previously showed excesses in $\Delta^{60}\text{Ni}^{*}$. High $^{60}\text{Ni}/^{58}\text{Ni}$ should have been readily found since the anomaly found by SIMS in $\Delta^{60}\text{Ni}^{*}$ is ~60‰ for the highest Fe/Ni elemental ratio reported by SIMS [2]. Our new measurements do not show any significant difference from zero, i.e., we found no excess in $\Delta^{60}\text{Ni}^{*}$.

Conclusion & Outlook: We analyzed the Semarkona DAP1 chondrule using RIMS, a sample that was previously analyzed by SIMS [2]. We found a slight mass-dependent fractionation of Ni isotopes in the sample. Correcting for this fractionation and using the Fe/Ni ratios determined previously by SIMS, results in a RIMS-determined initial $^{60}\text{Fe}/^{56}\text{Fe}$ of $(4.2\pm7.6)\times10^{-5}$. SIMS data for the same spots regressed in the same way give $(3.8\pm7.1)\times10^{-5}$, with MSWD of 15.8. Currently, we cannot determine the Fe/Ni ratio using RIMS since laser-desorbing atoms from the surface severely fractionates Fe/Ni ratios. In future analyses, we will use an ion gun or a femtosecond laser for sample removal. These techniques in combination with matrix-matched standards will ultimately allow us to determine the Fe/Ni ratio along with the isotopic composition of Ni isotopes in individual samples and further constrain the initial $^{60}\text{Fe}/^{56}\text{Fe}$ in the early Solar System.


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PETROGRAPHY AND GEOCHEMISTRY OF NORTHWEST AFRICA 11115: A NEW, ENRICHED, HIGH THORIUM BASALTIC SHERGOTTITE.

M. Melwani Daswani1, P. R. Heck1, N. D. Greber1 and R. C. Greenwood3, 1Dept. of the Geophys. Sci., University of Chicago, Chicago, IL 60637, USA, melwani.mohit@gmail.com, 2The Field Museum, Chicago, IL 60605, USA, 3Planetary and Space Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK.

Introduction: The martian shergottite meteorites show a remarkable variety in petrography and geochemical composition. Northwest Africa (NWA) 11115 is a shergottite found in Morocco in 2016 – an aliquot of the main mass (~247 g) was donated to the Field Museum of Natural History (FMNH) by T. Boudreaux [1]. We report bulk-rock major and trace element abundances of NWA 11115, oxygen isotope systematics, and petrography of a thick section, and compare the geochemistry of the recent finds to other martian meteorites.

Methods: SEM/EDS analyses were carried out at the FMNH and the University of Chicago on a thick section of NWA 11115. Approximately 31 mg of powder was fluxed with LiBO2 and then used for whole-rock chemical analyses by LA-ICP-MS at the FMNH, using NIST SRM 610 and 612 as standards. Oxygen isotope analyses were determined for two bulk aliquots by laser fluorination at the Open University.

Results: Petrography and mineralogy. The section was composed (by vol.) of ca. 9% Ol, 32% Pyx (mainly pigeonite, Wo11.12±0.5FeS4.5±0.2, Fe/Mn=30.4±2.8 (N=24)) and 55% maskelynite (An49.3±4.9±0.2AB8.3±5.2Or2.0±0.6 (N=74)), with the remainder made up of sulfides, spinels (mainly cromite), and large (up to 1 mm length) phosphates. Abundant secondary calcite (almost certainly terrestrial) infills pores, especially within cracks in and around olivine grains. Olivine phenocrysts up to 2 mm are visible, as well as Pyx+Msk melt pockets. Olivine phenocrysts are strongly zoned from core to rim (~Fas 30 to Fas 85), and smaller, groundmass Ol grains are more Fe-rich than phenocrysts.

Bulk-rock geochemistry. The bulk sample has a Mg#=57. NWA 11115 shows an enriched REE pattern, similar to other enriched shergottites, especially NWA 856 (Fig. 1). However, the whole-rock K/Th ratio (~453) is different to all other known martian meteorites and the martian surface (Fig. 2).

Oxygen isotopes. The aliquots gave an average isotopic composition of: δ17O=2.823 ‰, δ18O=4.796 ‰, Δ17O=0.329 ‰ (where Δ17O =δ17O – 0.52 δ18O), consistent with the Mars Fractionation Line [2].

Discussion: NWA 11115 is an enriched basaltic shergottite with some unusual properties. The K/Th ratio is distinctly low compared to other SNCs and the surface of Mars (analyzed by GRS, K/Th=5300 [3]), which could be related to fractional crystallization, as in some Zagami lithologies [4]. But the K abundance is not especially low compared to other SNCs. Instead, NWA 11115 is Th enriched. Most likely, the large phosphate crystals are the hosts of the Th (as well as U, also relatively enriched). Finally, while NWA 11115 is clearly altered, trace element proxies for alteration (e.g. Sr/Nd) do not correlate with other SNCs known to have experienced hot desert alteration (e.g. Dhofar 019 and Dar al Gani 476/489 [5,6]).


Figure 1. REE abundances in NWA 11115 (two averaged analyses of a glass bead; N=4+24) and other enriched shergottites, compared to CI chondrites.

Figure 2. Whole-rock K and Th in NWA 11115, martian meteorites (green crosses) and the surface of Mars (black line). Green line is a regression on all martian meteorite data except for NWA 11115, grey field is a 95% confidence interval.
NEW INSIGHTS INTO SOURCE CRATERS FOR THE MARTIAN METEORITES.

C. D. K. Herd1, L. L. Tornabene2, T. J. Bowling3, E. L. Walton1,4, T. G. Sharp3, and H. J. Melosh1, 1Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, AB, T6G 2E3, herd@ualberta.ca, 2Centre for Planetary Science and Exploration/Department of Earth Sciences, University of Western Ontario, London, ON, 3Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637. 4Department of Physical Sciences, MacEwan University, Edmonton, Alberta T5J 4S2, 5Arizona State University, School of Earth and Space Exploration, Tempe AZ, 85287-1404, 6Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana 47907.

Introduction: The martian meteorites provide invaluable information on the formation, differentiation, and geologic evolution of Mars. With the exception of ALH 84001, they crystallized within the Amazonian: the augite-rich shergottites ~2.4 Ga [1, 2]; the nakhlites and chassignites ~1.3 Ga [3]; and the youngest shergottites 575-175 Ma [3, 4]. Ejection ages indicate that ≤ 8 impact events between 0.7 and 20 Ma produced the martian meteorites [3]. Attempts at identifying the source craters for these meteorites using spectral matching [e.g., 5, 6] have met with limited success. The study of [7] assumed ages of 4.1-4.3 Ga for the shergottites, a postulation which has since been proven incorrect [e.g., 8]. The identification of rayed craters – indicative of high ejection velocities and young ages – on predominately Amazonian igneous surfaces has provided the best potential candidates [9]; however, since the visibility of rays depends on thermal contrast [9], the list of such craters are few and limited. Here we use the preservation of impactites (i.e., impact melt-bearing deposits) as an additional criterion for crater youth [10]. These additional craters, including the rayed craters, will be cross-referenced with the results of new modeling of martian meteorite impact ejection events to further constrain candidate source craters of the martian meteorites.

Modeling: Four martian meteorites were identified for which dwell times and bulk peak shock pressure have been determined (Table 1). These four meteorites cover the range of petrologic types, ages, and conditions of impact ejection. Following [11], we use the iSALE shock physics code [12-14] to simulate the dwell times and peak pressures reached during the ejection of material at greater than escape velocity from a Mars-like basaltic target following a vertical impact at 13.1 km s⁻¹. Model results are then compared to observationally inferred peak pressures and dwell times in order to constrain a size range of possible impactors. Other factors, including pre-impact burial depth, impact velocity, and impact obliquity, will be considered in future refinements to modeling.

Results: Application of the model to the four martian meteorites results in a range of impactor sizes for each; as expected, impactor size correlates with dwell time (Table 1). Impactor sizes are converted to crater sizes based on the formulation of [15]. NWA 8159 results are considered an upper limit, given current uncertainties in the dwell time estimate. The maximum crater size for Tissint is not supported by the shock petrography [16]. These results should be considered preliminary, since e.g., lower obliquity should produce smaller craters by up to a factor of two.

Discussion: Results demonstrate the potential utility of the model of [11] in narrowing the number of possible source craters for martian meteorites. At face value, our results corroborate the postulation that Tooting crater (28 km) may be the source of younger shergottites [22], and that smaller rayed craters such as Zunil (10.2 km) and Corinto (13.5 km) are excluded. However, smaller craters and narrower ranges are expected as the model is refined.


### Table 1. Ages, conditions of impact ejection, and modeling results for selected martian meteorites

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Crystallization age (Ma)</th>
<th>Ejection age (Ma)</th>
<th>Dwell time (ms)</th>
<th>P, bulk (GPa)</th>
<th>Impactor radius (m)</th>
<th>Crater diameter (km)</th>
</tr>
</thead>
</table>

*considered an upper limit
CORRELATIONS AMONG MICROSTRUCTURE, MORPHOLOGY, CHEMISTRY, AND ISOTOPIC SYSTEMATICS OF HIBONITE IN CM CHONDRITES.

J. Han1,2, M.-C. Liu1, L. Kööp1,3,5, L. P. Keller1, and A. M. Davis4,6, 1Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058, USA (jangmi.han@nasa.gov), 2ARES, Code X13, NASA Johnson Space Center, 2101 NASA Road 1, Houston, TX 77058, USA, 3Department of Earth, Planetary, and Space Sciences, UCLA, Los Angeles, CA 90095, USA, 4Department of the Geophysical Sciences, Chicago Center for Cosmochemistry, 5Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA.

Introduction: Hibonite is a primary refractory phase occurring in many CAIs, typically with spinel and perovskite [1]. Our microstructural studies of CAIs from carbonaceous chondrites reveal a range of stacking defect densities and correlated non-stoichiometry in hibonite [2,3]. We also conducted a series of annealing experiments, demonstrating that the Mg-Al substitution stabilized the formation of defect-structured hibonite [3-5]. Here, we continue a detailed TEM analysis of hibonite-bearing inclusions from CM chondrites that have been well-characterized isotopically [6-8]. We examine possible correlations of microstructure, morphology, mineralogy, and chemical and isotopic systematics of CM hibonites in order to better understand the formation history of hibonite in the early solar nebula.

Methods: Fifteen hibonite-bearing inclusions from the Paris CM chondrite [8] were analyzed using a JEOL 7600F SEM and a JEOL 8530F electron microprobe. In addition to three hibonite-bearing inclusions from the Murchison CM chondrite previously reported on [3,9], we selected three inclusions from Paris, Pmt1-6, 1-9, and 1-10, representing a range of 26Al/27Al ratios and minor element concentrations for a detailed TEM study. We extracted TEM sections from hibonite grains using a FEI Quanta 3D field emission gun SEM/FIB. The sections were then examined using a JEOL 2500SE field-emission scanning TEM equipped with a Thermo-Noran thin window EDX spectrometer.

Results and Discussion: A total of six hibonite-bearing inclusions, including two platy hibonite crystals (PLACs) and four spinel-hibonite inclusions (SHIBs), were studied. There are notable differences in chemical and isotopic compositions between the inclusions (Table 1), indicative of their different formation environment or timing.

Our TEM observations show perfectly-ordered, stoichiometric hibonite crystals without stacking defects in two PLACs, 2-7-1 and 2-8-2, and in three SHIBs, Pmt1-6, 1-9, and 1-10. In contrast, SHIB 1-9-5 hibonite grains contain a low density of stacking defects linked to an increase in MgO contents, indicating complex, disordered intergrowths of stoichiometric and MgO-enriched hibonites. From the data collected to date, we find no clear correlation between the microstructures of hibonite and its morphological and mineralogical types that reflect distinct chemical and isotopic systematics [6-8,10].

Interestingly, the presence of no or few stacking defects in hibonite from the PLACs and SHIBs are in contrast to our experimental studies that produced very high densities of stacking defects in hibonite [3-5]. Unlike our experiments, electron microprobe data from the PLACs and SHIBs hibonite grains show a strong correlation between (Ti4+Si4+) and Mg2+ cations, suggesting that coupled substitutions of (Ti4++Mg2+) and (Si4++Mg2+) for 2Al3+ inhibit the formation of defect-structured hibonite. However, our experimental studies suggest that kinetics (e.g., cooling rate) or other thermal effects also exert a strong control on the microstructures and chemical compositions of hibonite [3-5]. In Pmt1-6, elongated perovskite grains present at the hibonite grain boundaries display (121) twinning, indicative of a fast cooling (>50°C/min) after high-temperature events [11]. Therefore, the nebular microstructural characteristics of hibonite, at least in this inclusion, would not have destroyed by subsequent high-temperature annealing.

Conclusions: Our TEM observations thus far show no clear correlation in microstructures, morphological and mineralogical characteristics, and chemical and isotopic systematics of hibonites from CM chondrites. The observed variation in stacking defect densities in the hibonites may be controlled by thermal processes in the early solar nebula. A detailed TEM analysis of additional CM hibonite samples is underway to evaluate this hypothesis.

Table 1. A summary of inferred 26Al/27Al ratios and minor element concentrations from CM hibonite samples studied.

<table>
<thead>
<tr>
<th>classification</th>
<th>PLAC</th>
<th>SHIB</th>
</tr>
</thead>
<tbody>
<tr>
<td>inclusion #</td>
<td>2-7-1</td>
<td>2-8-2</td>
</tr>
<tr>
<td>(26Al/27Al)x10^-3</td>
<td>0.2±0.2</td>
<td>0.0±0.3</td>
</tr>
<tr>
<td>TiO2 (wt%)</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>MgO (wt%)</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>stacking defect density</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

STRONTIUM, MOLYBDENUM, AND BARIUM ISOTOPES IN THE MATRIX OF ACFER 094

K. L. Villalon\textsuperscript{1,2,3}, C. Floss\textsuperscript{4}, T. Stephan\textsuperscript{1,2,3}, P. Boehnke\textsuperscript{1,2}, I. Koch\textsuperscript{5}, L. Kööp\textsuperscript{1,2,3}, and A. M. Davis\textsuperscript{1,2,3,5}.

\textsuperscript{1}Department of the Geophysical Sciences, The University of Chicago, Chicago, IL, USA, \textsuperscript{2}Chicago Center for Cosmochemistry, \textsuperscript{3}Robert A. Pritzker Center for Meteoritics and Polar Studies, Field Museum of Natural History, Chicago, IL, USA, \textsuperscript{4}Laboratory for Space Sciences, Washington University in St. Louis, St. Louis, MO, USA, \textsuperscript{5}Enrico Fermi Institute, The University of Chicago, Chicago, IL, USA. E-mail: kvillalon@uchicago.edu

Introduction: Silicates are pervasive throughout the universe and are therefore integral to understanding the life cycle of matter. The silicate components of different primitive samples may represent various related stages in silicate dust evolution. Unfortunately, isotopic studies of these grains have been limited due to their small sizes (~250 nm) and analytical limitations. We have begun a thorough isotopic study of presolar silicates, GEMS (Glass with Embedded Metal and Sulfides), and Acfer 094 matrix grains with the unparalleled analytical capabilities afforded by the Chicago Instrument for Laser Ionization (CHILI)\textsuperscript{[1]} in order to reveal the ancestral connections, or lack thereof, between them. We previously reported the first trace element isotopic study of Sr, Mo, and Ba in seven Acfer 094 matrix grains\textsuperscript{[2]}. All but two measurements were isotopically normal within errors except one grain with a possibly resolved depletion in \(^{84}\text{Sr}\) and another with a possibly resolved depletion in \(^{134}\text{Ba}\) (3\(\sigma\)). Molybdenum isotopes showed a tendency towards negative delta values, similar to that observed in SiC grains from AGB stars (but lower in magnitude). Here we report new measurements on an additional seven matrix grains.

Methods: Acfer 094 is an ungrouped carbonaceous chondrite with a high abundance of presolar silicates and is considered to be one of the most primitive meteorites\textsuperscript{[3]}. Aliquots of disaggregated and size separated Acfer 094 grains were dispersed onto Au foil\textsuperscript{[4]}. The isotopic composition of trace elements Sr, Mo, and Ba were measured using CHILI, a new resonance ionization mass spectrometer designed to achieve an unprecedented lateral resolution of 10 nm and a useful yield of ~40\%\textsuperscript{[1]}. CHILI’s high spatial resolution, improved sensitivity, and ability to eliminate isobaric interferences makes it far better equipped than current SIMS instruments to resolve the isotopic composition of nanometer-sized grains. Measurements were carried out using a Nd:YLF desorption laser beam, frequency-tripled to 351 nm, and focused to ~1 \(\mu\)m\textsuperscript{[1]}.

Results: A summary of all Sr, Mo, and Ba isotopic measurements with CHILI in submicron primitive silicate matrix grains is shown in Fig. 1. No measureable Sr, Mo, or Ba were found in the matrix in preliminary measurements. EDS mapping of the sample was later used to locate phases more likely to host these elements, such as Ca-, K-, or Al-rich phases. These phases were subsequently confirmed to be carriers of Sr, Mo, and Ba while the surrounding phases contributed no signal.

Unlike the previous measurements\textsuperscript{[2]}, all seven matrix grains analyzed for this study are isotopically normal within errors for all isotopes. The trend toward negative delta values in Mo\textsuperscript{[2]} is also no longer observed with the expanded data set. Large uncertainties were found due to the small grain sizes paired with the low abundance of trace elements in silicates.

Outlook: While no anomalies were resolved in the Acfer 094 matrix grains, it is possible that resolvable Sr, Ba, and/or Mo isotopic anomalies are present in presolar silicates. We therefore plan to study these elements in presolar silicates previously identified by NanoSIMS in our Acfer 094 sample. We are also prepared to analyze the Fe and Ni isotopic in presolar silicates, matrix grains, and GEMS. Iron and Ni are highly abundant in these grains [e.g., 5]. Future analyses will benefit from the installation of a Ga ion gun in the upcoming months that will provide sub-100 nm lateral resolution. An isolation and lift-out technique has also been developed for isolating small grains\textsuperscript{[2]}.


\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Isotope patterns for Sr, Mo, and Ba measured in 14 Acfer 094 matrix grains using CHILI. Uncertainties are 2\(\sigma\). \(^{130}\text{Ba}\) and \(^{132}\text{Ba}\) not shown as too low in abundance. Gray points previously reported in [2] for reference.}
\end{figure}