VALENCES OF Ti, V and Cr in APOLLO 17 HIGH-Ti BASALTS. S. B. Simon and S. R. Sutton, Dept. Geophysical Sci., 5734 S. Ellis Ave.; Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA (sbs8@uchicago.edu).

Introduction: The presence of trivalent Ti in lunar pyroxene has been inferred from electron probe [1, 2] and spectroscopic [3, 4] analyses, even though (a) the $fO_2$ of the Ti$_2$O$_3$/TiO$_2$ buffer lies several orders of magnitude below the iron-wüstite (IW) buffer; and (b) Fe$^{3+}$ was reported [5], although [3] disputed the claim. The valences of Ti, V, and Cr in the olivine and pyroxene of lunar igneous rocks, important indicators of the $fO_2$ of their source regions, can be readily measured nondestructively by XANES (X-ray Absorption Near-Edge Structure) spectroscopy. Our initial work [6,7,8] showed little Ti$^{3+}$ but much higher than expected proportions of Ti in tetrahedral coordination; both observations call into question inferences of Ti$^{3+}$ based on Ti/Al ratios >0.5 [1, 2]. Sung et al. [4] reported absorption bands in the visible to near-infrared region of spectra A-17 pyroxene that were attributed to Ti$^{3+}$. They estimated Ti$^{3+}$ proportions to be 30-40% from electron probe analyses but assumed that Ti did not enter tetrahedral sites. XANES work on A-17 glasses and basalt compositions led Krawczynski et al. [9] to conclude that ~10% of the Ti in their source region could be trivalent, and Karner et al. [10] inferred an $fO_2$ of IW-2 for A-17 orange glass from its V valence. To see if the pyroxene and olivine in A-17 basalts do indeed contain Ti$^{3+}$ and/or reduced V and Cr, we analyzed two samples, 70017 and 74275.

Samples and Methods: One polished thin section of each sample was studied. Areas of the sections to be analyzed were documented by SEM and analyzed by energy-dispersive spectroscopy. XANES spectra were collected using the GSECARS X-ray microprobe in fluorescence mode, with a 1 µm X-ray beam. Valences were determined following the results of [11], who demonstrated that Ti K-edge XANES spectra of pure Ti$^{4+}$-bearing minerals fall into distinct valence-coordination clusters on a plot of pre-edge peak intensity vs. energy. Those with all Ti in tetrahedral coordination have high intensities and low energies, whereas those with all Ti in octahedral coordination have low intensities and high energies. Any Ti$^{3+}$ present in olivine and pyroxene is expected to be in octahedral coordination, yielding a third data cluster, pre-edge peaks with relatively low intensity and low energy. Titanium valences in unknowns were determined by applying the lever rule to mixing lines for XANES results for standards representing these three endmember occurrences. Valences are reported as values between 3 and 4, representing averages for the analytical volumes, with precisions based on spectral fitting uncertainties. The valence of V was determined from the absolute intensity of the pre-edge peak ensemble compared to glass standards as in [12]. The valence of Cr was determined using Fe-free glass standards with Cr$^{3+}$ or Cr$^{2+}$ as in [13]. For each analytical spot, spectra were collected at two to four different orientations and then merged to minimize orientation effects.

Sample petrography and mineral chemistry: 70017. The texture and mineral chemistry of this medium-grained vesicular basalt were reported by [14,15]. Its mode is 50% pyroxene, 26% plagioclase, 22% ilmenite, and minor amounts of olivine, troilite, metal, silica and mesostasis. Olivine and ilmenite crystallized before pyroxene and plagioclase. Early pyroxene is relatively Ti-, Al-rich augite; contents of these minor elements decreased as crystallization continued toward pigeonite composition [14].

74275. Also studied by [15], this sample is finer-grained than 70017. It has olivine phenocrysts, smaller pyroxene phenocrysts, and acicular armalcolite with ilmenite rims in a groundmass of augite and plagioclase. Olivine is more abundant in this sample than in 70017 (~15 vs. ~1 vol%) and more magnesian (Fo$_{76.85}$ vs. Fo$_{98.72}$). Pyroxene in this sample is richer in TiO$_2$ (3.6-6.1 wt%) than that in 70017 (1.6-3.6 wt%) [16].

Results: Preliminary XANES data for vanadium indicate mixtures of V$^{5+}$ and V$^{3+}$ for olivine and pyroxene. Average pyroxene valences are 2.75±0.07 in 70017 and 2.87±0.05 in 74275. Average V valences in olivine are lower, 2.60±0.16 in 70017 and 2.53±0.05 in 74275. More extensive results are available for Ti and Cr (50 pyroxene and 18 olivine analyses).

Valence of Ti and Cr in pyroxene. Results are summarized in Fig. 1. In 70017, Ti valence ranges from 3.65±0.08 to 3.94±0.10 and averages 3.79±0.08. For 74275, the range and average are 3.66±0.06 to 4.01±0.08 and 3.86±0.11, respectively, quite similar to 70017. The valences of Ti and Cr do not vary systematically with ferrosilite (Fs) (Fig. 1). The valence of Cr (Fig. 1b) has a wider range in 70017, 2.69±0.05 to 2.84±0.05, than in 74275, 2.81±0.05 to 2.86±0.05.

Valence of Ti and Cr in olivine. Results are summarized in Fig. 2. Just three analyses were obtained for 70017, all for olivine less magnesian than that analyzed in 74275, and containing no Ti$^{3+}$. Both Ti and Cr are more reduced in 74275 olivine than in 70017 olivine. In both samples Cr is more reduced in the olivine than in the coexisting pyroxene. As the plots show, in
pyroxene the Cr valence is ≥2.7, and in olivine it is ≤2.7. In 70017, Ti is more reduced in pyroxene (avg. 3.8) than in olivine (avg. 4.0), and in 74275 the Ti valences in olivine and pyroxene average 3.9.

**Proportions of Ti in tetrahedral coordination in pyroxene.** As in previous work [6,7,8] significant proportions are observed. Pyroxene in 74275 generally has lower proportions of tet Ti (11-27%) than that in 70017 (18-43%), likely due to its higher Al₂O₃ contents (5.0-9.6 wt% in 74275 vs. 1.3-4.9 wt% in 70017) [8].

**Discussion:** These two rocks have very similar bulk compositions but different crystallization sequences [15], accounting for the differences in pyroxene composition. Unlike that in 70017, pyroxene in 74275 crystallized before Fe-Ti oxides and plagioclase and thus has higher Al and Ti contents and lower tet Ti proportions. Although the latter feature has been associated with lower Ti⁴⁺ proportions, the range of valence of Ti in pyroxene is about the same in both samples (Fig. 1a), and it shows no correlation with Fs component, tet Ti proportions, or atomic Ti/Al ratio. It is worth noting that almost all pyroxene valence results are within error of 4.0. Pyroxene in both A-17 samples tends to have larger Ti⁴⁺ components than was found for pyroxene in A-14 aluminous basalts [7], but smaller ones than the 30-40% inferred by [4].

The large difference in average Cr valence between the pyroxene (2.83±0.02) and olivine (2.38±0.11) in 74275 is of interest. It was suggested [17] that the coarse, magnesian olivine “megacrysts” in this rock are exotic fragments; Delano and Lindsley [18] agreed with [17] that the 74275 bulk composition is not that of the parental melt but concluded that, unlike a dunite clast also found in 74275 [17], the coarse olivine grains could be related to the host rock. Our data are consistent with these suggestions that the olivine and pyx in 74275 did not crystallize from the same melt.

OXYGEN AND MAGNESIUM ISOTOPIC COMPOSITIONS OF GROSSITE-BEARING INCLUSIONS IN DOM 08004 (CO3.1) AND DOM 08006 (CO3.0) CHONDRIES. S. B. Simon1, A. N. Krot2, and K. Nagashima2.

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Introduction: Ca,Al-rich inclusions (CAIs) in the least metamorphosed chondrites show a bimodal distribution of the initial $^{26}$Al/$^{27}$Al ratio ($[^{26}\text{Al}/^{27}\text{Al}]_0$) with peaks at $\sim$0 and $\sim$5x$10^{-3}$ [1–5], most likely indicating heterogeneous distribution of $^{26}$Al in the protoplanetary disk during an apparently brief epoch of CAI formation [2]. Most CAIs in these chondrites are uniformly $^{16}$O-rich ($\Delta^{17}$O $\sim$ – 24‰) suggesting formation in a gas of $\sim$ solar composition [3,4]. The important exceptions are isotopically anomalous $^{26}$Al-poor CAIs with fractionation and unidentified nuclear effects (FUN) [5], $^{26}$Al-poor platy hibonite crystals (PLACs) [6], and $^{26}$Al-poor grossite-rich CAIs in CH chondrites showing a range of $\Delta^{17}$O, from $\sim$ ‒35‰ to $\sim$ – 10‰ [7,8]. Grossite, CaAl$_2$O$_4$, is one of the most refractory minerals predicted to condense from a cooling gas of solar composition [9]. Grossite-bearing inclusions are a relatively rare type of CAIs in most chondrite groups, except CH chondrites, the only group where they have been extensively studied [10–13]. Here, we report on the mineralogy, petrography, O and Al-Mg isotope systematics of six grossite-bearing CAIs in DOM 08004 (CO3.1) [14]) measured in situ with the UH Cameca ims-1280. For analytical conditions during SIMS measurements see [12]. Isotopic compositions of grossite-bearing CAIs in DOM 08006 (CO3.0) will be reported at the meeting.

Mineralogy and Petrography: For details, see [14].

**DOM 08004**: CAI 16-1 has a hibonite (in wt%: $\sim$0.9 MgO, $\sim$1.9 TiO$_2$)–grossite–perovskite core surrounded by the layers of spinel, melilitie ($\text{Alk}_{1.13}$), Al-diopside (0.6–9.6 Al$_2$O$_3$, 0–1 TiO$_2$), and forsterite (Fig. 1a). CAI 26-1 consists of platy hibonite ($\sim$0.7 MgO, $\sim$1.6 TiO$_2$) crystals surrounded by grossite (Fig. 1b). CAI 44-2 (Fig. 2a), 75-1 and 77-1 consist of several mineralogically-zoned bodies composed of grossite and perovskite, and surrounded by layers of spinel and melilitie ($\text{Alk}_{1.12}$). CAI 55-1 occurs inside a magnesium porphyritic olivine-pyroxene chondrule (Fig. 2b). Its core consists of grossite, melilitie ($\text{Alk}_{3.11}$) and perovskite; it is surrounded by layers of spinel+perovskite and plagioclase (Fig. 1f). The spinel layer is corroded by plagioclase and overgrown by Cr-bearing spinel. Grossite in all CAIs experienced incipient replacement by a secondary Eu-rich phase ("sec" in Figs. 1, 2).

**DOM 08006**: CAI 31-2 has a core composed of hibonite ($\sim$0.9 MgO, $\sim$1.8 TiO$_2$), grossite, and perovskite; it is surrounded by the layers of melilitie ($\text{Alk}_{2.44}$), Ti-free diopside ($\sim$0.2 Al$_2$O$_3$), forsterite (Fay) + FeNi-metal (oxidized to magnetite), and low-Ca pyroxene (Fs$_0$Wo$_{10}$) (Fig. 3a). CAI 56-1 has a corundum–hibonite ($\sim$0.6 MgO, $\sim$1.1 TiO$_2$)–grossite core surrounded by the melilitie ($\text{Alk}_{1.1}$) and Al-diopside rims. Corundum and hibonite are corroded by hibonite and grossite, respectively. CAI 99-1

![Fig. 1. BSE images of the $^{26}$Al-poor grossite-bearing CAIs 16-1 and 26-1 from DOM 08004 (CO3.1). Hereafter: cor = corundum; cpx = high-Ca pyroxene; grs = grossite; hib = hibonite; mel = melilitie; pv = perovskite; px = low-Ca pyroxene; sec = secondary phase; sp = spinel.](image-url)
Magnesium isotopes: Hibonite and grossite in CAIs 16-1 and 26-1 show no resolvable excesses of $^{26}$Mg*, $(^{26}\text{Al}/^{27}\text{Al})_0 < 5.7 \times 10^{-7}$ and $< 6.8 \times 10^{-7}$, respectively. Grossite in CAIs 44-2, 51-1, 75-1 and 77-1 shows large $^{26}$Mg* excesses correlated with their Al/Mg ratios, corresponding to inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ of $(4.4 \pm 0.3) \times 10^{-5}$, $(4.0 \pm 0.3) \times 10^{-5}$, $(4.5 \pm 0.3) \times 10^{-5}$ and $(4.3 \pm 0.3) \times 10^{-5}$, respectively. The $(^{26}\text{Al}/^{27}\text{Al})_0$ values systematically lower than the canonical ratio are probably due to use of an improper Al/Mg sensitivity factor for grossite, that was assumed to be the same as for hibonite [3].

Discussion: The $^{16}$O-depleted compositions of grossite and melilite in DOM 08004 CAIs may have resulted from postcrystallization exchange during fluid-rock interaction on the CO chondrite parent body [15]. The alteration appears to not have affected the Al-Mg systematics of the CAIs. Therefore, the inferred $(^{26}\text{Al}/^{27}\text{Al})_0$ likely reflect the heterogeneous distribution of $^{26}$Al in the CAI-forming region. The $^{26}$Al-poor CAIs could have formed prior to addition of $^{26}$Al to the protoplanetary disk.

DIVERSE ALTERATION OF DOM 08006 (CO3.0) AND DOM 08004 (CO3.1) AND ITS EFFECT ON OXYGEN ISOTOPIC COMPOSITIONS OF GROSSITE-BEARING REFRACTORY INCLUSIONS. A. N. Krot1, K. Nagashima1, and S. B. Simon21HIGP/SOEST, University of Hawai‘i at Mānoa, Honolulu, HI 96821, USA (*sasha@higp.hawaii.edu); 2Dept. of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637, USA.

Introduction: Most Ca,Al-rich inclusions (CAIs) in chondrites of petrologic type \( \leq 3.0 \) (CO, CR, CM) are uniformly \(^{16}\text{O}\)-rich \((\Delta^{17}\text{O} \approx -24\%\)) suggesting formation in a gas of approximately solar composition [1, 2]. In contrast, melilite and anorthite in CAIs from CO and CV chondrites of higher petrologic type \((\geq 3.1)\) are often \(^{16}\text{O}\)-depleted to various degrees [3,4], indicative of postcrystallization exchange with an \(^{16}\text{O}\)-poor external reservoir. The place and mechanism of this exchange (gas-melt or gas-solid in the nebula vs. fluid-rock on the parent bodies) remain controversial [4–6]. In our companion abstract [7], we reported on the mineralogy, petrography and O-isotope compositions (only in DOM 08004) of grossite-bearing CAIs in DOM 08004, 6 (CO3.1) and DOM 08006, 56 (CO3.00) (classification is based on \(\text{Cr}_2\text{O}_3\) contents in chondrule ferroan olivines [8–10, this study]). In DOM 08004, grossite-bearing CAIs are isotopically heterogeneous with grossite \((\Delta^{17}\text{O} = -11\%\) to \(0\%\)), and, in most cases, melilite \((\Delta^{17}\text{O} = -15\%\) to \(-1\%\)) being \(^{16}\text{O}\)-depleted relative to hibonite, clinopyroxene, and Al,Ti-diopside \((\Delta^{17}\text{O} \approx -24\%\)). In DOM 08004, grossite experienced incipient replacement by Fe-rich phases(s); in DOM 08006, it is petrographically pristine. Both meteorites experienced asteroidal alteration resulting in formation of phyllosilicates and abundant magnetite [9–12]. To understand possible effect of this alteration on the O-isotope compositions of grossite-bearing CAIs, we studied secondary mineralization of DOM 08004 and 08006 by the UH field emission electron microprobe JEOL JXA-8500F. Oxygen-isotope compositions of magnetite to be measured \textit{in situ} with the UH Cameca ims-1280 will be reported at the meeting.

Secondary mineralization in DOM 08004 (CO3.1): Most Fe,Ni-metal nodules in chondrules are pseudomorphically replaced by Cr-bearing magnetite and Ni-rich metal, and often overgrown by clean Cr-free magnetite (Fig. 1a). Chondrule mesostasis is partially replaced by phyllosilicates. The most extensive alteration was found in silica-bearing pyroxene chondrules, in which silica is nearly completely pseudomorphically replaced by Fe-rich hydrous phase(s) (in wt%, \(26.5\) \(\text{SiO}_2, 0.93\) \(\text{Al}_2\text{O}_3, 61.5\) \(\text{FeO}, 0.62\) \(\text{MnO}, 4.6\) \(\text{MgO}, 0.2\) \(\text{CaO}, 0.14\) \(\text{Na}_2\text{O}, \Sigma = 94.5\); “sec” in Fig. 1b). Some olivines in type I and type II chondrule fragments are overgrown by nearly pure fayalite (Figs. 1c,d). Matrix and fine-grained chondrule rims contain abundant submicron-sized grains of ferroan olivine, and are occasionally crosscut by fayalite veins (Fig. 1b). In addition, the matrix contains abundant coarse euhedral-to-subhedral magnetite grains associated with Ni-rich metal and

Fig. 1. Backscattered electron (BSE) images of secondary mineralization in DOM 08004 (CO3.1). \textit{met} = Fe,Ni-metal; \textit{mgt} = magnetite; \textit{ol} = olivine; \textit{phyl} = phyllosilicates; \textit{px} = low-\(\text{Ca}\) pyroxene; \textit{sec} = secondary Fe-rich hydrous phase(s); \textit{sf} = sulfide; \textit{sil} = silica.
troilite; Fe,Ni-carbides are exceptionally rare. Texturally and mineralogically similar secondary mineral assemblages have been described in MAC 88107 (CO3.1-like) and Kaba (CV3.1) [6,13]. DOM 08004 is brecciated and contains fragments of nearly completely hydrated chondritic clasts.

**Secondary mineralization in DOM 08006 (CO3.00):** Alteration of opaque nodules and mesostasis in chondrules is similar to that in DOM 08004. Matrix and fine-grained chondrule rims, however, contain abundant Fe,Ni-carbides (Figs. 2a–c), and, occasionally, crosscut by Fe,Ni-carbide veins (Fig. 2d); no secondary fayalite was found. In addition, the matrix contains abundant rounded magnetite nodules and coarse euhedral-to-subhedral magnetite grains associated with Ni-rich metal, troilite, pentlandite, and Fe,Ni-carbides. Texturally and mineralogically similar carbide-magnetite-bearing assemblages have been described in Semarkona (LL3.0) [14] and ALHA 77307 (CO3.0) [15]. DOM 08006 is brecciated and contains fragments of thermally metamorphosed chondritic material.

**Discussion:** Based on our mineralogical observations of DOM 08004, and thermodynamic analysis and isotopic data reported for fayalite-magnetite assemblages in Kaba and MAC 88107 [6, 13, 16], we infer that DOM 08004 experienced relatively high-temperature (±100–300°C) hydrothermal alteration at a low water/rock ratio (<0.2). Krot and Nagashima [6] showed that anorthite and melilite in Kaba CAIs experienced O-isotope exchange with an asteroidal fluid responsible for the formation of fayalite and magnetite in that meteorite. We suggest that the O-depleted compositions of grossite and melilite in the DOM 08004 CAIs [7] could have resulted from postcrystallization isotope exchange during fluid-rock interaction on the CO chondrite parent body. A3°O value of the fluid will be constrained by O-isotope compositions of fayalite and magnetite in DOM 08004, to be measured. DOM 08006 appears to have experienced relatively low temperature, Semarkona-like alteration, resulting in formation of carbide-magnetite assemblages. Therefore, it is expected that grossite-bearing CAIs in DOM 08006 have retained their initial O-isotope compositions. SIMS measurements of these CAIs are in progress and will be reported at the meeting.


Fig. 2. BSE images of secondary mineralization in DOM 08006 (CO3.0). Region outlined in “b” is shown in detail in “c”. crb = Fe,Ni-carbides; FGR = fine-grained rim; mgt = magnetite; ol = olivine; phyl = phyllosilicates; px = low-Ca pyroxene; sf = sulfide.
Introduction: The L-chondrite parent body breakup (LCPB) in the asteroid belt ~466 Ma ago produced ejecta that was discovered as >100 fossil L-chondrite meteorites (1-21 cm in diameter) in Sweden and abundant micrometeorites worldwide within post-LCPB Middle Ordovician sediments [1]. Elemental and oxygen isotope composition of relict chrome-spinel from the fossil meteorites confirm that they are L-chondritic [2-4] except one ungrouped achondrite, Österplana 065 (Öst 065) [5-6]. Whole-rock ε²⁴Cr and Δ¹⁷O values and elemental composition of chromite grains from Öst 065 show that the meteorite is different from any previously known meteorites [6]. The similarity of the cosmic-ray exposure age of Öst 065 [5] and fossil L chondrites [7] most probably suggests that they are related and Öst 065 could be a piece of the impactor that hit the L-chondrite parent body. Additional evidence for this hypothesis could be provided by the study of the shock history of relict chrome-spinel grains from Öst 065. Shock features of two fossil L chondrites were recently studied by comparing nanoscale features between chromite grains in fossil L chondrites as well as in recent L-chondrite falls/finds [8].

Here, we present a study of shock features in chrome spinels from the fossil ungrouped achondrite Öst 065. We present results from Raman spectroscopy and TEM of Öst 065 chrome spinel and compare with the features in chromite from highly shocked recent L chondrites.

Samples & Methods: We studied polished chrome-spinel grain mounts from Öst 065 using a HORIBA LabRAM HR Evolution confocal Raman system at the NUANCE facility, Northwestern University. A 473 nm Ar⁺ laser was focused to ~1 µm spot and spectra were accumulated for 120 sec. Raman spectra were obtained from 12 chrome-spinel grains. A TEM lamella was then prepared from one of the chrome-spinel grains using a Zeiss 1540XB FIB-SEM at the Electron Microscopy Center (EMC), Argonne National Laboratory (ANL). The TEM lamella was then studied using a FEI Tecnai F20ST TEM equipped with an EDAX SDD EDS detector also at EMC. Quantitative TEM-EDS analysis was performed by measuring the k-factors for Cr, Fe, Mg and Al on the UWCr-3 chromite standard [3]. For reference, highly shocked L chondrites Tenham (FMNH ME 2617 #4) and Catherwood (FMNH ME 3066 #2) were studied [8].

Fig. 1: Backscattered electron (BSE) image of a chrome-spinel grain from Öst 065. The region where the FIB lamella was prepared is shown by an open rectangle. Exsolution-like weathering-enhanced shock features are indicated by arrows.

Fig. 2: BSE image of a highly fractured chromite grain from Tenham. Oliv = Olivine; Plg = Plagioclase; Chr = Chromite; SMV = Shock melt vein.

Results: All chrome spinels from Öst 065 are heavily fractured and show planar features (Fig. 1). The fracturing is similar to the one in chromite in Tenham (Fig. 2) and Catherwood. In backscattered electron images of Öst 065 chrome-spinel features resembling mineral exsolution lamellae along planar fractures are apparent (Fig. 1). Chrome-spinel grains from
Öst 065 have distinct Raman spectra peaks at ~717 cm\(^{-1}\) and ~605 cm\(^{-1}\). In comparison, the chromite grains from Tenham and Catherwood have a distinct peak between 686-688 cm\(^{-1}\) and secondary peaks at ~600 cm\(^{-1}\) and 496-500 cm\(^{-1}\) (Fig. 3). This is expected as the elemental compositions of chrome spinel from Öst 065 and chromite from L chondrites are different. There is no difference between the Raman spectra from the host chrome spinel and the mineral exsolution-like features along the planar fractures in Öst 065 (Fig. 3). No xieite, a high-pressure phase of chromite, was detected within the 12 studied chrome-spinel grains from Öst 065. The TEM sample from the Öst 065 chrome-spinel grain shows planar fractures and many dislocations and defects throughout the lamella (Fig. 4). The dislocation density (1x10\(^{13}\) m\(^{-2}\)) is a factor of two lower than in a chromite from Tenham (2x10\(^{13}\) m\(^{-2}\)) outside a shock-melt vein (SMV) [Fig. 2; 8]. In the Öst 065 chrome-spinel grain the planar fractures are along (311) compared to (011) in Tenham chromite. In the TEM images, the mineral exsolution-like features along the planar fractures have a very irregular boundary (Fig. 4). These features are most probably due to terrestrial weathering which is indicated by higher concentrations of ZnO (~0.7 wt%) and MnO (~1 wt%) measured with TEM-EDS. The composition of the unweathered volume of the chrome spinel and the weathered features also differ in the Cr/Fe ratios: ~1.5 and ~1.8, respectively. The studied chrome-spinel grain is a single crystal with a diffraction pattern consistent with cubic spinel (Fd\(\bar{3}\)m) structure. There is no difference in the diffraction pattern between the unweathered and weathered part. No polycrystallinity, like in chromites from SMV of highly shocked Tenham and Catherwood meteorite was observed.

**Discussion:** The high density of fractures in Öst 065 chrome spinel confirms that it is highly shocked. Similar abundant planar features are not visible in SEM images of chromite from highly shocked L chondrites Tenham and Catherwood. The planar features in Öst 065 chrome spinel are most likely shock-produced and were enhanced by weathering and leaching processes during terrestrial residence in the marine sediment. The similarity of the planar fractures and dislocation density between Öst 065 and Tenham chrome spinel suggests that Öst 065 was also heavily shocked possibly up to shock stage S6. The chrome-spinel grain is certainly not from a SMV within Öst 065. Typically only about ~2% of all chromite or chrome spinel in a highly shocked meteorite are high-pressure polymorphs from a SMV [8]. Thus more than 100 chrome-spinel grains from Öst 065 would need to be studied to find one. However, chrome spinel from SMVs may also have been preferentially destroyed during sediment diagene-

![Fig. 3: Stacked Raman spectra of chrome spinel from Öst 065 and chromites from highly shocked L6 chondrites Tenham and Catherwood.](image)

![Fig. 4: BF-TEM image of Öst 065 chrome spinel. Arrows point to the weathering-enhanced shock features along the planar fractures. Inset: Selected area electron diffraction pattern.](image)

**Conclusion:** We conclude that the presence of abundant weathering-enhanced planar shock features along with a high density of planar fractures and dislocations such as observed in Öst 065 chrome spinel (Fig. 1,4) is good indicator of high shock state (up to S6) of fossil meteorites. Thus, our conclusion is consistent with the hypothesis that Öst 065 was possibly a piece of the impactor causing the LCPB.

**References:**
IMPACT FRAGMENTATION AND DEVELOPMENT OF THE LUNAR MEGAREGOLITH. S. E. Wiggins¹, B. C. Johnson¹, E. A. Silber¹, T. J. Bowling², and H. J. Melosh¹, ¹Department of Earth, Environmental, and Planetary Sciences, Brown University, 324 Brook Street, Providence, RI 02912, USA. (Sean_Wiggins@Brown.edu). ²Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637, USA. ³Department of Earth, Atmospheric, and Planetary Sciences, Purdue University, 550 Stadium Mall Drive, West Lafayette, Indiana 47907, USA.

Introduction: Understanding impact fragmentation and how megaregolith develops is paramount to our understanding of the thermal, magmatic, and hydrologic evolution of ancient planetary crusts [1,2]. The Lunar megaregolith remains as a pristine example of an ancient planetary crust and is thought to be composed of a thin regolith, 2-3 km of ballistically emplaced ejecta, and ~10 km of structurally disturbed fragmented crust [1]. Recent results from the GRAIL missions suggest that the lunar crust is highly porous [3] and that this porosity extends to depths of 10-25 km [4]. Although it is generally accepted that the megaregolith is the product of impact cratering, the dynamics of impact fragmentation and the dynamics of the megaregolith production have received little attention [5]. Here we estimate the extent of fragmentation and fragment sizes produced by lunar impacts as a first step toward understanding the production of lunar megaregolith. Although we focus on in situ fragmentation, estimating the sizes of ejected fragments will be the focus of future work.

Methods: We simulated impacts of spherical basalt impactors with a Moonlike target at 15 km/s using the iSALE shock physics code [6,7,8]. We varied the diameter of impactors from 10 m to 10 km, while keeping a resolution of 10 cells per projectile radius. We also produced runs at resolutions of 5 and 20 cells per projectile radius and found that our results are not resolution dependent. We use the ANEOS equations of state of basalt for both the impactor and the target [9]. We estimate fragment sizes using the Grady-Kipp fragmentation model [10] recently implemented in iSALE [11]. The Grady-Kipp fragmentation model is a dynamic model that tracks the damage caused by tensile stresses. The Weibull parameters used are k=10\(^{13}\) and m=9.5. These parameters produced the best fit to results of laboratory impact fragmentation experiments [11].

Results: An impact produces an expanding hemispherical shockwave in the target that is followed by a rarefaction wave. This rarefaction wave can produce tensile stresses in the material, causing dynamic fragmentation. Fig. 1-A and 1-B (10 and 100 m diameter impactors) show a nearly hemispherical zone where material is fragmented by this tensile pulse. The near surface shows additional structure consistent with an interference zone and spallation [12]. The size of this hemispherical zone scales nearly linearly with impactor size. As the size of the impactor increases further to 1 km (Fig. 1-C) the role of increasing overburden becomes apparent. When scaled by the size of the impactor, the region in which the rarefaction causes tensile failure becomes smaller until it can no longer be seen (Fig. 2). This zone is composed of fragments that are meter to tens of meters in scale regardless of impactor size (Fig. 1). The Grady-Kipp fragmentation model predicts that higher strain rates will produce smaller fragments (Fig. 1). Thus, the relatively constant fragment size demonstrates that strain rates in the rarefaction are independent of impactor size far from the point of impact. Although the impact by the 10 km diameter impactor causes limited fragmentation at depth relative to its size when compared to the smaller impactors (Figs. 1, 2), the near surface zone contains fragments 10 m to 1 km in size extending far away from the contact site and to a depth around 10 - 20 km.

Closer to the point of impact, especially directly beneath the point of impact (r=0), fragment size has a monotonic dependence on impactor size. This suggests that the strain rates in the rarefaction depend on impactor size in the nearfield (close to the point of impact) but that they are insensitive to changes in impactor size further from the impact point. This is consistent with recent discussion of shock rise times and dwell times experienced by the Martian meteorites [13].

The current implementation of Grady-Kipp fragmentation model only tracks accumulation of fracture area when material is in tension. In all frames of Fig. 1 and in Fig. 2 there are zones of large fragment sizes adjacent to the transient crater. This material becomes fractured predominantly through shear failure rather than tensile failure. Thus, the fragment size estimates in these regions are an upper bound and should be viewed with skepticism. An accurate fragment size calculation for this region will require estimates of how fracture area accumulates during shear failure. This may be the subject of future work.

Our preliminary results suggest that impacts could efficiently fracture the lunar crust to depths of ~20 km and the crust would be broken into blocks a few meters in scale. Future work will explore how variations of the Weibull parameters and impact velocity change these results.

Acknowledgements: We gratefully acknowledge the developers of iSALE-2D, including Gareth Collins, Kai Wünneumann, Dirk Elbeshausen, and Boris Ivanov.

Figure 1 (Left). Material colored according to average fragment size. The 10 m, 100 m, and 1 km impactor diameter simulations are given in A, B, and C, respectively. The plots only show fragments for material that was at least 99% damaged. Therefore, the white spaces in the fractured field represent material that is less than 99% damaged.

Figure 2 (Below). Material colored according to average fragment size for the 10 km diameter impactor simulation. The larger overburden pressure at great depths leads to a markedly different fracture field shape when compared to the smaller impact in Fig. 1. Note that the scale bar here is quite different than those of Fig. 1, going to fragment sizes up to $10^4$ m. The fragment sizes do exceed this level, but only in the shear damage zone.
THE ROLE OF OBLIQUITY IN POST-NOACHIAN MARTIAN SURFACE CONDITIONS.  M. Mansfield and E. Kite, University of Chicago Department of Geophysical Sciences, 5734 S. Ellis Ave., Chicago, IL 60637, meganmansfield@uchicago.edu

Introduction: Late-stage Martian alluvial fans suggest the presence of liquid water on post-Noachian Mars about 3.5 Gya[1], but by the late Noachian most of the conditions favorable to warm and wet climates no longer existed: much of Mars’s atmosphere was lost before the Noachian and the Martian dynamo shut down around the mid-Noachian[2,3]. Insolation changes driven by orbital variability could offer a potential explanation for why late-stage Martian rivers were able to form under these unfavorable conditions[4]. We seek to understand the role of orbital variability in the post-Noachian Martian climate.

Modeling: To investigate the influence of orbital variability on post-Noachian surface water, physically consistent orbital histories were constructed using the mercury6 N-body integrator [5] and an obliquity code [6]. The orbital histories include periodic variations in orbital parameters, and most importantly include changes in obliquity, which for Mars has jumped from low mean values around 20° to high mean values around 40° between two and four times in its history[7]. These orbital histories were combined with solar brightening and a variety of estimates of Martian atmospheric loss to produce potential insolation histories, which were then used to determine the surface energy balance of a hypothetical Mars surface covered in water ice at 273 K[8,9]. Additionally, melting was only allowed to occur at obliquities greater than 40°, because the fluvial features of interest are located at low latitudes and water ice on the surface of Mars is most stable near the equator only at high obliquity[10]. At low obliquity, water ice on the surface of Mars is most stable at the poles[10].

To be a possible explanation of Martian surface features, these energy balance histories must fit three geologic constraints. First, sediment transport in post-Noachian deltas indicates that liquid water must have been present for at least 10 kyr[11]. Second, the presence of olivine in the river networks means that liquid water must not have been present for longer than 10 Myr during the most recent melting period[12]. Additionally, counts of craters interbedded in post-Noachian alluvial fans indicate that the total time during which periods of melting occurred must have been at least 10 Myr[13].

Results: Preliminary results indicate that the rate of Martian atmospheric loss has a strong influence on favorability of surface conditions toward the presence of liquid water. Significant melting occurs only in cases where the Martian atmosphere was relatively thick 3.5 Gya. However, this result will be affected by values chosen for the albedo and thermal inertia of Martian water ice. The extent to which these two factors influence the potential of Mars to host liquid water is being determined. Additionally, the original model examined only a flat horizontal surface, while the water source regions for the alluvial fans could be better modeled by sloping surfaces. The difference between the insolation received by horizontal and sloping surfaces is also being investigated.

MOLECULE-FREE REE ABUNDANCES IN HIBONITE BY SIMS-SSAMS. E. E. Groopman1,2, L. Kööp3, K. S. Grabowski2, and A. J. Fahey4 1National Research Council Postdoctoral Fellow, 500 Fifth Street NW, Washington, DC 20001 (evan.groopman.ctr@nrl.navy.mil) at 2Materials Science & Technology Division, U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375. 3Dept. of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637. 4Microscopy & Surface Analysis, Corning, Inc., Corning, NY 14831.

Introduction: Rare Earth element (REE) abundances in calcium-aluminum-rich inclusions (CAIs) reflect oxygen fugacity and fractionation processes present during their formation. In situ analysis of REEs in small (<100 µm) grains is possible with Secondary Ion Mass Spectrometry (SIMS), though it is complicated by the presence of molecular isobars, especially oxides, over the heavy REEs (HREE, see Figure 1). High mass resolving power is not sufficient to separate these interferences. To achieve percent-level uncertainties in REE abundances by SIMS, time-intensive calibration of the oxide-to-atomic-ion yields (MO+/M+) must be performed while biasing the sample voltage, which reduces all ion yields, but suppresses molecules more intensely than atomic ions [1–3]. Ion intensities are then measured on the tails of the energy distributions, thus the overall yield is at least one order of magnitude lower than without a bias voltage, but the interferences are minimized. Abundances are further deconvolved through a least-squares fit of some 47+ atomic and oxide masses, which relies upon knowing the isotopic abundances a priori. Resonance Ionization Mass Spectrometry (RIMS) can eliminate many of these issues, however only 2 to 3 elements may be typically measured in an analysis before laser retuning is required. Using a Single-Stage Accelerator Mass Spectrometer (SSAMS) connected to the output of a SIMS instrument, we are able to directly measure the REEs in standards and samples without molecular interferences.

Methods: The NRL SIMS-SSAMS consists of a Cameca ims 4f SIMS connected to a National Electrostatics Corporation (NEC) SSAMS, both significantly modified [4]. 4.5 keV ions from the SIMS are accelerated by 300 kV in the SSAMS and transit a gas stripping cell filled with Ar where collisions with the gas dissociate molecules. Molecular fragments or atomic ions are selected magnetically and electrostatically on the high-voltage “Deck” following the stripping cell. Electrostatic peak switching (EPS) allows for the selection of masses up to ±6.5% of the Deck magnet’s central mass. An electron multiplier (EM) counts the high-energy ions.

Wavelength- & Energy-Dispersive X-Ray Spectroscopy (WDS; EDS; U. Chicago) were used to quantify the major and minor elements in polished chips of Madagascar hibonite (MH; Table 1). The NRL SIMS-SSAMS was used to measure the REEs, Ba, and Hf from chip G4 of MH, using NIST Standard Reference Material (SRM) 610 as a standard [5]. While not an ideal matrix match, the ion yields of REE+ relative to Ca+ have been found to be similar between phosphates, silicates, and hibonite [1,2]. The La abundance of MH, quantified by WDS, was used as an anchor for the REE abundances measured by SIMS-SSAMS. Four analyses each of the light REE (LREE) and HREE from two

Table 1: WDS & EDS quantification of different MH chips (wt. %). Average for each chip shown, plus mean of all analyses.

<table>
<thead>
<tr>
<th>Chip</th>
<th>MgO</th>
<th>Al2O3</th>
<th>CaO</th>
<th>TiO2</th>
<th>FeO</th>
<th>La2O3</th>
<th>CeO3</th>
<th>ThO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>2.46</td>
<td>77.40</td>
<td>5.58</td>
<td>2.92</td>
<td>4.85</td>
<td>2.14</td>
<td>3.45</td>
<td>1.20</td>
</tr>
<tr>
<td>G2</td>
<td>2.36</td>
<td>77.91</td>
<td>5.84</td>
<td>2.98</td>
<td>4.79</td>
<td>1.98</td>
<td>3.25</td>
<td>0.89</td>
</tr>
<tr>
<td>G4</td>
<td>2.47</td>
<td>77.29</td>
<td>5.65</td>
<td>3.00</td>
<td>4.85</td>
<td>2.10</td>
<td>3.51</td>
<td>1.13</td>
</tr>
<tr>
<td>Mean</td>
<td>2.45</td>
<td>77.42</td>
<td>5.64</td>
<td>2.96</td>
<td>4.84</td>
<td>2.11</td>
<td>3.44</td>
<td>1.13</td>
</tr>
<tr>
<td>1σ</td>
<td>0.05</td>
<td>0.29</td>
<td>0.11</td>
<td>0.08</td>
<td>0.04</td>
<td>0.07</td>
<td>0.25</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure 1: Mass scan of Madagascar hibonite on SIMS EM. Gd isotopes (measured with SSAMS) in red.
spots were performed with a 10 nA, 15 keV $^{16}$O Köhler beam focused on a 65-µm-sized spot. From a 150 µm imaged field, a 100 µm aperture was used to limit the analyzed area at the crater centers to ~40 µm to avoid crater wall effects. Higher transmission would be achieved without this aperture. Two Deck magnetic fields were used to measure the REE, centered on mass ~146.5 u for LREE and mass ~166.5 u for HREE. EPS was used to select $^{139}$Ba, $^{149}$La, $^{146}$Ce, $^{141}$Pr, $^{146}$Nd, $^{147}$Sm, $^{152}$Sm, $^{152}$Eu, $^{155}$Gd, and $^{156}$Gd for LREE; and $^{155}$Gd, $^{158}$Gd, $^{159}$Tb, $^{163}$Dy, $^{166}$Ho, $^{166}$Er, $^{169}$Tm, $^{172}$Yb, $^{175}$Lu, and $^{178}$Hf for HREE. Gd isotopes were used to check for fractionation between the two Deck fields. Analyzed isotopes were chosen to be the most abundant species lacking or with minimal nuclear isobars. An Ar flow rate of 0.3 standard cubic centimeters per minute (SCCM) was used during the measurements, as this satisfactorily eliminated molecular isobars in NIST610 glass (Figure 2) where all elements are of roughly equal abundance. In hibonite, the oxide isobars over HREE are relatively more intense, so 0.3 SCCM was chosen over 0.2 SCCM as a precaution, even though it further lowered transmission.

**Results:** The CI chondrite-normalized [6] REE elemental abundance pattern in MH is shown in Figure 3, ranging from 0.26 ± 0.01 at. % La to 6.2 ± 3.5 at. ppm Tm, Hf and Ba abundances are 1.0 ± 0.2 and 8 ± 0.4 at. ppm, respectively, though the Ba concentration in NIST610 was found to be heterogeneous spot-to-spot, limiting its usefulness in determining Ba’s relative sensitivity. Our measurements qualitatively agree with those reported in [2,7] for MH determined by spark source mass spectrometry, neutron activation, and SIMS, though we have additionally directly measured Ba, Gd, Er, Tm, Lu, and Hf. Our abundances are ~5× lower than previously measured for MH, either a reflection of heterogeneous concentration in different samples or our increased ability to remove molecular isobars. Lu is enhanced over Yb by ~10× relative to an extrapolation from HREE, though this feature has also been observed in the meteoritic HAL hibonite [8,9]. Gd and Sm isotope ratios matched terrestrial composition, within uncertainties. Counting statistics were the largest component of the total propagated uncertainties.

**Discussion:** We have directly measured the REE abundances in MH by SIMS-SSAMS. These measurements provide high sensitivity, even to the low-abundance HREE, and enable their quantification from single analysis spots. This analysis, no more complex than a routine SIMS measurement, would facilitate greater throughput of CAIs and other samples where REEs are of interest, e.g. [8-10]. The ability to directly measured REEs free of molecules also facilitates REE imaging. These measurements allow MH to be used as a reference for REE measurements of CAIs and presolar grains.


![Figure 2: Gd isotope ratio deviation vs. Ar flow rate. Interferences are labeled.](image1)

![Figure 3: CI chondrite-normalized REE abundances in Madagasc hibonite chip G4 by SIMS spot analysis.](image2)
**Introduction:** PLAty hibonite Crystals (PLACs) and isotopically related hibonite-rich CAIs (i.e., non-platy hibonite crystals and hibonite aggregates; hereafter collectively referred to as PLAC-like CAIs) have the largest nucleosynthetic anomalies of all materials believed to have formed inside the Solar System (e.g., variations >100‰ in 50Ti and 48Ca [1–3]). This and their 26Al-poor character have been attributed to an early formation, prior to a widespread distribution of 26Al and large-scale homogenization of nucleosynthetic components in the solar nebula [2,3]. As PLAC-like CAIs may be among the first materials to have formed inside the Solar System, they are key samples to search for evidence of irradiation by cosmic rays, which may include a record for an early active Sun [e.g., 4,5]. Evidence for this would be found in the presence of noble gas isotopes created by spallation inside PLAC-like CAIs (in addition to those produced by exposure to cosmic rays in the meteoroid phase). Recently, we reported high cosmogenic 21Ne and 3He in two PLAC-like CAIs from the Murchison meteorite (PLACs 28 and 77, analyzed in bulk) [6]. These high gas amounts suggest that at least one of the two grains experienced a precompaction exposure to cosmic rays. However, since some components in the Murchison meteorite appear to have been exposed to cosmic rays in the parent body regolith [7,8], it was unclear if the excess 3He and 21Ne is the result of exposure in the regolith or in the nebula.

To investigate whether high amounts of cosmogenic 21Ne and 3He are characteristic of PLAC-like CAIs, we have studied 18 additional PLAC-like CAIs for He and Ne isotopes. To better understand whether the high gas amounts are due to regolith exposure, we have also analyzed other components from the same Murchison acid residue (i.e., spinel-hibonite inclusions, SHIBs, N=5, and single grains of spinel, N=3). Here, we present preliminary results.

**Samples and Methods:** The samples were picked from the same Murchison HCl-HF-treated density separate of the Murchison meteorite (ME 2752, Field Museum of Natural History) as PLACs 28 & 77, which we presented previously [6]. All samples were placed on carbon tape for SEM imaging and EDS analyses. The morphology of the PLAC-like CAIs resembles those presented in [3], and includes platy and irregular, non-platy single grains and hibonite aggregates. SHIBs are typically dense, round objects, and the shapes of spinel crystals range from platy to octahedral. The sample heights (i.e., smallest dimensions) span the following ranges: Single hibonite crystals 3–39 µm (av. 13 µm), hibonite aggregates 18–45 µm (av. 28 µm), single spinel crystals 4–214 µm (av. 84 µm), SHIBs 18–65 µm (av. 38 µm). After removal from the tape, the grains were cleaned in acetone, isopropanol and water, dried and pressed into a clean gold foil. To remove adsorbed air molecules, the grains were baked for 3 days at 80°C and pumped down for over a week prior to noble gas analysis. Noble gases were extracted with a Nd-YAG 1064 nm laser and He and Ne isotopes were measured with an ultra-high-sensitivity noble gas mass spectrometer at ETH Zurich [9]. The analytical protocol was developed specifically for analyses of low gas amounts [10]. To convert He and Ne amounts to concentrations, the sample masses were estimated using the density of hibonite and spinel and volumes estimated from SEM images obtained at varying tilt and rotation angles. For simplicity, we use maximum volumes calculated as prisms (base × maximum height) enveloping the true shapes of the particles. Therefore, all concentrations and exposure ages are minimum values. We estimate that for some grains, ages and concentrations could be up to a factor of 3 higher than reported here.

**Results:** The ranges of measured 3He and 21Ne amounts and minimum concentrations are summarized in Table 1 for each sample type. Analyses with sufficiently precise Ne isotope ratios have 26Ne/22Ne ratios <2, suggesting that our heating and evacuation procedure efficiently removed adsorbed air Ne. Therefore, all measured 21Ne is considered to be cosmogenic (i.e., 21Ne$_{cosm}$).

**Table 1.** Range of gas amounts, concentrations and production rates. STP refers to standard temperature and pressure; 1 cm$^3$ STP = 2.6868×10$^{19}$ atoms.

<table>
<thead>
<tr>
<th>Amounts:</th>
<th>PLAC-like CAIs</th>
<th>SHIBs</th>
<th>Spinel crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_e$-3 (10$^{-16}$ cm$^3$ STP)</td>
<td>0.9 245.1</td>
<td>1.9 7.9</td>
<td>2.9 520.4</td>
</tr>
<tr>
<td>Ne$_{21}$ (10$^{-13}$ cm$^3$ STP)</td>
<td>1.9 63.4</td>
<td>2.9 1.4</td>
<td>3.9 140.4</td>
</tr>
<tr>
<td>Concentrations:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_e$-3 (10$^{-6}$ cm$^3$ STP g$^{-1}$)</td>
<td>1.2 110.4</td>
<td>1.3 2.4</td>
<td>1.6 4.3</td>
</tr>
<tr>
<td>Ne$_{21}$ (10$^{-6}$ cm$^3$ STP g$^{-1}$)</td>
<td>0.9 28.8</td>
<td>0.2 0.7</td>
<td>0.5 1.0</td>
</tr>
<tr>
<td>Production rates:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_e$-3 (10$^{-4}$ cm$^3$ g$^{-1}$ Ma$^{-1}$)</td>
<td>1.77 1.82</td>
<td>1.81 1.84</td>
<td>1.79 1.94</td>
</tr>
<tr>
<td>Ne$_{21}$ (10$^{-4}$ cm$^3$ g$^{-1}$ Ma$^{-1}$)</td>
<td>0.30 0.31</td>
<td>0.37 0.38</td>
<td>0.41 0.46</td>
</tr>
</tbody>
</table>

The data show a systematic relationship between 3He and 21Ne concentrations and mineralogy (Table 1, Fig. 1). On average, spinel-bearing samples (single crystals and SHIBs) have lower minimum 3He and 21Ne concen-
trations than the spinel-free PLAC-like CAIs. In particular, the seven samples with the lowest concentrations contain (or are entirely composed of) spinel. Only one spinel grain overlaps with the lower end of the concentrations found in PLAC-like CAIs.

**Discussion:** Assuming that cosmogenic $^3\text{He}$ and $^{21}\text{Ne}$ was entirely acquired in the Murchison meteoroid, nominal exposure ages can be calculated for each sample. For this, we use the same shielding assumptions for the Murchison meteoroid as [7] and production rates calculated by [11] as well as elemental abundances of the samples obtained by EDS. For the eight spinel-bearing samples (single crystals and SHIBs), we calculate minimum exposure ages between $-1$ and $2$ Ma (Figs. 1, 2), which are comparable to many Murchison chondrules and the bulk meteoroid exposure age of $\sim 1.6$ Ma ([7], Fig. 3). This suggests that the spinel-bearing samples did not experience significant exposure to cosmic rays prior to compaction of the parent body. In contrast, the nominal exposure ages of the 18 spinel-free PLAC-like CAIs range from $-3$ to 93 Ma ($T_3$, based on cosmogenic $^{21}\text{Ne}$) and $-1$ to 60 Ma ($T_1$ based on cosmogenic $^3\text{He}$), indicating that they experienced additional, variable exposure to cosmic rays. The discrepancy between $T_{21}$ and $T_3$ (Fig. 1) is small for most grains and since $T_{21} \geq T_3$ this is consistent with preferential diffusive loss of the lighter element He.

Since Murchison is known to include materials from the parent body regolith, we need to consider whether the measured excess $^3\text{He}$ and $^{21}\text{Ne}$ in most PLAC-like CAIs are due to irradiation in the regolith. Therefore, we compare our dataset to [7], who found evidence for pre-exposure (i.e., $T_{21} > 4$ Ma) in 7 of 32 studied Murchison chondrules ($\sim 22\%$). The fraction of PLAC-like CAIs with $T_{21} > 4$ Ma is significantly higher ($\sim 78\%$). In the regolith exposure scenario favored by [7], this observation could be explained if our Murchison fragment had a higher relative abundance of regolith material. However, if this were the case, we would expect to find similar $^3\text{He}$ and $^{21}\text{Ne}$ excesses in spinel grains and SHIBs, as they were recovered from the same acid residue. This is contrary to our observations. Instead, the mineralogy dependence of the presence of excess $^3\text{He}$ and $^{21}\text{Ne}$ may point to a different precompaction exposure origin. If the eight spinel-bearing samples are representative for the exposure history of this rock while it was part of the Murchison parent body, the new data would indicate that most PLAC-like CAIs acquired excess $^{21}\text{Ne}$ and $^3\text{He}$ in a different location, likely prior to incorporation into the Murchison parent body. As PLAC-like CAIs are thought to have formed in the solar nebula, but earlier than regular, $^{26}\text{Al}$-rich CAIs, this exposure may have occurred early in Solar System history, perhaps while located close to the young Sun or during a period of high cosmic ray fluxes, e.g., from an early active Sun. Alternatively, these anomalous CAIs may predate the formation of the Solar System. The excess $^3\text{He}$ and $^{21}\text{Ne}$ could then be the result of prolonged exposure to galactic cosmic rays in the interstellar medium.

Overall, our preliminary results suggest that the presence of excess cosmogenic $^{21}\text{Ne}$ and $^3\text{He}$ can be added to the growing list of isotopic properties in which PLAC-like CAIs are distinct from ‘regular CAIs’ [3,12,13] and SHIBs.


![Figure 1](image1.png)
**Figure 1.** Minimum nominal meteoroid exposure ages: The ages of spinel-bearing samples are comparable to the exposure age of Murchison ($\sim 1.6$ Ma) and typically younger than those in PLAC-like CAIs. For many samples, $^{21}\text{Ne}$ ages are $>^3\text{He}$ ages, likely due to diffusive He loss. Plotted uncertainties are from noble gas analysis only (uncertainties from mass estimates and production rates are not considered).

![Figure 2](image2.png)
**Figure 2.** Comparison of nominal exposure ages of different sample types with those found in chondrules without evidence for regolith exposure [7].
HYDROGEN IN EVAPORATION EXPERIMENTS AND LINKS TO CAIs AND CHONDRULES. E. H. Hauri¹, C. M. O’D. Alexander¹, J. Wang¹, R. A. Mendybaev², and S. D. Jacobsen¹, ¹Department of Terrestrial Magnetism, Carnegie Institute of Washington, 5241 Broad Branch Rd, Washington, DC 20015, USA (ehauri@ciw.edu), ²Dept. Geophysical Sciences, University of Chicago, Chicago, IL 60637, USA, ³Department of Earth and Planetary Sciences, Northwestern University, Evanston, IL 60208, USA.

Introduction: The abundances and isotopic compositions of H and other highly volatile elements (C, S, halogens) in glasses and minerals from chondrules and CAIs can potentially provide information on the immediate environment in which they formed, as well as subsequent modification on chondrite parent bodies. In the early inner solar system, end member volatile sources include nebular gas and water ice. These two sources have D/H ratios that differ by up to an order of magnitude, and are also characterized by very different O isotope compositions. Additionally, coupled data on the degrees of hydration and the O isotope compositions of chondrules and CAIs can potentially identify open-system behavior in phases that are used for Al-Mg, Pb-Pb, Sm-Nd and Hf-W chronometry.

Thus, CAIs and chondrules in the most primitive chondrites (i.e., those least metamorphosed and aqueously altered) may preserve evidence for volatiles incorporated from the solar nebula, potentially recording the partial pressure of H during their formation; however, subsequent alteration by late-stage water derived from the outer solar system could overprint these signatures. Before attempting to unravel the potentially complicated processes of late-stage alteration, it is important to determine how much H can be expected to be present in high-temperature nebular-derived materials. Thus, as a first step we have chosen to investigate the abundances of H and other volatiles in analog vacuum evaporation experiments. For this purpose we have selected to determine volatile abundances (H, C, F, S, P, Cl) in four groups of evaporation experiments that were originally conducted for other purposes: (i) a solar CMAS-Fe composition melt heated under vacuum (1.3×10⁻⁹ bar, 1800–2000°C) [1]; (ii) a CMAS CAI composition melt heated at 1 bar of H₂ (1600°C); (iii) one CMAS CAI composition melt heated at 1 bar of H₂O (1600°C); and (iv) a CMAS diopside composition heated at variable pressures of H₂O from 1 bar down to 1.6×10⁻⁶ bar (1350–1450°C) [2].

Analytical Methods & Results: Volatiles in the evaporation experiments were measured using the Cameca NanoSIMS 50L in the Dept. of Terrestrial Magnetism, Carnegie Institute of Washington, following established techniques for low-H₂O analyses [3]. Calibration reference materials ranged from 1.66 ppm H₂O (Suprasil SiO₂ glass) to 2 wt% H₂O and drift was monitored using ALV519-4-1 basaltic glass (1700 ppm H₂O). The raw NanoSIMS data (¹²C/³⁰Si, ¹⁶OH/³⁰Si, etc) were normalized by the SiO₂ content of each material before calculating abundances of C, H₂O, F, P and Cl. After analysis of the highest-H₂O experiments during the first day of the session, subsequent analyses of Hauri quartz glass (71 ppm H₂O) were reproducible to ±14% (all errors are 2 sigma), while the abundance of H₂O in Suprasil quartz glass (1.66 ppm H₂O) was similarly reproducible at ±15%.

Here we concentrate on the H₂O abundances in the CMAS-Fe experiments of Wang et al. [1], which showed systematic evaporative mass loss as a combined function of temperature and heating duration. The least-evaporated experiment (SC12, 0.4% mass loss) contained 19 ppm H₂O, while the next-least evaporated experiment (SC11, 3.4% mass loss) contained 1.6 ppm H₂O; these experiments also contained measurable C, F, P and Cl. All the other experiments of this group, ranging from 21% to 90% evaporative mass loss under vacuum (1.3×10⁻⁹ bar) have relatively constant H₂O abundances averaging 2.13 ppm H₂O (±45%) and clearly resolved from the 1.66 ppm H₂O (±15%) in Suprasil SiO₂ glass. In contrast, the abundances of C, F and Cl in the highly-evaporated experiments are at the NanoSIMS detection limits (0.1 to 0.01 ppm and 2 sigma errors ~100%). Phosphorus shows a systematically declining abundance as a function of mass loss, starting at 20 ppm and reaching the P detection limit (0.013 ppm) at 50% mass loss.

Discussion & Preliminary Conclusions: H₂O data collected during the first day of measurements showed steadily declining H₂O abundances for Suprasil SiO₂ glass from ~6 ppm one hour after insertion of the mount in the NanoSIMS sample chamber, to ~2 ppm at the end of the first day; this is the result of improving H₂O detection limits during the first 24 hours of exposure to the sample chamber vacuum, a well-known phenomenon observed at other SIMS labs [4]. Beginning on the second day of the session, however, the very good reproducibility of the Suprasil analyses (±15%) indicates that conditions were favorable such that our actual detection limit for H₂O was very likely << 1 ppm, as demonstrated by our ability to clearly resolve the higher abundance of H₂O in the Wang et al. vacuum evaporation experiments (Fig. 1).

In the absence of silicate materials with demonstrably less than 1 ppm H₂O, we have estimated the NanoSIMS H₂O detection limit by plotting the error
envelopes for repeat analyses of reference materials as a function of their H$_2$O abundance and extrapolating toward ±100% error; this provides a semi-quantitative estimate of H$_2$O detection limit (0.01-0.1 ppm) and suggests that the NanoSIMS is capable of measuring H$_2$O abundances in-situ at concentration levels in the parts-per-billion range.

The partial pressure of H in the primordial solar nebula is unknown, but may be estimated from the H abundances of unaltered CAIs and chondrules if (A) they are not overprinted by later alteration; and (B) their H abundances can be constrained or measured directly. Furthermore, our results suggest that extrapolation of existing solubility models for H in silicate melt are a poor guide to predicting the H abundances of primitive CAIs and chondrules, and indicate that further measurements of experiments conducted under controlled H fugacities are warranted.

![Figure 1](image1.png) **Figure 1.** Measured OH/Si ratios in Herasil SiO$_2$ glass (red), Suprasil SiO$_2$ glass (green), and vacuum evaporation experiments (blue) versus analysis order. OH/Si ratios are normalized by the SiO$_2$ content.

![Figure 2](image2.png) **Figure 2.** Plot of hydrogen (as H$_2$O) content of mafic-ultramafic silicate melt (thin lines) and pyroxene (thick lines) as a function of H pressure and fO$_2$, extrapolated from experiments conducted at >1 bar. Thin lines show silicate melt saturation surface for gas phase composed of pure H$_2$O (blue) and pure H$_2$ (orange); thick lines show estimated H$_2$O concentrations in pyroxene, based on melt saturation and H partitioning [3]. All silicate melt solubility will lie between the curves for pure H$_2$ (orange) and pure H$_2$O (blue). The pure H$_2$O curve at high fO$_2$ is from [5]; the inset is for molecular H$_2$ solubility at low fO$_2$ [6]. Intermediate curves with error envelope are from [7].

Was our Solar System Born inside a Wolf-Rayet Bubble? Vikram V. Dwarkadas, Peter H. Boyajian, Michael Bojazi, Alex Heger, Bradley. S. Meyer, and Nicolas Dauphas, Dept. of Astronomy and Astrophysics, University of Chicago, 5640 S Ellis Ave, ERC 569, Chicago, IL 60637 (vikram@oddjob.uchicago.edu), Dept. of Physics and Astronomy, Clemson University, Clemson, SC, Monash University, Wellington Road, Victoria, Australia, Origins Lab, Department of the Geophysical Sciences and Enrico Fermi Institute, University of Chicago

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

Almost 40 years ago, [11] suggested that a nearby supernova (SN) explosion triggered the collapse of a molecular cloud and the formation of the solar system. $^{26}$Al created via stellar and SN nucleosynthesis, was 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). Recent work instead found that the $^{60}$Fe/$^{56}$Fe ratio at solar system formation is about an order of magnitude lower than 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 $\gtrsim 25$ M$_\odot$, which have lost their H and possibly He envelopes. In a study of the Carina region using INTEGRAL data, [21] found that the $^{26}$Al signal could not be accounted for by supernovae alone, and the fraction of $^{26}$Al ejected in W-R stars is high, indicating strong wind ejection of $^{26}$Al.

$^{26}$Al has also been seen towards other star forming regions such as Cygnus [22], Orion [23], and Scorpius-Centaurus [24]. 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, 19].

Using a combination of semi-analytic calculations, astronomical observations, and numerical modeling, in this presentation we advance the idea that our solar system was born inside a Wolf-Rayet wind bubble.

$^{26}$Al Yields from massive stars: In Figure 1 we have plotted the $^{26}$Al yields from stars with initial mass $\gtrsim 20$ M$_\odot$ [25,26,27,28,29,30].

Newer yields (1-4) take into account new metallicities, stellar rotation and improved mass-loss rates [25,26,27]. It is clear that a single massive star provides at least $10^{-4}$ M$_\odot$ of $^{26}$Al, sufficient (even after some dilution) for the entire early solar system budget [16], where the initial concentration was 3.3 parts per billion [19]. The more massive the star the higher the $^{26}$Al yield. The $^{60}$Fe yield from the wind itself is negligible - $^{60}$Fe in the proto-solar nebula arises from the swept-up material, expelled by a previous generation of stars.

Wolf-Rayet Bubbles: W-R stars form the post-main-sequence phase of massive O and B-type main sequence stars. These stars have winds with terminal velocities of 1000-2000 km s$^{-1}$ [31]. The high surface temperature of these hot stars results in a large number of ionizing photons. The combined action of the supersonic winds and ionizing radiation results in the formation of photo-ionized wind-blown bubbles around the stars, consisting of a low-density interior surrounded by a high-density shell (Fig. 2). Most of the volume is occupied by a low-density high-temperature plasma.

Wind Bubbles as Stellar Nurseries: Star formation at the boundaries of wind-bubbles around O and B stars has been revealed in astronomical observations [32,33,34,35]. Molecular cores undergoing gravitational collapse due to external pressure from the surrounding gas have been found around W-R star HD 211853 [36]. This triggered or stochastic star-formation is well understood in the context of two models, the 'collect and collapse model' [37] and the 'radiation-driven implosion' model [38].
Injection of $^{26}$Al from the Wind to the Solar System: The important ingredient remaining is the injection of the $^{26}$Al from the wind into the early solar system. This topic has been studied mainly in the context of injection by a SN. [12,13] have shown that the injection efficiency due to hydrodynamic mixing between the SN shock wave and the collapsing cores is small, of order a few percent. This occurs late in the SN evolution, when it has reached the radiative stage and slowed down $< 100$ km s$^{-1}$ (although see [40]). The W-R wind velocity substantially exceeds this value, and they have a much lower density than SN ejecta. The efficiency of mixing will therefore be reduced. Winds sweeping past high-density cores will lead to shearing and the growth of Kelvin-Helmholtz instabilities at the interface, stripping material away. Hydrodynamic mixing does not appear a viable mechanism.

We suggest instead that $^{26}$Al condenses onto, and is injected mainly via dust grains (see also [17,41]). Dust is seen around WN and WC stars [42,43], although the formation mechanism at high temperatures is not well understood. Analysis of IR emission shows that dust forms close in to the star, with the grains estimated to be large in size, $\sim 1$ μm [44]. The stopping distance of μm size grains in bubbles is several parsecs, exceeding the size of the bubble in the high density molecular cloud. The grains can survive passage through the reverse shock and the low density shocked wind, and reach the outer dense shell. The grains would then be injected into the high density cores, penetrating depths of 1 to several hundred AU depending on the density.

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.

AN ACHONDRITE-DOMINATED METEORITE FLUX BEFORE THE L-CHONDRITE PARENT ASTEROID BREAKUP EVENT 466 MYR AGO? P. R. Heck1,2, B. Schmitz1,3, W. F. Bottke1, S. S. Roul1,2, N. T. Kitā5, A. Cronholm1, C. Defouilloy5, A. Dröns4,5, F. Terfelt4. 1Robert A. Pritzker Center for Meteoritics and Planetary Studies, The Field Museum of Natural History, 1400 South Lake Shore Drive, Chicago, Illinois 60605, USA. e-mail: prheck@fieldmuseum.org. 2Chicago Center for Cosmochemistry and Department of the Geophysical Sciences, The University of Chicago, 5734 South Ellis Avenue, Chicago, Illinois 60637, USA. 3Astrogeobiology Laboratory, Department of Physics, Lund University, PO Box 118, SE-22100 Lund, Sweden. 4Department of Space Studies, Southwest Research Institute, 1050 Walnut Street, Suite 300, Boulder, Colorado 80302, USA. 5WiscSIMS, Department of Geoscience, University of Wisconsin-Madison, 1215 W. Dayton Street, Madison, Wisconsin 53706-1692, USA. 6Geological Institute, Russian Academy of Sciences, Pyzhevsky Pereulok 7, 119017 Moscow, Russia. 7Kazan (Volga Region) Federal University, Kremlevskaya ulitsa 18, 420008 Kazan, Russia.

Introduction: Today, ordinary chondrites dominate the meteorite flux to Earth, with L chondrites being the most abundant group. The type abundances of meteorites that fall today are different than the types of asteroids that are best positioned to deliver them [1,2]. This implies that today’s meteorites originated predominantly in a few asteroid breakup events [3,4] and that today’s meteorite flux is not representative over 100-Myr-time scales. In order to investigate the past meteorite flux at such timescales an approach has been developed in which extraterrestrial minerals are extracted from ancient slowly formed sea-floor sediments [5]. Here we studied relict extraterrestrial chrome-spinel grains recovered from Middle Ordovician sediments that were deposited 467 Myr ago, before the L-chondrite parent body breakup (LCPB) event.

Samples and Methods: We extracted chrome-spinel grains from marine limestone from the Lymna River section near St. Petersburg, Russia [6] by acid dissolution. The sampling interval GAP7 was chosen to avoid contributions from the LCPB [7]. The first sample consisted of 46 coarse chrome-spinel grains (63–200 μm) extracted from 270 kg of rock, the second sample comprised 184 chrome-spinel grains 32–63 μm from ~114 kg of rock. Opaque grains were handpicked under a reflected light microscope and chrome-spinel was identified with SEM/EDS [8]. Major and minor elements were analyzed with quantitative SEM/EDS or EPMA on polished epoxy grain mounts. We used previously established methods for a Cameca IMS-1280 to analyze three oxygen isotopes in the 230 grains in two sessions [7,9,10]. Unkowns were bracketed with UWCr-3 chromite standard [8]. Hydride peak tailing interferences of 16O1H on 17O were corrected for. Data with hydride corrections >1% was rejected as justified previously [10].

Lower noise levels due to an improved detector system allowed us to use a smaller primary Cs+ beam (~11 μm spot size compared to ~15 μm previously) for the smaller grains of the second sample with shorter analyses times and similar external reproducibility [11].

We use three oxygen isotopes in conjunction with diagnostic TiO2 concentrations to classify relict chrome-spinel grains as demonstrated in previous studies [9,10]. In some cases an unambiguous classification was not possible due to overlap between different types of meteorites in oxygen isotope space and in elemental compositions [9,10]. Sediment-dispersed extraterrestrial chrome-spinel grains (SECs) originate mostly from coarse micrometeorites [12,13]. We argued that coarse micrometeorites are useful to reconstruct the composition of the flux of coarse-chromite bearing meteorites [7,9,10].

In addition to SECs we also extracted chrome-spinels from recent surface-recovered meteorites to determine the chrome-spinel abundances in different types of meteorites.

Results and Discussion: The chrome-spinel abundance is variable in different types and sometimes even in the same types of meteorites [7]. However, our study on the recent falls and finds also shows that the abundances of coarse chrome-spinels are not very different on average in HED meteorites and in primitive achondrites, and slightly higher in equilibrated ordinary chondrites (EOCs) [7]. From our SEC data we find a large diversity of meteorite types that include ordinary chondrites, HED achondrites, primitive achondrites and ungrouped achondrites, including some that are not found today (Fig. 1). Surprisingly, the fraction of achondrites before the LCPB was very high and comprised at least 44% of the coarse chrome-spinel bearing meteorite flux (based on the coarsest SECs, the 63–200 μm size fraction), whereas it is only ~7% today. Today, ungrouped and primitive achondrites are rare in the meteorite and micrometeorite populations. The recovered achondritic SECs in our study include a sample that matches the composition of ungrouped fossil achondrite Osterplana 065 which was found in slightly younger sediments of the same epoch [14]. This suggests that this type of meteorite, which is
Lunar eruption events were probably small compared to the number of partially differentiated asteroids that had disrupted and generated the high flux of achondrites that L chondrites were less abundant at that time and are rare today. The high flux of LL chondrites, the rarest achondrites, was closer to the source of the LL chondrites was regarded as a meteorite flux after the LCPB, where they made up >99% in sediments immediately deposited after the event [10]. The distribution of meteorite types in pre-LCPB sediments is confirmed by our results from the smaller size fraction of SECs (32–63 μm).

The high abundance of LL chondrites and HED achondrites 467 Myr ago can be explained by the fact that this time window was closer to the respective peak meteorite flux after major collisional events that can be regarded as the most probable sources. The main source of the LL chondrites was likely the Flora asteroid family-forming event 950 ±200/−170 Myr ago [15] and of the HED meteorites the formation of the ∼500 km wide Rhea Silvia impact basin on asteroid 4 Vesta ~1 Gyr ago [16]. The high abundances of primitive and related ungrouped achondrites indicate that some of the partially differentiated asteroids had disrupted and generated the higher flux that we observed. These disruption events were probably small compared to the LCPB so that the collisional cascade did not result in a large flux today.

Conclusions: Our study shows that the meteorite flux before the LCPB was strikingly different than it is today. We provide clear evidence from the sedimentary record that the composition of the flux of extraterrestrial material to Earth is biased today and varies on timescales of 10-100 Myr and larger. Studies of extraterrestrial material from different time windows [5] are in progress and, together with this study, will contribute to our understanding of the evolution of the asteroid belt.


Figure 1. Relict chrome-spinel grains can be classified by comparing their Δ¹⁷O values, the deviation from the terrestrial mass fractionation line (dotted line), and their TiO₂ concentrations to data from different meteorite types (reference data compilation from [7]). Error bars are 2σ and shown if larger than the symbol.
CLIMATE OPTIMUM ON MARS INITIATED BY ATMOSPHERIC COLLAPSE? Edwin S. Kite, Michael Mischna, Peter Gao, Yuk Yung. 1University of Chicago (kite@uchicago.edu) 2JPL, 3NASA Ames, 4Caltech.

Introduction: The progressive drying-out of Mars’ surface was punctuated by a dramatic transient increase in fluvial erosion around the Noachian-Hesperian boundary [1]. Standard explanations of this climate optimum appeal to volcano- or impact-triggered climates and imply that individual runoff episodes were brief, apparently inconsistent with evidence for persistent run-off. We examine a scenario in which the duration, intensity and uniqueness of the Noachian-Hesperian climate optimum result from degassing of CH4-clathrate consequent to Mars’ first atmospheric collapse. Atmospheric collapse causes low-latitude surface H2O-ice to sublimate, depressurizing and destabilizing CH4 clathrate in subglacial pore space. Subsequent atmospheric re-inflation leads to further warming and further destabilizes CH4-clathrate. CH4-induced warming is efficient, permitting strong positive feedbacks, and possibly raising Mars into a climate optimum. The optimum is brought to a close by photolysis of CH4, and drawdown of the clathrate reservoir prevents recurrence. This scenario predicts a $10^5-10^6$ yr climate optimum, transient connections between the deep hydrosphere and the surface, and strong surface weathering, all of which are consistent with recent observations. Crustal hydrothermal circulation very early in Mars history could yield CH4 that would be incorporated into clathrate on a prograde to the cold surface. The scenario explains why regional watershed integration on Mars occurred relatively late and only once, and suggests that the contrasts between Noachian versus Hesperian climate-sensitive deposits on Mars correspond to a transition from a never-collapsed atmosphere to a collapse prone climate, ultimately driven by slow loss of CO2 to space.

Figure 1. Overview of proposed scenario. (a) Left: schematic of the long-term evolution of a column of the Mars highlands. Right: obliquity diffusion and slow CO2 loss lead to polar temperatures dropping below a pressure-dependent critical value for atmospheric collapse initiation, $\phi_c$. (b) Below $\phi_c$, >90% of the atmosphere will condense in 1-10 Kyr (step 1). This unloads high ground (step 2), releasing CH4 from sub-ice clathrate. Re-inflation of the atmosphere leads to climate optimum (steps 3-4).
Overview of the climate optimum scenario.

Step 1. Collapse of an initially-thick CO₂ atmosphere. As Mars’ atmosphere is thinned by escape-to-space and carbonate formation, the remaining atmospheric CO₂ becomes increasingly vulnerable to collapse. Collapse is triggered if polar CO₂-ice caps grow from year to year. Cap growth occurs below a critical polar temperature. Polar temperature is set by insolation, which increases with obliquity, and by heating from the CO₂ atmosphere (both the greenhouse effect, and equator-to-pole heat transport, increase with atmospheric pressure). Given secular atmospheric-pressure decline, obliquity variations will eventually lower insolation below the threshold for perennial CO₂-ice caps. Once nucleated, caps grow in <10⁴ yrs [2] and typically sequester >90% of the planets’ CO₂. Post-collapse pCO₂ is in equilibrium with polar-CO₂-ice-cap surface temperature. Cap thickness is ~1200 m/bar CO₂. Atmospheric collapse involves a hysteresis, but obliquity rise will eventually trigger rapid re-sublimation of CO₂. Cooling of the surface due to loss of the greenhouse effect helps to stabilize CH₄-clathrate, outweighing the destabilizing effect of loss of the weight of the atmosphere. Cold post-collapse conditions are unfavorable for liquid water.

Step 2: H₂O-ice unloading of low latitudes triggers CH₄ release. Following Mars’ first-ever atmospheric collapse, the atmosphere can longer provide much heat to the poles; these are now the stable location for H₂O ice. H₂O ice condenses at the poles, and sublimes away from low-latitude highlands for the first time in Mars history. The low-latitude ice sublimes in <10⁵ yr (the scenario assumes a net rate of ~10 mm/yr; e.g. [3]). On this timescale H₂O-ice glacial flow is negligible [3]. This latitudinal shift in ice overburden is the first such shift in Mars history, and (in the collapse trigger scenario) it has an effect on CH₄-clathrate decomposition that is unsurpassed. Unloading of the highlands due to removal of H₂O-ice causes irreversible decomposition of sub-ice within-regolith pore-space CH₄ clathrate. The corresponding CH₄(g) release can be very large. The clathrate is charged up with CH₄ produced by water-rock reactions over >10⁸ yr. It is released in <10⁴ yr. Once in the atmosphere CH₄ is photolyzed at a rate of 0.1 mbar/Kyr [4]. CH₄ is ineffective at warming Mars at this stage because CH₄’s principal greenhouse band at 7.7 µm is mismatched with the cold-Mars Planck function, and CH₄-CO₂ Collision-Induced Absorption (CIA) is also ineffective because the collapsed-atmosphere pCO₂ is low [5]. The collapsed-atmosphere CH₄/CO₂ ratio may exceed the threshold for forming haze, which will scatter sunlight and further suppress temperatures.

Step 3. CO₂-atmosphere reflation and further CH₄ release. Mars’ first atmospheric collapse occurs at the bottom of a (20⁰ amplitude) quasi-periodic obliquity cycle. As the obliquity cycle continues, pCO₂ initially rises in vapor-pressure equilibrium with polar temperature, and with most CO₂ sequestered in ice. pCO₂ rises in equilibrium with CO₂-ice temperature because, although stiff H₂O-ice may enshroud the CO₂-ice, flow of thick, soft CO₂-ice opens crevasses. When obliquity rises to the point where no value of pressure yields a polar temperature below the condensation point, the remaining polar CO₂-ice caps rapidly (10⁴ year) and completely sublimate. Because the duration of quasi-periodic orbital cycles is known for the post-4.0 Ga solar system, the time between Mars’ first atmospheric collapse and reflation is 1-5 × 10⁴ yr for reasonable parameter choices. Loss of H₂O-ice overburden exposes clathrate to the CO₂-greenhouse warming associated with reflation, and clathrate irreversibly decomposes, releasing CH₄. The wait time for CH₄ clathrate decomposition is (reflation time + subsurface conductive-warming time + decomposition time) = (10⁴ yr + ~10⁶ yr + <10 yr) = 10⁵ yr. This is much quicker than the 10⁻³⁵ yrs needed for H₂O ice to return to the low latitudes. In the simulations, the amount of CH₄ released at this point is larger than in Step 2. For methane clathrate stability zone occupancy fractions larger than a few percent, the atmosphere now contains abundant CO₂, with 1-5% CH₄. These are ideal conditions for strong CH₄-CO₂ CIA warming [5].

Step 4. CH₄+CO₂ = Mars climate optimum. The cocktail of circumstances enabled by Mars’ first atmospheric collapse (a massive CH₄ pulse, a thick CO₂ atmosphere, low-latitude water ice) now permits low-latitude rivers and lakes. H₂O snow falling on the equator (plus any H₂O ice that did not have time to sublimate) encounters high insolation and high greenhouse forcing. Seasonal snowmelt runoff forms valleys that drain into perennial ice-covered lakes, which overspill to form valley networks. High lake-bottom temperatures destabilize sub-lake methane clathrates. CH₄-induced warming is strong to destabilize additional CH₄ in the regolith (and under some circumstances this positive feedback can produce a runaway).

Step 5. CH₄ loss shuts down of wet climate in 10⁴-10⁶ yr. The wet climate ends when atmospheric CH₄ is photolyzed. So long as CH₄-induced warming persists, atmospheric re-collapse is unlikely. As CH₄ is destroyed without resupply, eventually the rivers dry up. Wet conditions persist for 10⁵-10⁶ yr, consistent with geomorphic estimates of the number of wet years needed to form the VN and reconciling the geomorphic data with mineralogic upper limits on the interval of surface liquid water (e.g., Ref. 6).

Possible tests will be discussed at the conference.

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THE AGE OF THE MOON. M. Barboni\textsuperscript{1}, P. Boehnke\textsuperscript{2,3}, C. B. Keller\textsuperscript{4,5}, I. E. Kohl\textsuperscript{1}, B. Schoene\textsuperscript{5}, E. D. Young\textsuperscript{1}, K. D. McKeegan\textsuperscript{1}; \textsuperscript{1}Department of Earth, Planetary, and Space Sciences; University of California Los Angeles, Los Angeles, CA 90095, USA; \textsuperscript{2}Department of the Geophysical Sciences, \textsuperscript{3}Chicago Center for Cosmochemistry, The University of Chicago, Chicago, IL 60637, USA; \textsuperscript{4}Berkeley Geochronology Center, Berkeley, CA 94709, USA, \textsuperscript{5}Department of Geosciences, Princeton University, Princeton, NJ 08544, USA.

Introduction: Knowledge of the age of the Moon is important for understanding the early evolution of the solar system, including the timing of the hypothesized Giant Impact (GI). There have been many attempts to determine the Moon’s age, but significant disagreement remains with some planetary scientists favoring formation within $\sim$100 million years after the formation of the solar system (4.45-4.47 Ga) \textsuperscript{[1-4]} and others arguing for a relatively late GI (4.35-4.42 Ga), approximately 150 to 200 million years after the beginning of the solar system \textsuperscript{[5-7]}. The “young” ages for lunar formation are difficult to reconcile with the zircon records from the Hadean era of Earth’s history \textsuperscript{[8]} and from the Moon \textsuperscript{[9]}, which show ages as old as 4.38 Ga and 4.4 Ga respectively. Attempts to determine an age for the formation of the Moon can be divided into two main approaches: dating the GI event through its possible collateral effects on other solar system bodies \textsuperscript{[1-4]}, or dating products of the solidification of the Lunar Magma Ocean (LMO) itself \textsuperscript{[5-7]}. An insurmountable problem with indirectly dating the GI is that there is no way to ascertain if the measured collateral effects are associated with the GI. Determining the timing of the LMO crystallization provides a more direct constraint on the age of the Moon, but interpreting the chronologic significance of LMO products is complicated by the fact that the only rock samples available are breccias, which were disturbed by post-crystallization impacts. Therefore, LMO products cannot be used to accurately date the Moon.

Method: A better approach to date the Moon is to construct a model age for the fractional crystallization of the LMO. Zircons from the Apollo samples are ancient; robust against later disturbances; and amenable to precise U-Pb geochronology and Hf isotope analyses. The results from the U-Pb and Hf isotope measurements can then be used to construct Lu-Hf model ages for the silicate differentiation of the Moon. Previous isotopic studies of Apollo zircons \textsuperscript{[10]} yielded incorrectly young Hf model ages because of the (then unknown) effect of neutron capture, resulting from cosmic ray exposure, on the Hf isotopic ratios. Additionally, previous studies \textsuperscript{[10]} were unable to determine whether or not their U-Pb dates were concordant due to insufficient precision of in situ dating techniques. We have addressed these issues by carrying out isotope dilution thermal ionization mass spectrometry U-Pb geochronology on chemically abraded Apollo 14 zircon fragments, followed by Hf isotope determination by solution multi-collector inductively coupled plasma mass spectrometry on the same volume of zircon. The effects of possible neutron capture on the Apollo 14 zircon Hf isotopic ratios were assessed by examining the deviation of their $^{178}$Hf/$^{177}$Hf ratios the chondritic value and corrected for by using the data and procedure proposed by \textsuperscript{[11]}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{U-Pb Concordia diagram for Apollo 14 zircons. Residue analyses are indicated by filled ellipses, 2\textsuperscript{nd} leachates by open symbols. All errors are 2\textsigma.}
\end{figure}

Results: Fragments from 8 zircon grains, separated from polymict breccias 14304 and 14321 and from soil sample 14163, were dated by U-Pb and analyzed for Hf isotope and rare earth element compositions \textsuperscript{[12]}. The U-Pb ages of the zircon residues and second leachates are highly concordant, with crystallization ages spanning a range from 4335 to 3969 Ma (Fig. 1). We obtained $\varepsilon^{176}$Hf(t) values that are the lowest measured in lunar materials, with the least radiogenic samples in the Apollo 14 population having $\varepsilon^{176}$Hf(t) within 1 to 2 $\varepsilon$ units of the solar system initial value (Fig. 2). The fact that our zircons are concordant at the subpermil level and the development of corrections for cosmic ray exposure permit accurate determination of
$\varepsilon^{176}$Hf(t) values on individual zircons. Our results place tight constraints on the timing of Lu/Hf fractionation during crystallization of the LMO. By considering the maximum Lu/Hf fractionation possible (i.e., Lu/Hf approaching zero in the residual melt, corresponding to the horizontal dashed line in Fig. 2), we compute that the minimum age for the end of differentiation of the LMO, and by extension, the formation of the Moon, is $4.51 \pm 0.01$ Ga [2].

**Fig. 2.** Hf isotope evolution diagram for Apollo 14 zircons analyzed in this study. Absissa plots the U-Pb age for each zircon residue or leachate, and ordinate shows the measured Hf isotope ratio corrected for neutron capture. Also shown is the initial solar system $^{176}$Hf/$^{177}$Hf determined by [13] and the chondritic evolution line (CHUR). Error bars are 1σ.

**Discussion and conclusion:** Our model age is ~120 to 200 Myr older than estimates based on isochron dating of various LMO products [5-7]. The zircon data containing the least radiogenic Hf unambiguously show that the Moon was differentiated and mostly solidified by 4.51 Ga. Therefore the “young” ages obtained on LMO products cannot be directly dating the age of the Moon. Our results are consistent with constraints given by the short-lived $^{182}$Hf/$^{182}$W system that indicate that formation of the Moon must have occurred later than ~50 Myr after the beginning of the solar system [14]. Because the Hf isotopic composition of the lunar zircons require solidification of the LMO by ~4.51 Ga (Fig. 3), we conclude that the Giant Impact and formation of the Earth-Moon system must have occurred within the first ~60 million years of the formation of the solar system, with an uncertainty on the order of 10 million years.

**Fig. 3.** Lu-Hf model ages vs. crystallization age for Apollo 14 zircons (blue) and leachates (red) analyzed in this study. Also shown are the neutron-corrected data from Taylor et al. [10] and the range of prior estimates for the timing of the Giant Impact / age of the Moon. Error bars are 1σ.

**Impact Spall and Fragmentation by Near-Surface Stress Wave Interactions.**

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**Introduction:** The impact ejection of fast, lightly shocked material is one of the important insights stemming from the discovery of meteorites that originated on Mars and the Moon [1]. The sizes of such fragments as a function of ejection velocity is presently one of the most poorly understood aspects of impact cratering, in spite of its importance for meteoritics as well as the sizes of secondary craters. To better understand this process we have carefully studied the interaction of the stress wave with the free surface at very high resolution in a simplified impact scenario. In addition, we present a new model for impact fragmentation of rock overtaken by a sudden compressional shock wave and deduce its consequences.

**Modeling Near-Surface Stress Waves:** We used the iSALE computer code to model a vertical impact of a 10 km diameter Al projectile onto a planar Al target at 20 km/sec at a resolution of 6.25 m/cell. We chose Al because it lacks high pressure phase transition that might complicate the free-surface interactions and because we have an accurate (and simple) Tillotson equation of state that we can solve analytically. Figure 1 illustrates the pressure contours 0.36 sec after the impact, when the projectile is still penetrating the target and the shock wave adjacent to the target is already damped by near-surface interactions beginning at the complex region near the projectile’s edge.

**Figure 1.** Pressure near a vertical Al on Al impact at 20 km/sec. Highest contour is 150 GPa, lowest is 0.

We traced the time evolution of the shock front and pressure contours, shown in Figure 2. Note that the area of pressure relief forms a near-triangle beginning at the former edge of the projectile. This region is known as an “irregular reflection” and is created by rarefaction waves propagating downward from the free surface through previously shocked material. The angle Ψ of the steepest contour is approximately given by [2]

$$\tan \Psi = \frac{\sqrt{c^2 - (U - u)^2}}{U}$$

where $c$ is the sound speed behind the shock, $U$ is the shock velocity and $u$ is the particle velocity. For Al at 150 GPa the tangent equals 0.7, implying an angle of 35°, close to that in Figure 2.

**Figure 2.** Contours of maximum shock pressure ever achieved (color) in the irregular reflection region and successive shock front positions (black) at intervals of 0.02 sec. Scale is in km.

The maximum shock pressure in this region is given approximately by $P_{max} = 150*z/s*\tan\Psi$, where $z$ is depth below the surface and $s$ is horizontal distance from the projectile edge (at 5.0 km on the left). This estimate is not valid very close to the surface, where numerical problems may have arisen from iSALE’s interface tracking algorithm—in any case, no Eulerian code does an adequate job close to a free surface because it cannot resolve the surface to better than one cell. We are currently exploring a Lagrangian code to better define this important region.

Figure 1 shows that the maximum pressure is only achieved for a short time. After the arrival of the sharp shock front, the pressure decays gradually through a stepwise release that is often approximated as a Prandtl-Meyer expansion fan [3], even though this is strictly not applicable because the flow is entirely subsonic (within the rapidly moving material) behind the shock. The pressure release fan forms an angle of about 45° to the vertical in these computations, so near-surface material is decompressed quickly as the
shock sweeps outward at 10.4 km/sec, while deeper material resides longer at high pressure.

**Compressional fragmentation at the shock front:** Although the iSALE computation did not implement a fragmentation model (none exists for crushing), so far, and the basalt HEL at 2 GPa is exceeded at nearly all depths this close to the impact), the stress history of material at different depths invites us to attempt to construct a post-processing algorithm for dynamic fragmentation.

Previous work [4] adapted a model of Grady and Kipp [5] to successfully model tensile fragmentation long after the arrival of the initial compressional shock. This model envisages that tensile stresses activate Griffith crack-like flaws that then grow at the speed of sound to finally intersect and define a distribution of fragments, whose mean size is inversely proportional to the strain rate. Although such flaw-activation models are currently used in the fragmentation literature [6], they are closely tied to estimates of the strain rate. Although such flaw-activation models are currently used in the fragmentation literature [6], they are closely tied to estimates of the strain rate. We then determined the constant k from the measured crushing strength at a characteristic strain rate. For basalt, with a strength of 200 MPa at a strain rate of 1000 sec^{-1} [6, Table 1], we find that k = 2.6 x 10^9 m^3, much smaller than is typical for tension, where k is approximately 10^{15}.

Following a development similar to that for tension, but assuming a fixed strain instead of a constant strain rate, expressions for time to complete fracture and mean fragment size can be derived in terms of m and k. The final result for the mode of the fracture size distribution l in terms of a suddenly imposed deviatoric strain ε_o above the HEL (in uniaxial compression):

\[ l = 4 \left( \frac{(m+1)(m+3)^{1/3}}{8\pi k(m+2)^{5/3}} \right)^{1/3} \epsilon_o^{m/3} \]

This predicts, for example, that for a shock of 3 GPa (just above the Hugoniot Elastic Limit for basalt) the fragment size in basalt is about 1.1 cm and at 10 GPa, l is 3.5 mm. Unfortunately we do not presently have adequate fragmentation data to check this theory.

We apply this theory to the stresses in the irregular shock wedge in Figure 3. Note that the duration at high pressure exceeds the time for complete fracture at all depths, so any tensile stresses that would develop in this region are proceeded (and thus prevented) by the complete fragmentation under compression computed by this model. Fragment sizes are much smaller than the surface spall layer (defined as the region where the HEL of 2 GPa is not exceeded). We do not show ejection velocities directly here, but they are high, typically about 10 km/sec this close to the impact site.

**Figure 3.** Log10 of fragment sizes in the irregular reflection wedge, all dimensions in meters. Intact spall shown in black at top. Contours for shock pressures above 50 GPa are not shown because the rock is melted, not fragmented. Note 50X vertical exaggeration.

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PROGRESS TOWARDS ESTABLISHING EARLY EARTH’S CRUSTAL Rb/Sr RATIO.
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Introduction: Understanding the Hadean (>4 Ga) Earth requires knowledge of its crust. The composition of the crust and volatiles migrating through it directly influences the makeup of the atmosphere, the composition of seawater, and nutrient availability. Despite its importance, there is little known and less agreed upon regarding the nature of the Hadean crust. In part, this is because our only direct geologic record of the Hadean comes from zircons, a robust zirconium silicate that is well suited for U-Pb geochronology. While Hadean zircons have been extensively studied for everything from oxygen isotopes to mineral inclusions to hafnium isotopes to their trace element distributions, interpretation of these data remains controversial [1,2].

One path forward to addressing these controversies would be to study how rubidium and strontium vary in the early crust. Understanding the Rb/Sr ratio of the source for the Hadean zircons may provide valuable insights into the source SiO₂ content and permit selection between several competing models for the Hadean. For example, if the Hadean zircons formed in intermediate magmas or from melting a mafic crust then the associated Rb/Sr ratio of the source magmas should be low [1,2]. Alternatively, if the Hadean zircons formed in felsic magmas, then the Rb/Sr ratio should be high [1,2].

Currently, there is only one study of Rb/Sr ratios of Archean igneous rocks, which proposed that the Archean crust had generally low Rb/Sr ratios [3]. These authors argue that the strong correlation between Rb/Sr ratio and SiO₂ content in modern igneous rocks extends into the Archean, and therefore, the low Rb/Sr ratios in the Archean suggest a dominantly mafic crust. However, the Rb/Sr system is easily disturbed by aqueous alteration [4], and therefore, it is unlikely that Archean rocks will accurately preserve their original Rb/Sr ratios.

In order to avoid the difficulty of ascertaining Rb/Sr ratios from whole rock samples, we will analyze the strontium isotopic compositions ofapatites included in Archean zircons. Apatite is a calcium phosphate mineral that includes significant strontium while excluding rubidium. Therefore, the Rb/Sr ratio in apatite provides a record of the time-integrated Rb/Sr ratio, while requiring only a minimal correction due to the ingrowth of Sr from the decay of Rb following crystallization.

While apatite inclusions in zircon could provide an important record of Rb/Sr ratios for the Archean and Hadean, this record has not previously been exploited due to their small (<10 μm in diameter) size. We used resonance ionization mass spectrometry (RIMS) to analyze strontium isotopes in apatite inclusions in zircons.

Methods: RIMS is a technique in which atoms are liberated from the sample surface and then photoionized using lasers before being introduced into a time-of-flight mass spectrometer [5]. The advantages to this technique are that it is element-specific and has very high sensitivity. Specifically, we used the Chicago Instrument for Laser Ionization (CHILI) [5] which has a 351 nm desorption laser with ~0.8 μm spatial resolution for sample removal and has achieved precisions of ~2‰, as determined in this study. Therefore, CHILI is in the unique position to analyze strontium isotopes in apatite inclusions in zircons and unlock an im-
important, previously inaccessible geochemical record.

Figure 1. Shown are the results from preliminary analyses of two standardapatites. The measurements of Durango were used to correct the Madagascar apatite analyses. Because we use Durango as our primary standard, the Durango results cluster around the true value of 0.7063 [6]. The longest analysis took ~60 minutes, i.e., is the sum of 3.6 million individual desorption laser shots. Longer analysis times would result in smaller statistical uncertainties as the error is currently dominated by counting statistics. Uncertainties are 1σ.

Preliminary Results and Discussion: Our analyses show that precisions of 2% are readily attainable on our two standards with CHILI (Fig. 1). When using Durango apatite as a standard for Madagascar apatite, our measured $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio is 0.7123±0.0015 (1σ), which agrees well with the true value of 0.7118 [6]. We also analyzed apatite inclusions in one zircon from a phanerzoic granite from San Jacinto Mountains, CA and our results (0.711±0.004 at 1σ) agree well with the whole rock $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio (~0.707) [7].

While our precision is significantly worse than typical strontium isotope analyses (e.g., by using TIMS), it is sufficient for the geologic questions we are interested in. For example, a reservoir that has ~70 wt% SiO$_2$ with an initial $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio of 0.699 will evolve to a $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio of 0.703 after 200 Myr [3]. This difference would be resolvable (at the 2σ level) with our current uncertainties.

From hafnium isotope studies of Hadean zircons, reservoirs can evolve for periods of 200–500 Myr [1,2], which would further increase the differences in $^{87}\text{Sr} / ^{86}\text{Sr}$ ratios between mafic and felsic reservoirs.

**Outlook:** Our next step is to investigate apatite inclusions in 3.6–3.8 Ga zircons from Nuvvuagittuq, Canada. These results will place some of the tightest constraints on Rb/Sr ratios in the Archean crust and serve as a stepping stone to our ultimate goal of analyzing apatite inclusions in Hadean zircons from the Jack Hills, Western Australia. Finally, our approach is not restricted to terrestrial samples and will also be applied to martian apatites [e.g., 8] to study the Rb/Sr ratios of the crust of Mars.

MODELING THE EFFECT OF OBLIQUITY ON MARS ELLIPTICAL CRATER ORIENTATIONS.

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**Introduction:** Obliquity is a strong control on post-Noachian Martian climate [1]. However, Martian obliquity is chaotic and dynamical models produce a wide range of instantaneous and long-term average values [2]. Here, we model the effect of Mars mean obliquity on the distribution of fresh elliptic crater orientations. To achieve this we used an N-body simulation to estimate the time-averaged distribution of asteroid close encounter inclinations and speeds. These close encounters seeded an analytic forward model of asteroid trajectories that tracked impact orientations and angles. Preliminary comparison of model output and elliptic crater orientation data from the Robbins database [3] suggest that mean Mars obliquity after the Mars impactor population stabilized was low, \(< \sim 30^\circ\).

**Close Encounter Simulation:** We started with the Minor Planet Center database of asteroid orbital elements and selected Mars crossing objects defined as having perihelion distance less than \(a \times (1 + e)\) and aphelion distance greater than \(a \times (1 - e)\) where \(a = 1.52\)AU is the semi-major axis of Mars and \(e = 0.15\) was chosen to include the entire range of Mars eccentricities observed in our simulations. We also required that the objects have magnitude less than 14 to ensure population completeness and more than one opposition to ensure accuracy of orbital elements. Using the *Mercury* N-body hybrid symplectic code [4], we integrated the solar system forward 10Myr with these objects as massless test particles. Each instance of a test particle passing within 1 Hill radius of Mars was counted as a close encounter, and from these close encounters we obtained a distribution of impactor speeds and inclinations relative to Mars’s orbital plane (Figure 1).

**Impact Model:** From each of the \(~43,000\) close encounters, we constructed 100 impacts following a method similar to [5]. In particular, for each inclination-speed pair we randomly generate impact parameters and arguments uniformly in the disk where hyperbolic orbits with focus at Mars’ center of mass are guaranteed to impact Mars. The trajectories of the hyperbolic orbits were solved analytically, the precessional season of the axial tilt (i.e. the angle between the axes of rotation for inclination and obliquity) was sampled uniformly from \([0, 2\pi]\), and obliquity was varied as a free parameter from 0 to \(90^\circ\). The set of impacts with impact angle (relative to the planet’s surface) in the bottom 5% were assumed to produce elliptic craters. Model outputs show that the most abundant crater orientation shifts from North-South to East-West as obliquity increases.

**Validation of Elliptic Crater Data:** The Robbins Mars crater database [3] contains measurements of crater ellipticities and major axis orientations obtained from fitting ellipses to points traced around crater rims. To validate this data, we retraced a random sample of elliptic craters from [3] spanning all ellipticities greater than \(1.1\) and major axes greater than \(1\)km and performed the direct ellipse fitting procedure from [6] that was used in [3]. When retracing craters, we displayed only the reported centers and not the best fit circles to avoid biasing our traced rim locations. Filtering out highly degraded craters (degradation state \(\leq 2\) in [3]) and crater-matching blunders, agreement between our measurements and measurements in [3] of ellipticity and orientation is good (Figure 3).

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**Figure 1.** Relative frequency of 30x30 binned close encounter speeds and absolute inclinations.

**Figure 2.** Probability density of elliptic crater orientations predicted by our forward model.
Preliminary Model-Data Comparison: Considering fresh craters (degradation state ≥3) with major axis greater than 10km and ellipticities greater than 1.1, we see that most craters are oriented in the North-South direction (Figure 4). This is consistent with a low obliquity in our model predictions. Minimizing the chi-squared statistic between our model distribution and the Robbins distribution indicate a best-fit long-term mean obliquity of ~5° (Figure 4).

Discussion and Future Work: In our model-data comparison, we included only relatively fresh craters with degradation state ≥3. Degradation state is a proxy for individual crater age, and thus this filter was chosen to remove ancient craters from the target sample. Our estimate of the impactor population on Mars is seeded from modern observations of asteroids and thus cannot be representative of the chaotic early solar system. Recent work in [7] suggests that solar system stabilization occurred ~3.5Gyr ago. We plan to include a more quantitative estimate of crater degradation in future analyses.

The distribution of close encounters are limited to objects with magnitude less than 14, where the cumulative number of objects deviates from a power law (following the method in [8]), to ensure completion of the population. However, if there is an albedo bias with asteroid inclination, we may be biasing the contribution of different inclination groups to the crater record. Comparison with NEOWISE [9] data should allow us to estimate the magnitude of this albedo bias.

Our inter-analyst comparison of ellipticity and orientation showed generally good agreement, which allowed us to take a simple data-cut for our model-data comparison. However, we plan to perform more rigorous tests of the relative contribution of systematic and random error. This will allow us to carefully decide which craters to accept as elliptical.

The current model assumes a single obliquity value for every impact seeded from the close encounters. We hope that with bootstrapping over the dataset we will be able to invert higher-order information about the obliquity probability distribution function.

Preliminary model fits suggest that Mars obliquity since solar system stabilization was often low (Figure 4). At high obliquities (> ~40°), seasonal melting is more likely to occur, even at low latitudes, while at low obliquities, atmospheric collapse could occur [1,10,11]. Thus, our results may have implications for the frequency and duration of periods during which liquid water was stable at the Martian surface and could potentially produce runoff.

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QUANTITATIVE PROCESSING OF X-RAY MAPS: A PRESENTATION OF MAPPING ARTIFACTS, SOLUTIONS AND APPLICATIONS TO METEORITES. L. Kööp\textsuperscript{1,2} and A. M. Davis\textsuperscript{1,2,3}, \textsuperscript{1}Department of the Geophysical Sciences, \textsuperscript{2}Chicago Center for Cosmochemistry, \textsuperscript{3}Enrico Fermi Institute, University of Chicago, Chicago, IL, USA (E-mail: kooep@uchicago.edu).

Introduction: X-ray mapping by scanning electron microscopy (SEM) is a common technique in geo- and cosmochemistry that provides a wealth of petrologic information. With the arrival of large-area silicon drift detectors, large amounts of chemical data can be collected on relatively short timescales. To control the quality of x-ray maps, it is often useful to produce unnormalized maps and reject analyses from spots that have totals deviating from 100\% by more than a defined threshold (e.g., 2\%). However, this requires that a constant beam current and a constant working distance are maintained. In addition, an appropriate beam measurement standard and exact knowledge of the thickness of the conductive coating are required. Often, these conditions cannot be met, and it is useful to normalize each point analysis in a map to 100\%. In such cases, deviations from 100\% cannot be used for an internal quality control.

Here, we present examples of artifacts of normalized x-ray maps and a quantitative approach to improve the quality of x-ray maps after data collection. We also show how the processed data can be used for further analysis, e.g., to constrain chemical zoning in minerals.

Samples: We present unprocessed and processed elemental maps for CAIs 2-2-8 and 1-6-7. CAI 2-2-8 is a zoned single hibonite crystal with abundant holes filled with epoxy (Fig. 1). It was previously presented in \cite{1} and interpreted as a spinel-hibonite inclusion fragment. CAI 1-6-7 was also presented in \cite{1} and is a dense aggregate of spinel, gehlenite and hibonite (Fig. 2). CAI 1-6-7 has multiple cavities, some are filled with epoxy, others are depressions in the polished surface. Alteration phases are present near the edge of the CAI.

Analysis and Results: The ‘raw’ data for our quantitative treatment are datafiles that can be exported from EDS operating software. For each element of interest (here: Mg, Al, Ca, Ti, Fe, Si), we export both raw counts and concentration files. For the coating element C, we only export a raw counts file.

The data processing is performed in Python, making use of the pandas library, which facilitates efficient analysis of multiple large datafiles. Here, we summarize the main analytical steps to improve the quality of x-ray maps. All steps are optional and can be performed independently of each other. Figures of maps and datafiles can be exported for each step.

Step 1: Filtering out analyses from uneven surfaces, and/or embedding material. To reject embedding material analyses, we use a raw counts map of an element that is abundant in the embedding material, but rare in the sample (here, we use C, as the CAIs are cast in epoxy) and reject analyses from spots that have C counts above a defined number (here, we rejected analyses with C counts >400). To remove analyses from uneven surfaces, we simply remove data from spots where counts of the most abundant element are unusually low for a given concentration. A comparison of Figs. 1b & 1c as well as 2b & 2c shows that this step efficiently removed analyses of epoxy as well as uneven surfaces.

Step 2: Filtering out data with high relative uncertainties. For each element, we can calculate the relative uncertainties using raw counts. Here, we rejected concentrations with relative uncertainties >20\%.

Step 3: Rejection of data with low totals. This step should be performed for unnormalized maps and can be performed for normalized data if step 2 has been performed. Here, we rejected spot analyses with totals deviating from 100 wt\% by 3.0 wt\% or more.

Additional steps: We have also implemented algorithms that produce RGB images for any chosen set of three elements (Fig. 2d) and color-coded phase maps. Furthermore, we can calculate formulae for selected minerals. Such data can be used to assess the chemical variation inside minerals (Fig. 3). Here, we find that hibonite compositions are more variable in 2-2-8 than in 1-6-7 (Fig. 3).

The advantages of our quantitative processing are shown in Figs. 1 & 2. In the unprocessed Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} maps, epoxy-filled holes seem to increase the zoning in the hibonite grain (low Al\textsubscript{2}O\textsubscript{3}, high SiO\textsubscript{2}; Figs. 1b & d). In the processed maps, the holes are excluded and the maps show a more appropriate Al\textsubscript{2}O\textsubscript{3} zoning that is complemented by zoning in MgO and TiO\textsubscript{2} (see Fig. 3).

The importance of step 2 is shown in Fig. 2. The unprocessed map (Fig. 2e) suggests that FeO is present in low concentrations and is approximately uniformly distributed between hibonite, spinel and gehlenite. The processing (Fig 2f) reveals that FeO abundances in these primary minerals are associated with high uncertainties. Significant amounts of FeO only appear to be present in alteration phases at the edges of the inclusion.

Conclusions and Outlook: Quantitative processing of x-ray maps is a useful approach to improve the quality of x-ray maps and to remove artifacts. It further allows exporting and analyzing the processed data for individual minerals, which is useful to compare the range of zoning between samples.

Fig. 1: CAI 2-2-8. a) Secondary electron image of the CAI showing holes filled with epoxy. Al$_2$O$_3$ (b, c) and SiO$_2$ (d, e) maps are shown. b) and d) show elemental maps before quantitative processing, c) and e) show the results of full processing.

Fig. 2. CAI 1-6-7. a) Backscattered electron image of the CAI. MgO (b, c) and FeO (e, f) maps are shown. b) and e) show elemental maps before quantitative processing, c) and f) show the results of full processing. d) RGB image.

Fig. 3. Comparison of compositions measured in the mineral hibonite in CAIs 2-2-8 and 1-6-7. For both CAIs, the hibonite data is consistent with a coupled substitution of Mg$^{2+}$ and Ti$^{4+}$ for 2Al$^{3+}$. The comparison shows that the range of Mg, Ti and Al contents is more restricted in hibonites in 1-6-7 than in 2-2-8.
GAS TRAPPING BY AMORPHOUS ICE IN THE SOLAR NEBULA. F. J. Ciesla¹ and S. Krijt¹,
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**Introduction:** The origin of noble gases in comets and icy planetesimals remains uncertain. As pure materials, these elements are not expected to condense out of the solar nebula until very low temperatures (<30 K) are reached. While planetesimals may have formed in such environments, as pure substances these elements would vaporize as the comets moved to warmer environments. As comets appear to be releasing these gases at much higher temperatures than this, it appears these species must have been incorporated into solid bodies in another way.

Experiments show that amorphous water ice formed at low temperatures is able to trap noble gases within its structure [e.g. 1-4]. As a result of this trapping, the noble gases are thus locked up within the water ice, being released only when the water ice itself is vaporized. However, trapping experiments were performed at conditions which differed significantly from those expected in the solar nebula or molecular clouds. Thus, it remains unclear what the trapping efficiency would be in actual astrophysical environments. Here we report our progress on developing numerical models which are tuned to reproduce experimental results and applying them to determine how efficient trapping is real astrophysical environments.

**Modeling Noble Gas Trapping:** Early experimental work on noble gas trapping were carried out at very low temperatures (<30 K) and high deposition rates resulting in the growth of a layer of ice 0.1 microns in thickness in a matter of minutes to hours (deposition fluxes of order ~10^15 molecules/cm²/s). In these experiments, it was found that the guest-to-H₂O ratio in the ice was identical to that of the ambient gas in the experiment [1]. This led many to conclude that the abundances of trapped gases would be the same as the solar ratio provided the amorphous ice formed at these temperatures [e.g. 4]. However, more recent experimental work has shown that noble gases can still be trapped at higher temperatures and lower deposition rates, but the concentration of the trapped species is much less than that found in the ambient gas [2,3]. This suggests that trapping is actually kinetic controlled, and not just a simple function of temperature.

Given that astrophysical environments are likely to have water deposition rates that are many orders of magnitude lower than what the experimental conditions have been carried out at [e.g. 5], we have developed a theoretical model for trapping of noble gases based on the three-layer astrochemical framework used to study ice evolution in molecular clouds [6]. This model tracks adsorption and desorption of water and a guest species (Ar is used here as a representative species) as the vapor freezes out onto a substrate. The guest species is considered “trapped” when it is covered by a monolayer of ice while it resides on a solid surface, moving from the “surface” of the ice to the covered “mantle”. In addition to adsorption and desorption, guest molecules are allowed to diffuse through the water ice, moving from the mantle to the surface.

The key parameters in the model are the binding energy of the guest molecule to the solid and the fraction of guest molecules the number of ice layers that can allow guest molecules to reach the surface via diffusion [6]. As these parameters have not been directly measured for noble gases, we have carried out a parameter space exploration to determine which values best fit the experimental results of [2].

We then applied these models to extrapolate the trapping efficiency down to lower deposition rates. The results are shown in Figure 1. Here we have simulated the freeze-out of a 1:1 H₂O-Ar gas mixture onto a substrate at temperatures of 27, 37, and 50 K, the same temperatures used in the experiments of [2] for a variety of deposition rates of ice (the experiments considered 0.1 and 0.001 micron/minute deposition rates), and we reproduce the experimental results here (at the highest deposition rate, the thin ice layers were found to have Ar/H₂O ratios of 0.1, at the lower deposition rate, that same ratio was found for T=27 and 37 K, but ~0.05 for T=50 K).

At lower deposition rates, we find that the trapping efficiency for Ar begins to decrease, though the decrease occurs at different deposition rates for different temperatures. This can be explained as the timescale for the formation of a monolayer of ice increases with decreasing deposition rate, while the residence time of a noble gas atom on the surface of a grain is just a function of temperature. As such, the likelihood of an atom adsorbing onto a solid and then being covered by a layer of ice to be trapped decreases with decreasing deposition rate. This leads to two trapping regimes: (1) **Burial** where high deposition rates lead to the rapid trapping of temporarily adsorbed guest atoms (water layer formation is rapid compared to desorption timescale of the atoms) and (2) **Equilibrium** where the abundance of guest atoms reaches a steady-state between adsorption and desorption as water slowly freez-
es out (water layer formation is slow compared to the desorption time of the atoms).

**Trapping Conditions in the Solar Nebula:** To date, it is unclear where, if at all, amorphous ice may form in a young planetary system. Based on the observation of cold water vapor in other protoplanetary disks that arises from photodesorption of ice off of solid grains [7], it has been suggested that such ice could form as the liberated water molecules freeze-out again onto solid grains [5,8]. The rate of amorphous ice formation, and thus the efficiency of noble gas trapping would thus depend on where this water vapor froze out again onto solids.

To investigate this, we have developed a model to track the 2D dynamics and freeze out of vapor in a protoplanetary disk [9]. By assuming a structure for the disk, we can calculate the flux of water molecules onto the surfaces of dust grains. An example is shown in Fig 2, where we use a disk structure based on that used by [7] to match the presence of a cold water vapor reservoir and assume that water vapor is present at a mixing ratio of $H_2O/H_2=10^{-5}$. Under these assumptions, freeze-out rates of water are expected to be $\sim$7-12 orders of magnitude less than used in the experiments of [2], and within the range where Equilibrium Trapping is largely predicted by our models where photodesorption would occur. Exact freeze-out rates and temperatures will depend on how the water molecules are liberated and transported within the disk and the size distribution of the dust that is present. This remains the focus of ongoing work [9].

**Discussion:** The conditions under which amorphous ice could form within the solar nebula is highly variable, with temperatures ranging from 10-50 K and freeze-out rates ranging many orders of magnitude. The amount of noble gas trapping that could occur will thus depend sensitively on where in the disk the amorphous ice forms. Efficient trapping would occur in regions at low temperatures and high deposition rates. Observations and protoplanetary disk models suggest that cold water vapor is present at high altitudes in the outer regions of disks as these regions are most easily bathed in UV [7]. Preliminary modeling suggests that volatiles will freeze-out in a narrow range of heights immediately below their effective ice lines in this disk which would be at somewhat elevated temperatures and low rates of water freeze-out [e.g. 9]. This could limit the ability for noble gases to be trapped in this way. We continue to explore the effects of dust growth and transport in the disks to quantify the extent of noble gas trapping by this mechanism in a self-consistent way.


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**Figure 1:** Contour map of Ar trapping efficiency in a gas of solar composition for typical pressures and temperatures expected in the solar nebula based on the model described in the abstract.

**Figure 2:** Freeze-out fluxes of water in a protoplanetary disk following the structure assumed by [7], taking the water vapor as being present at an $H_2O/H_2$ ratio of $10^{-5}$.
**Introduction:** The spatial distribution of the abundances of major volatile species (e.g., water, CO) in protoplanetary disks is expected to change dramatically during the disk’s 1-10 Myr lifetime. Astrochemical models indicate volatiles freeze out in cold, dense regions while remaining in the gas-phase in hot, tenuous, and/or UV-irradiated regions [e.g., 1]. At the same time, various mechanisms can transport large amounts of gas (through diffusion and advection) and solids (gravitational settling, turbulent mixing, and radial drift) in the vertical and radial directions [2,3]. Recent observations of mm-dust, molecular CO and various other tracers [4,5,6] hint at a common narrative: (i) volatiles are depleted from disk surfaces and presumed to be locked up in solids at the disk midplane; (ii) these solids then drift inward, redistributing the volatiles and potentially enriching the planet formation zone in carbon and oxygen [7]. At this point however, we lack a complete understanding of the interplay of these various processes and how they influence each other, making it difficult to connect different observables in single, well-studied systems (e.g., TW Hya or HL Tau), let alone draw comparisons between disks in different evolutionary stages.

**Towards a New Hybrid Model:** We present a new global, two-dimensional model that is capable of simulating the transport and interaction between volatile species (both in the form of vapor or ice), small microscopic dust grains, and larger coagulated pebbles in a simultaneous and self-consistent manner.

The method is based on treating these three ingredients separately, but not independently (see Fig. 1). The CO vapor and small dust components are treated as concentrations on a 2D Cartesian grid with logarithmically spaced grid cells, while the pebbles are described using Lagrangian tracer particles, each representing a larger number of physical particles. The transport of vapor and small dust is simulated by solving 2D transport equations (including advection and diffusion) on the logarithmic grid, while pebble motions are calculated using a random-walk-like Monte Carlo scheme that includes the effects of turbulent diffusion, vertical settling, and radial drift [2,3]. Different interactions between the components are included, such as freeze-out of CO molecules onto small dust, evaporation of CO ice present on dust grains or pebbles, and sweep-up of small grains by pebbles. The key advantage of this hybrid approach is that we can describe the pebbles as particles with unique histories (every pebble’s current size and chemical make-up is a function of its journey through the disk) and still solve interactions between vapor and microscopic grains in regions where the total mass of solids is small.

![Figure 1: Conceptual model of the hybrid approach.](2291.pdf)

**Results:** Figure 2 shows snapshots of models for a disk resembling the Minimum Mass Solar Nebula. The initial conditions (Fig. 2A) assume small dust is present everywhere with a constant dust-to-gas mass ratio of 0.005, while pebbles start out in a settled disk between 100-140 AU, with individual sizes around 1 mm and a surface density (relative to the gas) of 0.005. At $t=0$, we assume freeze-out/desorption equilibrium, which results in very little vapor in the midplane outside of $r\sim70$ AU.

Figure 2B shows the situation after 0.5 Myr of evolution, assuming all solids (dust & pebbles) are stationary. In this scenario, transport of ices is non-existent, and the continuous mixing of CO vapor to the midplane depletes the upper layers of the disk at those radii where freeze-out closer to the midplane is possible [5,8]. In this particular case, most vapor does not make it all the way down to the midplane, but freezes...
out onto small dust grains (not shown here) in the region highlighted by the blue contour. Knowing where and under which conditions ices are being formed is relevant for understanding their structure [e.g., 9].

In Fig. 2C, both the small dust grains and the pebbles are allowed to diffuse, settle, and drift. Since small, ice-covered grains can now return CO to the upper layers of the disk, the depletion as seen in case B practically vanishes. Thus, the removal of volatiles from the upper layers of the outer disk depends heavily on the ability of (small) grains to replenish vapor by transporting ices to these regions. After 0.5 Myr, most pebbles have moved inside the midplane snowline; their CO ice has evaporated and the disk has been enriched in CO vapor between 40-70 AU, with the radial extent of this enriched region depending on the height above the disk midplane.

For the simulations of Fig. 2, we have ignored dust-pebble interactions. If pebbles can efficiently accrete small grains however, the ability of small grains to replenish the vapor in the disk atmosphere will be reduced [10]. In that case, we still expect a considerable depletion of vapor from the upper layers [11]. A realistic disk is therefore expected to resemble an intermediate case between Figs. 2B and 2C.

The snapshots shown in Fig. 2 are by no means steady-state configurations. In fact, one of the outcomes of our simulations is that the abundances of ice, vapor, etc. vary significantly in time. Nonetheless, it is clear from Fig. 2 that both vertical and radial transport of volatiles, be it as vapor or ice, has a major impact on the spatial distribution of CO molecules.

Discussion: We introduce a novel 'hybrid' approach for modeling 2D transport of volatile species and solids in protoplanetary disks. The method is designed to intuitively connect several key observables: (1) vapor abundances in the upper parts of the outer disk; (2) vapor abundances close to, and inside of the midplane snowline; (3) the radial extent of the pebble disk; and (4) the distribution of small, microscopic grains. Solving the vapor abundance in two dimensions is critical for comparing to observations, as different tracers/wavelengths probe different layers of the protoplanetary nebula [e.g., 12].

By creating synthetic images of the model’s output and comparing these predictions to resolved observations of nearby protoplanetary disks, we will be able to constrain the efficiency of various transport mechanisms in those systems (e.g., vertical settling/stirring, radial drift), allowing us in turn to extract key parameters such as the turbulence strength and the dust-to-gas ratio — parameters that, despite being very important for understanding disk evolution and planet formation, are notoriously hard to measure directly.


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Figure 2: Snapshots of our model for different scenarios assuming an alpha turbulence of $5 \times 10^{-4}$. The background color indicates CO vapor density (relative to H$_2$) and the spherical symbols represent the pebble population (blue is ice-rich, white is ice-poor).
COLLISIONAL HISTORIES OF SMALL PLANETESIMALS T. M. Davison1, E. Shivarani1, G. S. Collins1, D. P. O’Brien2, F. J. Ciesla3, and P. A. Bland4. 1Impacts and Astromaterials Research Centre, Department of Earth Science and Engineering, Imperial College London, London, SW7 2AZ, United Kingdom (E-mail: thomas.davison@imperial.ac.uk). 2Planetary Science Institute, 1700 E. Ft. Lowell, Suite 106, Tucson, AZ 85719, U.S.A. 3Department of the Geophysical Sciences, The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637, U.S.A. 4Department of Applied Geology, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

Introduction: Most asteroids smaller than 500 km are porous [1]. This porosity may be primordial microporosity and/or macroporosity introduced by fragmentation and reaccumulation. Recent work suggests that impacts may have been influential in compacting chondritic precursor materials [2, 3]. To place those results in context requires an understanding of collisional histories of meteorite parent bodies. Models of solar system evolution suggest that objects > 100 km are difficult to disrupt [4, 5]; thus, a significant fraction of their porosity should be primordial. Objects below this size are generally assumed to be collisional fragments; however, their collisional histories and the nature of their internal structure is uncertain.

Here we investigate the fraction of small primitive asteroids that is disrupted; the nature of those disruptive events; and the nature of the largest and most influential impacts on surviving (non-disrupted) bodies.

Modelling: For this work, an analytic collision physics model [6, 7] was incorporated into an existing Monte Carlo planetesimal collisional history model [5, 8].

Collisional outcomes: The analytic model [6, 7] defines 6 categories of collisional outcomes based on the impact velocity, impact angle and the masses of the impacting and parent bodies. As erosive impacts dominate, we refine these outcomes by further subdividing impacts that cause partial erosion based on the fraction of the target that is eroded. We also treat as a special case any impact where the impactor mass exceeds the target mass. In this case, we mark the parent body as accreted on a larger body, calculate no further impacts on that parent body, and remove it from any further analysis.

Parent body collisional histories: To determine the frequency and intensity of different collisional outcomes, a Monte Carlo model [5, 8] was used to predict impact histories for a range of parent body sizes (1 – 250 km radius) over the first 100 Myr of solar system evolution. For each parent body size, $10^5$ parent bodies were simulated in the Monte Carlo model. For each parent body, a set of impact parameters was determined using time-varying asteroid size-frequency distributions, impact velocity-frequency distributions and intrinsic collisional probabilities that were calculated using collisional and dynamical evolution modelling of terrestrial planet growth [e.g. 9, 10]. For each impact that was determined to have taken place, the impactor mass, impact velocity and a randomly selected impact angle (where $P(\theta) = \cos^2 \theta$ [11]) were used as inputs to the collisional outcome calculation.

Limitations/future work: The analytic collision physics model does not consider the strength of bodies when determining the catastrophic disruption threshold. This assumption is reasonable at large parent body sizes, but to extend our model to smaller sizes the disruption criterion should transition to a strength-dominated regime.

Currently the mass of the parent body is fixed in the Monte Carlo calculation: each subsequent impact occurs on the same mass of target. Future calculations will track the changing mass of the target, as it accretes or loses mass by collisions.

Results: Figure 1 shows the average number of disruptive collisional events per parent body during the first 100 Myr of Solar System history, as a function of parent body size.

![Figure 1: Average number of disruptive collisional events per parent body during the first 100 Myr of Solar System history.](image)

The average number of disruptive events is shown as a function of parent body radius. The average number of disruptive events increases with increasing parent body radius. At parent body radii between 2–20 km, the number of disruptive events is low (3–8% of parent bodies). For parent bodies with radii 20–250 km, the average number of disruptive events is 25% – 45%. Only at a parent body radius of 1000 km does it become more likely than not that a parent body is disrupted during 100 Myr (71% of parent bodies).

Our simulations calculate the amount of mass lost or gained ($\Delta M$) during each collision on a parent body. Figure 2 shows the average net mass change, as a fraction of the total parent body mass ($M_p$) for all parent bodies (black circles), parent bodies disrupted in the first
100 Myr (red diamonds) and parent bodies that survive without disruption during 100 Myr (blue squares). For all objects considered here (up to a maximum radius of 250 km), there is net erosion of the bodies, consistent with previous work [12, 13]. For 1 km objects, almost the entire mass of the object is eroded away during 100 Myr; however, approximately 50% of the total mass of bodies in the 2–20 km size range survives the same period. Of those asteroids that survive 100 Myr, 1-km radius objects tend to lose more than half of their mass, whereas 2–20 km radius bodies tend to lose a much smaller proportion of their mass (10–20%) in the same time period.

We note that mass changes of less than −1 on Figure 2 are an unphysical consequence of assuming a fixed target mass. They show bodies that were eroded extensively prior to disruption. This limitation will be addressed by future simulations that track the changing mass of the parent body.

Surviving objects: Those objects that are not disrupted in the first 100 Myr still experience some large sub-catastrophic impacts. The nature of these events will determine whether any primordial porosity remains. For a 10-km body (and other target sizes), most mass is eroded by impacts in the region $-0.1 > \Delta M/M_t > -0.5$ (Fig. 3). At a typical impact velocity of 5 km s$^{-1}$ and angle of $45^\circ$, a ~ 1 km impactor would erode 10% of the parent body mass, and a 2 km impactor would erode 50% of the mass. Impacts on this scale will cause significant localised heating and compaction, but not global scale effects [8, 14], suggesting that if the object had primordial porosity to begin with, it should be largely retained after 100 Myrs.

Discussion: Asteroids smaller than 1 km seem unlikely to contain any primordial porosity, even if it existed to begin with. Asteroids larger than $\sim 100$ km are likely to be primordial [4]. However, in the transition region between these two sizes, any porosity present could be a mix of primordial microporosity (if it existed to begin with) and macroporosity, resulting from impact fracturing or re-accretion following partial disruption events. Future modelling will use these collisional histories combined with shock physics modelling [3] to track compaction as a function of time and depth on a meteorite parent body.

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Introduction: Stony-iron meteorites, mixtures of silicate and metal thought to have formed during collisions between differentiated planetesimals, are the least common subset in the terrestrial collection. The canonical theory of stony-iron meteorite formation requires low velocity, glancing ('hit and run') collisions between relatively large planetary embryos [1-2]. However, such collisions within a terrestrial planet forming region dynamically excited by Jupiter [3] were likely quite rare. Because there are several distinct genetic groupings of stony-irons [2], implying different parent bodies and hence multiple rare hit-and-run collisions, it is worthwhile to quantify the ability of smaller, more common impacts to produce silicate-iron mixtures within differentiated planetesimals.

Collision Models: Using the iSALE-2D [4-6] shock physics code, we modeled 10 km radius dunite impactors colliding head-on into a 100 km radius differentiated target planetesimal at 3 and 6 km/s at various points in their evolution (10, 50, and 88 Myr after formation). Pre-impact target temperature profiles are determined using an internal differentiation and cooling model [7]. All impact models assume a cylindrically symmetric geometry, have a spatial resolution of 666 m, and use self gravity. Material thermodynamics are addressed using the ANEOS equation of state package [8]. The mantle is treated as a visco-elastic-plastic solid [9], with flow laws appropriate for the terrestrial mantle [10], and a temperature dependent yield strength with a melting point of 1436 K. In the 10 Myr scenario, the entire core is above the melt temperature of most iron alloys and is assumed to be a fluid with viscosity $\eta=100$ Pa s. For the 50 Myr scenario the core has an initial temperature of ~1200 K, and depending on composition, could reasonably be either entirely molten or entirely crystallized before impact. As such, we consider both liquid ($\eta=100$ Pa s) and solid cores; in the latter case assuming a strain- and temperature-dependent yield strength [11] appropriate for metals and a melt temperature of 1300 K. For the 88 Myr scenario, the temperature of the core is ~750 K and is treated as a solid for all impact scenarios.

Turbulent Mixing of Iron and Silicate: A Lagrangian tracer, which tracks the motion of material through iSALE’s fixed Eulerian computational mesh, is embedded within each cell of the pre-impact target. Each tracer is initially composed of 100% iron or 100% silicate. At each post-impact timestep, tracer pairs in close proximity with large differences in composition are identified. For each such tracer pair, we find a second set of nearby, orthogonally oriented tracers in order to build a quadrilateral set. The deformation of this quadrilateral allows us to calculate a shear strain rate for each tracer pair [12]. We then allow material to flux from one tracer into another assuming a Prandtl [13] turbulent mixing velocity that is proportional in scale to this shear, such that the rate at which material is exchanged is highest for tracer pairs in close proximity and with high shear rates. Because each tracer may form more than one pair in a given timestep, concentrations are updated in such a way as to conserve total system mass. To avoid rapid diffusion of material across the target, we only allow tracers to exchange material if they have a difference of composition greater than 10%.

Results: Immediately after passage of the shock wave, a small amount of material interchange takes place at the core mantle boundary of the target, but the degree of mixing is relatively minor. In simulations where the transient crater is deep enough to significantly deform the core, crater collapse induces large shear strains at the core mantle boundary, rapidly mixing silicate and metal. The amount of mixing can be considerable: in the 10 Myr scenario [Fig. 1 a-d] where the majority of the target’s interior is molten, ~35 impact masses worth of material are >50% mixed at the end of the simulation [Fig. 1 d]. While most tracers that become heavily mixed are ultimately emplaced near the core mantle boundary, a considerable amount of mixed material is advected into both the mantle and the interior of the core. Mixtures which end up in the planetesimal’s upper mantle may record vastly different post-impact cooling rates than mixtures in the deep interior of the body. This may help to explain the diverse cooling rates reported for stony iron meteorites [13], depending on whether or not these metal rich plumes reach closure temperature before being gravitationally driven back deeper into the interior of the body.

While some mixing does occur in late (50 and 88 Myr post-accretion) impact scenarios, the total mass of thoroughly mixed material produced is considerably lower than for early (10 Myr) impacts [Fig. 1 d-f]. This is because the elastic strength of the cooler targets greatly suppresses the amount of shear that can occur.
During crater collapse. In these cases, the majority of thoroughly mixed material ends up near the target’s final core mantle boundary, and as such, the cooling rates recorded by these mixtures should be fairly uniform. The exception to this rule is very energetic [Fig. 1 e-f] late collisions in which part of the core is melted by the impact shockwave, allowing for an enhanced degree of mixing, but the strength of the unmelted mantle prevents the planetesimal from completely collapsing back into a spherical, isostatic shape.

Discussion: There are several limitations to the mixing model as implemented in this work. First, the parameterization of sub-grid scale turbulent advection is quite simple, with a linear dependence on shear rates, and relies on tuneable free parameters that can alter the total amount of mixing induced by a given impact. Secondly, because the mixing analysis is done as a post-processing step, silicate-iron mixture thermodynamics and rheologies do not influence the bulk advection of material within the impact simulations. Nonetheless, our results are sufficient a) to demonstrate the efficacy of small impacts in producing silicate-iron mixtures within differentiated planetesimals; and b) for quantifying how the magnitude of mixing depends on how long after accretion an impact occurs.

Conclusions: Relatively small impacts into differentiated planetesimals are capable of producing large quantities of iron-silicate mixtures. The degree of mixing that occurs is a function of both impact energy and epoch of impact (with early impacts producing several orders of magnitude more mixed mass than late impacts).


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![Figure 1](2323.pdf)  
**Figure 1:** [a-c] Time series showing (a) pre impact state (b) mixing at the onset of transient crater collapse and (c) mixing at the onset of central uplift collapse. [d-f] Final states for impacts into targets 10 (d), 50 (e), and 88 (f) Myr after formation. The color scale represents the degree of mixing, with 0 corresponding to pure metal or pure silicate, and 100 corresponding to a fully mixed, 50% silicate/50% iron material. Completely unmixed tracers are plotted in grey. All targets have initial radius of 100 km.
STRONTIUM STABLE ISOTOPE COMPOSITION OF ALLENDE FINE-GRAINED INCLUSIONS

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Introduction: Isotopic anomalies are departures from the laws of mass-dependent fractionation that cannot be explained by radioactive decay, cosmogenic effects, or exotic isotopic fractionation processes such as nuclear field shift or magnetic effects [1 and references therein]. These anomalies often have a nucleosynthetic origin and provide clues on the stellar origin and solar system processing of presolar dust. Anomalies are most often found in refractory elements of relatively low mass, so Sr is a prime target for study. The four stable isotopes of strontium are useful for discerning the various nucleosynthetic origins of early solar system building blocks and the timing of accretion processes. Strontium-84 is the least abundant (0.56%) of these isotopes, but is particularly significant in being a p-process only nuclide that is produced in core-collapse or type Ia supernovae [2,3]. The more abundant isotopes 86Sr (9.86%), 87Sr (7.00%) and 88Sr (82.58%) are produced in s- and r-processes in asymptotic giant branch stars and other stellar types [4]. Additionally, 87Sr is produced by 87Rb decay in proportions that dominate over possible nucleosynthetic variations but provide timings of early solar system processes, most notably volatile element depletion [5-7]. Furthermore, variations in strontium isotopic ratios caused by high-temperature mass-dependent fractionation [8] are also important [9-12], as they provide insights into nebular and accretionary processes.

Studies of stable Sr variations have thus far been limited to three approaches. Firstly, the classical approach is correction of instrumental mass fractionation by internal normalization to 86Sr/88Sr = 0.1194. Taken at face value, such data indicate potential small positive 86Sr anomalies in bulk carbonaceous chondrites [13], but information about natural stable isotope fractionation is lost. Second, those that resolve fractionation in one of the isotope pairs – usually 86Sr/88Sr - using fractionation correction to an external element [11,12]. Thirdly, double-spike methodologies that resolve all the isotope ratios without recourse to internal or external normalisation, providing true relative isotopic compositions [9,10]. In the case of the latter examples, this early work was limited to a precision of ~0.25 and ~0.5 ‰ for the 87Sr/86Sr and 84Sr/86Sr ratios respectively and only broad trends in mass-dependent fractionation could be determined. Measurements of 84Sr/86Sr ratios were well below the necessary precision to reveal any non-mass-dependent anomalies in the 86Sr abundance in the separated CAIs from Allende.

Here, we present new high-precision TIMS 84Sr/86Sr results for a suite of previously studied fine- and coarse-grained CAIs from Allende [14] in order to investigate nucleosynthetic anomalies associated with variations in p-process 84Sr abundances. Measurements of spiked aliquots are underway to determine the Sr stable isotopic fractionation on the same samples.

Experimental: Initial digestions were carried out for the study of [14] and an aliquot was taken for Sr isotope analysis. This aliquot was further divided into two equal portions, one of which was optimally spiked with an 84Sr/86Sr double spike (DS), the other left unspiked. The spike amount required for optimal spiking was based on the amount of Sr present from measurements of trace elements in separate aliquots of the same samples. Natural and DS aliquots were dealt with independently and all manipulations and separations were carried out in separate laminar flow cabinets only using beakers and columns specifically designated for use with spiked and natural samples, respectively. The number and type of manipulations for the DS and natural aliquots were identical in order to remove the possibility of differential blank issues. The spike was added to the samples prior to column separation in order to circumvent possible column-induced fractionation. Sr was separated from both aliquots using identical protocols involving sorbing the Sr onto Sr-spec resin in 8M HNO3, followed by recovery of Sr in 0.05 M HNO3 [15].

Measurements were carried out on the VUW Thermo-Finnigan Triton TIMS in static mode with a standard configuration using 6 Faraday collectors and 1011 Ω feedback resistors. Samples were loaded on outgassed zone-refined single Re filaments with a Ta2O5 activator. Runs used amplifier rotation and consisted of 540 ratios, 16 sec integrations with two minute baselines measured every block. Mass fractionation was corrected by assuming 86Sr/88Sr = 0.1194.

Results: Results are shown Figure 1, where 84Sr/86Sr ratios are reported in μ-units (μ84Sr = 106 relative deviations from average NBS-987). External reproducibility was 13.3 μ84Sr and is denoted by the
shaded band. CAI data define a range in $\mu^{\delta_4}Sr$ values from +30.3 (within error of the standard data) to +286.5. Four terrestrial rock standards - two each of granite G3 and basalt BCR-2 - are shown for comparison and agree well with the standard data (i.e., no anomaly detectable). A compilation of previously published data for normal (i.e., non-FUN) refractory inclusions from CV3 is also plotted for comparison.

**Discussion and conclusion:**

FUN inclusions show large negative $\mu^{\delta_4}Sr$ anomalies that can reach $\sim$5000 [16,17]. In contrast, non-FUN CAIs display positive anomalies that cluster around $\sim$120 [7,18]. Recent measurements of other elements have suggested that non-FUN CAI could have formed from a uniform isotopic reservoir of non-terrestrial isotopic composition [18]. Our new results show that this view is correct to first order but that significant variations are present between CAIs. In particular, we report the largest $\mu^{\delta_4}Sr$ excess measured thus far in a bulk CAI of +286.5. Because this value is more anomalous than the isotopic compositions defined by other meteorites, this cannot be due to dilution by matrix or terrestrial Sr, which have near-normal compositions. Instead, it must reflect some heterogeneity in the isotopic composition of the region in which non-FUN CAIs formed.

Several scenarios exist for explaining the presence of isotopic anomalies in meteorites and their components. One is that those anomalies were simply inherited from large scale heterogeneities that existed in regions of the molecular cloud core that collapsed to form the Sun [19]. Another is that the solar system started with a more or less uniform isocopic composition and isotopic anomalies were created by thermal processing [20] or grain size sorting [21] that separated components with distinct isotopic signatures. One possible consequence of the thermal processing model is that the creation of isotopic anomalies would be accompanied by mass-dependent fractionation that is usually a characteristic of evaporation/condensation processes. Measurements are currently underway to document the mass-dependent component of the isotopic variations to search for correlations with isotopic anomalies. The large range of $\mu^{\delta_4}Sr$ variations measured among the studied CAIs makes this an ideal sample set to test this idea.

**References:**


![Figure 1. $\mu^{\delta_4}Sr$ compositions of 16 Allende CAIs previously studied by [14] compared to terrestrial rock standard and previously published CAI data.](image-url)

Introduction: Iron meteorites come from the cores of differentiated planetesimals. The cooling rates of these samples provide valuable insight into the thermal evolution and structures of their parent bodies. Haack et al. [1] simulated the thermal evolution of differentiated bodies using a one-dimensional conductive thermal model. They found that a core would cool uniformly and that the cooling rate was a function of the planetesimal size. However, for many iron meteorite groups, the measured cooling rates exhibit values that range over orders of magnitude. For example, IVA iron meteorites have measured cooling rates from 100 to 6600 K/Myr [2]. Additionally, [1] inferred the parent body sizes for iron meteorites would be <100 km in radius. This is at odds with the idea that asteroids are “born big,” with initial sizes from 100 - 1000 km [3].

The Haack et al. [1] model did not allow for collisions to occur as the body cooled. However, during the first 100 Myr of solar system evolution, planetesimals would have experienced frequent and energetic collisions [4]. Ciesla et al. [5] found that an impact onto a radiogenically heated body could uplift material at depth, bringing it closer to surface, where it would cool more quickly than expected for where it originated. Similarly, it has been shown that hit-and-run collisions could strip large planetesimals of their mantles, expose the cores, and produce the non-uniform cooling rates found for iron meteorite groups such as the IVA’s [2,6]. However, hit-and-run impacts in the first 100 Myr would be much less frequent than collisions between smaller bodies. Therefore, it is useful to investigate the effect small, energetic impacts would have.

Here we report preliminary results of our investigation of whether energetic collisions in the early Solar System could produce scatter in metallographic cooling rates throughout the core of a differentiated body. To do so we follow a planetesimal as it is heated, differentiates, is impacted, and subsequently cools.

Differentiation Model: Our modeling pipeline starts with a cold purely chondritic body and is then heated by Al26. Thermal evolution is found by solving the 1D heat equation, assuming spherical symmetry [1]. The thermal properties of the materials and heat production rates are taken from [7].

When regions of the planetesimal reach temperatures of 1673 K (the midpoint between the assumed liquidus and solidus) differentiation occurs, forming a core and molten silicate mantle. The size of the iron core is determined from the metal fraction in the original chondritic material and the volume of the molten region. Additional melting of the planetesimal would lead to further growth of the core. In the models reported here, the cores are 44 km in radius for fully differentiated 100 km radius bodies.

The molten mantle is assumed to convect when the temperature is above the 50% partial melt threshold, producing a roughly isothermal region [7]. The rapid heat transfer in a convecting mantle is modeled by increasing the thermal diffusivity of the hot silicate material by three orders of magnitude [8,9].

Impact Model: Using the iSALE-2D [10-12] shock physics code, we modeled 10 km radius dunite impactors colliding head-on into the 100 km radius differentiated target planetesimals formed simultaneously with CAIs (t=0) at 3 and 6 km/s at various points in their evolution (10, 50, and 88 Myr after formation). All models assume a cylindrically symmetric geometry and have a spatial resolution of 666 m. Material thermodynamics are addressed using the ANEOS equation of state package [13]. The mantle is treated as a viscoelastic-plastic solid [14], with flow laws appropriate for the terrestrial mantle [15], and a temperature dependent yield strength with a melting point of 1436 K. In the 10 Myr scenario, the entire core is above the melt temperature of most iron alloys and is assumed to be a fluid with viscosity $\eta=100$ Pa s. For the 50 Myr scenario the core has an initial temperature of ~1200 K, and depending on composition, could reasonably be either entirely molten or entirely crystallized before impact. As such, we consider both liquid ($\eta=100$ Pa s) and solid cores; in the latter case assuming a strain- and temperature-dependent yield strength [16] appropriate for metals and a melt temperature of 1300 K. For the 88 Myr scenario, the temperature of the core is ~750 K and is treated as a solid for all impact scenarios. These simulations were also used to investigate the mixing of silicate and metal during impacts [17].

Thermal Evolution: The cooling of the post-impact planetesimals is calculated using a 2D, cylindrically symmetric heat equation. Cooling rates at the metallographic closure temperature of the iron core, 773 K, are recorded throughout the body.

Figure 1a shows the initial conditions for a simulation of a 100 km body impacted head-on with a 10 km impactor at 6 km/s 50 Myr after its formation. The core was assumed to be solid. The colors denote the temperature profile of the planetesimal as calculated using our differentiation model. The black line marks the core-mantle boundary. Figure 1b shows the same body
about 7 hours post-impact. The iron core has been disturbed slightly, with the silicate mantle experiencing some erosion and thinning.

Figure 2 shows cooling rates near the impact zone. Only material with temperature exceeding 773 K post impact had cooling rates recorded. The gray regions are parts of the mantle that remained at $T<773$ K after the impact occurs, and thus retain their onion-shell cooling rate. The black line marks the core-mantle boundary. The mantle near the impact site cools very quickly as it is now closer to the surface than before the impact. The core, however, still cools uniformly at a rate of $\sim 10$ K/Myr which is the same as a non-impacted body. We explored impacts at 10, 50, and 88 Myr after formation with a 10 km impactor at 3 and 6 km/s. All simulations show similar outcomes, the cores cool at the same rate as an unimpacted body. A more energetic impact would likely excavate even more mantle, reducing the size of the insulating silicate layer at the impact site. This would lead to faster cooling in the core. Such simulations are now being performed.

Future Plans/Discussion: We are currently running a suite of simulations of more energetic collisions, varying time of impact, impactor size, and impact velocity. If we continue to find that disturbing the cooling rates of the core is difficult in this scenario, it would suggest that more rare low velocity, hit-and-run collisions among large bodies were the dominant mechanism for producing spread among the iron meteorite cooling rates. However, if more energetic collisions involving small impactors can also enhance cooling, this would suggest that these meteorites possibly are sampling the high velocity impacts predicted in planetary accretion simulations [4,18]. Either way, this research will constrain the dynamical evolution of meteorite parent bodies in the early Solar System.


Figure 1: An impact onto a differentiated planetesimal occurring 50 Myr after formation with a 10 km/s impactor at 6 km/s head-on. The black line marks the location of the core. The mantle at the impact site is displaced bringing the core closer to the surface.

Figure 2: The cooling rate of the above impacted body near the impact site. The gray regions are mantle that were not hotter than 773 K post-impact. The core is outlined in black. The core cools uniformly at $\sim 10$ K/Myr while the uplifted hot mantle cools very quickly at the surface.
FACULAE ON CERES: POSSIBLE FORMATION MECHANISMS


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Introduction: On Ceres’ low albedo surface there occur localized bright areas usually associated with impact craters [1]. The brightest and largest spots, Vinalia and Cerealia Faculae, are found within the young (~21 Ma) Occator crater [2] (Fig.1) and consist predominantly of sodium carbonate [3]. The localized, high concentration of carbonate is interpreted as the solid residue of a crystallized salt solution (i.e., brine) [1, 3, 4-6]. Occator crater also hosts lobate flows suggestive of brine-based cryovolcanism [7] and/or collapsed walls [5]. Whether a relationship between the faculae and cryovolcanism exists is currently under debate.

Here we use clear-filter framing camera (FC) LAMO images (~35 m/pixel) to perform a morphological analysis of Cerealia and Vinalia Faculae (Fig. 1), and discuss possible formation mechanisms.

Observations - Vinalia Faculae: Vinalia Faculae consist of several localized bright areas adjacent to each other, found on top of a large lobate flow covering the floor of Occator crater [2, 5, 7]. Only the two largest bright areas are described here (Fig. 2) as the smaller spots are not spatially resolved. The facula at 20°N-242°E (site 1) is characterized by a 500 m wide circular feature (hereafter pit) and a surrounding bright halo, 5 km in width. The pit is rimless and has a relatively flat floor, distinct from a bowl-shaped crater of such a size. One of the pit sides corresponds to a dark-er, linear fracture [8] running several kilometers across the halo. The halo has a continuous distribution and is brighter closer to the pit, and discontinuous and patchy farther away. This pattern seems to be controlled by the underlying ropy surface of the lobate flow. This morphology can be described as a discontinuous mantling, as the halo material has no discernible relief.

Six km NE of this facula, another localized bright area of similar dimension is found (site 2, Fig. 2). This spot shares the same distal patchy distribution as the first facula, but displays a continuous, smooth material distribution in its center. Most importantly, the smooth bright material forms two ridges in a V-shaped configuration, separated by a possible topographic depression (trough-like morphology). As site 1, linear fractures [8] and depressions are found across this facula. However, the texture and relief of the bright material at the center of this facula suggests it is thicker than that at site 1.

Observations - Cerealia Facula: This bright area is located within Occator crater’s central pit (Fig. 2, 20°N-240°E). It has an irregular shape and is approximately 6 km wide. In addition, it is uplifted in its center, creating a domical feature 3 km wide and 0.25 km high relative to the surroundings, and is dissected by fractures up to 300 m wide and pits. The bright material surrounding the dome has a smooth texture with darker patches and darker fractures circumferential to the dome. The contact between the bright material and the surrounding darker central pit material is characterized by patches. Small -200 m wide- bright zones are found scattered in the darker central pit material and, less frequently, small dark zones are found scattered in the bright material. The width of the contact between the different zone is sharp (<70 m). In one location, we observe the scattered bright patches to have an elongated shape radial to the central dome, similar to discontinuous impact crater rays.

Discussion: Morphologies at sites 1 and 2 indicate that surface disruption (pit, trough) as well as redistribution of adjacent bright material (i.e., mantling by fine grained material) occurred. At site 3 the above processes took place (pits on dome, radial elongated patches), as well as build-up and/or upwarping of thicker (>100 m) bright material. We note that fractures and pits on a carbonate-rich material are also observed on the summit of the cryovolcanic dome Ahuna Mons [9, 10]. Here we consider several mechanisms that could have produced the entire range of morphologies described at sites 1, 2 and 3.

Impact cratering leads to a central depression and mantling of the surrounding terrain, similar to site 1. However, the morphologic characteristics of a pit and the extensive halo at site 1 lacking a rayed pattern argue against an impact induced-origin. An impact origin is also inconsistent with our observations at site 2 and 3.

Sublimation is a process known to create depressions or pits. On Ceres, this process is known to occur
at the crater Oxo, where a conspicuous ice deposit is observed [11]. There, however, the morphologies are different and no pits or mantling is observed [12].

Another mechanism is fragmentation by decompression of gas-rich ice. The ascent of gas-rich ice to the surface and exposure to the vacuum of space might lead to an explosive event [e.g., 13]. The rate of ascent of solid ice from few kilometers depth and through a <500 m wide conduit will depend on the ice’s initial temperature and cooling by the surrounding rock. Once extruded, particulate, fragmented material might be ejected and subsequently distributed around the upris-
Introduction: We have measured Sr, Zr, Mo, and Ba isotopes in presolar SiC grains using CHILI, the Chicago Instrument for Laser Ionization [1]. This continues a preliminary study in which we successfully measured Sr and Ba in 10 out of 22 presolar SiC grains, including three X grains [2–4]. Zr, although searched for, was not detected in any of the previously investigated grains. However, with a technically improved CHILI, we were able to measure Zr in presolar SiC grains. In addition, we analyzed Mo, another element that is particularly important for understanding the $s$-process in asymptotic giant branch (AGB) stars [5,6].

Samples: Thirty-one presolar SiC grains from the 1.5–3 μm size separate (KJG), extracted from the Murchison CM2 meteorite more than 20 years ago [7] and mounted on gold foil, were analyzed in this study. In contrast to recent work on SiC grains [8–12], the samples in this study were not additionally treated with concentrated acids to remove parent-body and terrestrial contamination. Energy dispersive X-ray images of the mount were acquired in a scanning electron microscope to locate SiC grains on the mount.

RIMS analysis: CHILI is a resonance ionization mass spectrometry (RIMS) instrument, which is equipped with six tunable Ti:sapphire lasers. This allows simultaneous resonance ionization of three elements with independent two-photon ionization schemes. All six laser beams with different wavelengths are brought onto a single line before entering the analysis chamber. Using a broadband mirror, the laser beams are reflected so that they travel twice through a cloud of neutrals, which were desorbed from the sample by a 351 nm Nd:YLF laser beam, focused to ~1 μm onto the center of the respective grain.

We first measured 15 grains simultaneously for their Sr, Zr, and Ba isotopes and then 18 grains for Sr, Mo, and Ba, including two grains that had been measured for Sr, Zr, and Ba. We used previously developed ionization schemes (Table 1). Only the Zr scheme (Table 1) was slightly modified after performing a wavelength scan for the second (ionization) step laser. This increased the sensitivity by 25–30%. Another increase in Zr sensitivity was achieved by replacing some mirrors, bringing the combined laser beams into the analysis chamber, with mirrors that have higher reflectance especially at lower wavelength, important for the first (excitation) step (296.172 nm) in the Zr scheme. The analytical precision for Sr, Zr, and Ba was increased, compared to the preliminary study [2–4], due to various improvements in the time-of-flight mass spectrometer, ionization laser system, desorption laser stability, and instrument control and data collection software.

Single-shot data were recorded and corrected for dead time effects [1,14]. Standards (Table 1), which were assumed to be of normal terrestrial isotopic composition, were used for correction of mass-dependent and non-mass-dependent isotope fractionation [1].

Results: All 31 investigated SiC grains showed detectable amounts of all elements the ionization lasers were tuned for in the respective measurement. Meaningful isotope ratios, which showed deviations from terrestrial values beyond 3σ for at least one isotope ratio in one element, were found for 26 grains. Nine out of 31 grains had anomalies beyond 3σ in Sr, five out of 15 grains in Zr, 16 out of 18 grains in Mo, and 16 out of 31 grains in Ba. All isotope results are shown in Fig. 1 as δ-values (deviation from terrestrial ratio in ‰). Figure 2 shows three-isotope plots for Mo in comparison with literature data [6]. A striking observation is that the analytical precision is much higher than in the earlier study.

Discussion: All isotope patterns shown in Fig. 1 are consistent with mainstream SiC grains formed in low-mass AGB stars [5,9,10,15]. The pure $s$-process isotopes $^{86}$Sr, $^{87}$Sr, $^{96}$Mo, $^{134}$Ba, and $^{136}$Ba are relatively enriched, whereas isotopes dominated by $p$-process ($^{64}$Sr, $^{92}$Mo, $^{95}$Mo, $^{130}$Ba, $^{132}$Ba) and $r$-process ($^{96}$Zr, $^{106}$Mo, $^{135}$Ba) show the strongest depletions. The neutron-magic $^{88}$Sr is also mostly of $s$-process origin and therefore only slightly depleted. Branch points at $^{89}$Sr, $^{90}$Sr, and $^{91}$Y and the strength of the $^{13}$C pocket ultimately determine the relative abundances of the various Zr isotopes [5]. $^{93}$Zr with its 1.61 Ma half-life behaves as a stable isotope during $s$-process. Mo is an ideal element for this kind of study. Resonance ionization is very effective for this element,

Table 1: Resonance ionization schemes and standards

<table>
<thead>
<tr>
<th>$\lambda_1$ [nm]</th>
<th>$\lambda_2$ [nm]</th>
<th>Ref.</th>
<th>Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr 460.862</td>
<td>405.214</td>
<td>[10]</td>
<td>SRM 855a¹</td>
</tr>
<tr>
<td>Zr 296.172</td>
<td>442.575</td>
<td>[6]</td>
<td>Zr metal</td>
</tr>
<tr>
<td>Mo 313.350</td>
<td>388.337</td>
<td>[6]</td>
<td>SRM 855a, 1264a³</td>
</tr>
</tbody>
</table>

¹NIST SRM 855a (180 ppm Sr and noncertified Mo)
²modified for $\lambda_2$ from 442.533 nm in reference [6]
³NIST SRM 1264a with 0.49 wt% Mo
which has seven stable isotopes (two $p$-only, one $s$-only, and one $r$-only isotope) with terrestrial abundances between 9 and 24%. The relative abundances of $^{95,98}\text{Mo}$ depend on the branch point at $^{95}\text{Zr}$ [5]. The relative abundances of $^{134–138}\text{Ba}$ mostly depend on the branch point at $^{134}\text{Cs}$ [5].

Conclusions: For the first time, three elements have been successfully analyzed simultaneously in presolar SiC grains with CHILI. Besides Sr and Ba, which have been analyzed in SiC with CHILI before, we have added Zr and Mo as possible choices for these measurements. Mo showed the most promising results with regard to analytic precision, surpassing previous measurements with RIMS. The results will help to further constrain models of the $s$-process in low-mass AGB stars.


Fig. 2: Three-isotope plots for Mo for 16 grains from this study in comparison with literature data [6]. Uncertainties are 2σ.

Fig. 1: Isotope patterns for Sr, Zr, Mo, and Ba measured in presolar SiC grains using CHILI. Uncertainties are 2σ.
DEFINING THE BASELINE OF THE REE STABLE ISOTOPE VARIATIONS IN SOLAR SYSTEM MATERIALS: EARTH. J.Y. Hu, F.L.H. Tissot, R. Yokochi, T.J. Ireland and N. Dauphas, Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, Chicago IL, Department of the Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, MA, Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, IL.

Introduction: Mass-dependent fractionations (MDFs) of stable isotopes record critical information regarding the origin and evolution of planetary materials [1]. Studies of MDF of refractory lithophile elements (RLEs) can provide insights into condensation/evaporation and planetary accretion processes in the early solar system. For example, the lighter calcium isotope composition observed in carbonaceous meteorites compared to that of the bulk silicate Earth, enstatite and ordinary chondrites [2, 3] may be due to the contribution of refractory dust [4, 5], which has a light Ca isotope composition [6, 7]. In contrast, titanium, another RLE with similar chemical behavior in the early solar system, was found to have uniform isotope compositions among different groups of meteorites including carbonaceous chondrites [8]. A potential explanation for the dichotomy of these two refractory elements could be connected to the higher 50% condensation temperature of Ti relative to Ca [9]. The isotopic results suggest that no Ti net loss took place from the CAI-forming region, while not all Ca condensed in the CAIs [7, 8]. Clearly, more proxies are needed to better understand the processes that occurred during the condensation of the solar nebula.

Particularly promising are the rare earth elements (REEs), a group of RLEs that cover a significant range in terms of volatility (50% condensation temperatures ranging from ~1659 to 1356 K [9]). The wide range of volatility and their relatively immobile chemical property makes REE isotopes ideal tracers to unravel the thermal and accretion processes in the earliest stages of the solar system.

To date, study on isotopes of REEs has mainly focused on radiogenic systems (e.g., $^{147}$Sm/$^{144}$Nd, $^{146}$Sm/$^{142}$Nd). As such, isotope data about REE MDFs are very limited, especially for heavy REEs (HREEs) [10, 11]. Thus, we have started analyzing the isotope compositions of Nd, Sm, Eu, Gd, Dy, Er and Yb in different geological reference materials, in order to get a first approximate bulk silicate Earth isotope composition for these systems. The geological reference materials comprise four basalts (BIR-1a, BHVO-2, BCR-2, W-2a), one andesite (AGV-2), one granite (G3), and one carbonatite (COQ-1).

Methodology: As the REEs behave very similarly during column chemistry, a major problem for the accurate measurement of their mass-dependent isotope composition is the proper separation of the individual REEs from one another by ion exchange chromatography. To overcome this challenge, we developed an all-Teflon, pneumatically actuated high-performance liquid chromatography system, called ChRobot (short for Chromatography Robot; Fig. 1). The most distinctive features of ChRobot are: 1) The elution scheme is controlled by a computer via a LabView software interface, making it possible to achieve fine-step ramp elutions through the fresh mixing of as many as 6 reagents during an extensively long time period (e.g., 48h). Both features are possible to achieve through traditional gravity-driven columns. 2) Almost all parts related to elution are made out of solid Teflon and are pneumatically actuated. Electronics are housed in a box that is pneumatically pressurized and is spatially isolated from the liquid flow path. Compared to the first iteration of the instrument [12], this updated design reduces chances of contamination and ensures that ChRobot remains intact under the harsh clean lab environment that a commercial HPLC could not sustain. 3) The elution temperature is adjustable (up to 80 °C) thanks to a water circulation system, in order to achieve optimal separation. Mixed reagents are forced through the column via a pressurized chemically inert gas (N2).
The pressure of N\textsubscript{2} is also adjustable (0 to 55 psi) to control the elution rate.

The use of ChRobot dramatically improves the efficiency of the chemical separations while maintaining a low blank and high reliability that is superior to traditional gravity-driven chromatography. The elution tests performed on the ChRobot show that all REEs isotope systems can be separated from each other with close to 100% yields and minor overlap (Fig. 2). The procedural blank during ChRobot elution is low, accounting for less than 30% of the overall blank; including digestion and preconcentration is 0.05 ng for Yb).

All geostandards were doped with double spikes (Nd, Sm, Eu, Gd, Dy and Yb) before digestion. REEs are first extracted from the major elements using the TODGA resin, after which they are loaded into ChRobot for individual separation. Isolated REE solutions are evaporated to dryness and re-dissolved to concentrations between 10 to 20 ppb and measured for their isotope compositions using a Thermo Scientific MC-ICPMS upgraded to Neptune Plus specifications with the addition of an OnTool Booster pump. As there are no well-established isotope standards for REE isotopes, the isotope ratios of geostandards are normalized to our lab standards. These REE isotope standards are prepared from homogeneous, high purity oxide powder purchased from ESPI and are available upon request.

**Results and Discussion:** The typical external reproducibility of the isotopic measurements is approximately 0.02 per mil per amu for Nd, Sm, Gd, Dy, Er and Yb when using a double-spike, and 0.03 per mil per amu for Eu when using Dy external normalization. This is by about a factor of 4 smaller than the observed variation in the Ca isotope composition between different groups of chondrites [2, 3].

For most REEs, the isotope compositions of the geostandards that have been analyzed are found to be very homogeneous, which is consistent with the results reported in earlier study on europium and ytterbium isotopes for terrestrial samples [10]. Small variations are observed mainly between basaltic rocks and granites. This might be due to magmatic isotope fractionation. A first order estimated of the terrestrial isotope composition relative to our lab isotope standards yields $\delta^{146/144}$Nd = -0.02 \%, $\delta^{149/147}$Sm = +0.20 \%, $\delta^{153/151}$Eu = +0.35 \%, $\delta^{157/155}$Gd = +0.08 \%, $\delta^{163/162}$Dy = -0.02 \%, $\delta^{166/164}$Er = +0.07 \% and $\delta^{173/174}$Yb = -0.05 \%.

**Conclusions:** We show that it is possible to measure the mass-dependent fractionation of Nd, Sm, Eu, Gd, Dy, Er and Yb to a precision of around 0.03 \%/amu, which is expected to be sufficient to resolve MDF effects due to processes taking place during the condensation in the solar nebula. Isotope variations among different terrestrial geostandards is limited, which allows us to define a first estimate of the stable isotope compositions of REEs for the bulk silicate Earth.

**References:**

\[ ^{36}\text{Cl}/^{35}\text{Cl} \] in Allende CAIs: Implication for the Origins of \[ ^{36}\text{Cl} \] in the Early Solar System.

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**Introduction:** Chlorine-36 (t\(_{1/2} = 3.0\) Myr) decays to either \[ ^{36}\text{Ar} \] (98%, \(\beta^+ \)) or \[ ^{36}\text{S} \] (1.9%, \(\beta^- \) and \(\beta^+ \)). This radionuclide can be produced by either charged particle irradiation [1,2] or stellar nucleosynthesis [3]. Evidence for the prior existence of \[ ^{36}\text{Cl} \] in the Early Solar System (ESS) comes from radiogenic excesses of \[ ^{36}\text{Ar} \] [4,5] and/or \[ ^{36}\text{S} \] [6-9] in secondary phases (e.g., sodalite and wadalite) of ESS materials such as Ca, Al-rich inclusions (CAIs) and chondrules. However, the inferred initial \[ ^{36}\text{Cl}/^{35}\text{Cl} \] ratios vary over three orders of magnitude among different chondrite constituents \((5 \times 10^{-6} \sim 10^{-3})\) [6-9]. Interestingly, although the initial \[ ^{36}\text{Cl}/^{35}\text{Cl} \] ratios inferred in previous studies vary widely, all secondary phases bearing evidence for live \[ ^{36}\text{Cl} \] in the ESS measured so far lack resolvable \[ ^{26}\text{Mg} \] excesses due to the decay of \[ ^{26}\text{Al} \] (t\(_{1/2} = 0.7\) Myr), implying that \[ ^{36}\text{Cl} \] and \[ ^{26}\text{Al} \] may have been produced by different processes and/or incorporated into ESS solids at different times. Given that secondary phases may have formed late, the \(^{36}\text{Cl}/^{35}\text{Cl} \) anomalies in secondary phases point to either a very high \[ ^{36}\text{Cl}/^{35}\text{Cl} \] initial ratio \((\sim 10^{-5})\) in the ESS, or a late irradiation scenario for the local production of \[ ^{36}\text{Cl} \] \((\sim 3\) Myr after CAI formation) [9]. The elevated ESS ratio of \[ ^{36}\text{Cl}/^{35}\text{Cl} \sim 10^{-2} \] inferred from [9] far exceeds the predictions from any model of stellar nucleosynthesis; therefore, a late irradiation scenario producing \[ ^{36}\text{Cl} \] is currently the favored idea. In this framework, \[ ^{36}\text{Cl} \] would be produced in the nebular gas and then incorporated into the CAIs via aequous alteration, which formed secondary phases.

To further investigate the origin and distribution of \[ ^{36}\text{Cl} \] in the early solar nebula, we analyzed \[ ^{36}\text{Cl}/^{35}\text{Cl} \] systems in secondary minerals of three fine-grained CAIs and one coarse-grain CAI from Allende.

**Sample description and Method:** The fine-grained Allende CAIs (Curious Marie, AL10S1, and 4321-FG-1) consist of widely-distributed powdery, porous aggregates of sodalite \([\text{Na}_8(\text{Al},\text{Si},\text{O}_4)\text{Cl}_3]\), nepheline \([\text{Na}_3\text{K}\text{Al}_8\text{Si}_6\text{O}_{24}]\), grossular \((\text{Ca}_4\text{Al}_2\text{Si}_3\text{O}_{12})\), and melilitite \([\text{Ca}_2\text{Na}_{3}](\text{AlMgFe})^2[(\text{AlSi})\text{Si}_2\text{O}_{7}])\), suggesting that these CAIs have been intensely altered from their primary mineralogy. Three wadalite grains \([\text{Ca}_6(\text{Al},\text{Si},\text{Mg})\text{O}_3\text{Cl}_3]\) are observed in the coarse-grained CAI (4322-CG-1), occurring as anhedral grains intergrown with grossular replacing melilitite. The high chlorine content in sodalite \((\sim 7\text{ wt\%})\) and wadalite \((\sim 12\text{ wt\%})\) and extremely low sulfur content \((<0.01\text{ wt\%})\) make them ideal minerals for resolving potential \[ ^{36}\text{S} \] excess due to decay of \[ ^{36}\text{Cl} \].

Measurements were performed on the Cameca IMS-1290 at UCLA. Negative S and Cl secondary ions were produced by a 0.6 nA Cs\(^{+}\) primary ion beam focused to a \(<10\text{ \mu m}^2\) spot in mono-collection mode. A long pre-sputtering time was required (>20 minutes) to minimize surface S contamination. A mass resolving power of 5,000 was used to resolve interferences from the peaks of interest. Typical count rates of \[ ^{36}\text{S} \] from the sodalite and wadalite in the CAI samples were 4-10 counts per second.

The instrumental mass fractionation was internally corrected by comparison to standards of Balmat pyrite, Canyon Diablo troilite, and CAR 123 pyrite. The transmission was deliberately decreased to minimize the QSA effect (Quasi-Simultaneous Arrival) [10] when measuring the pyrite and troilite standards. Sulfur isotopic ratios were calculated by using total counts due to relatively low \[ ^{36}\text{S} \] count rate. A systematic offset of 15‰ on the \[ ^{35}\text{S}/^{34}\text{S} \] ratio was observed on all the standards when normalizing measured \[ ^{36}\text{S}/^{34}\text{S} \] to the reported value of CDT (11) with corrected \[ ^{36}\text{S}/^{34}\text{S}_{\text{CDT}} = 0.0034200 \]. A terrestrial sodalite \((^{32}\text{Cl}/^{34}\text{S} = 15,000)\) was measured to monitor the accuracy of the measurement on \[ ^{36}\text{S} \] excess.

The bulk \[ ^{35}\text{Cl}/^{34}\text{S} \] ratio of Curious Marie was measured by making 25 \(\mu \text{m} \times 25 \mu \text{m} \) raster squares on the sample and then averaging the measured \[ ^{35}\text{Cl}/^{34}\text{S} \] ratios. The signals of \[ ^{32}\text{S} \] and \[ ^{35}\text{Cl} \] were simultaneously collected with L1 (EM) and H2* (FC) with a mass resolution of ~5,000. The relative sensitivity factor (RSF) of \[ ^{35}\text{Cl}/^{34}\text{S} \] (-1.24) used throughout this study was estimated from analyses of NIST 610 glass (Cl/S=1).

**Result and discussion:** No elevated \[ ^{36}\text{Cl}/^{35}\text{Cl} \] initial ratio \((\sim 10^{-2})\) was observed in our study. As shown in Fig. 1, no resolvable \[ ^{36}\text{S} \] excesses were found in the sodalite of AL10S1. Sodalite grains in 4321-FG-1 and wadalite in 4332-CG-1 exhibit resolvable \[ ^{36}\text{S} \] excesses, giving a \[ ^{36}\text{Cl}/^{35}\text{Cl} \] ratio of \(-1.6\times10^{-7} \) and \(-8.3\times10^{-10} \), respectively. Assuming an alteration timescale of \(-2.5\) Myr based on \[ ^{26}\text{Al}/^{27}\text{Mg} \] systematics in secondary phases of CAIs (e.g., [9]), the two CAIs yield an upper limit for the ESS initial \[ ^{35}\text{Cl}/^{35}\text{Cl} \] ratio \(<2.7\times10^{-4} \). Curious Marie is a U-depleted Allende CAI with highly elevated \[ ^{235}\text{U}/^{238}\text{U} \), most likely due to the decay of \(247\text{Cm} \) [12]. Significant excesses in \[ ^{36}\text{S} \] are clearly resolved in this sample over a large range of \[ ^{35}\text{Cl}/^{34}\text{S} \] values (from 500 to 20,000). However, the \[ ^{35}\text{S} \] excesses are uniformly elevated, with a weighted average of 97±12‰, independent of the Cl/S ratio, indicating late closed-system homogenization of the \[ ^{36}\text{S} \] excesses after \[ ^{36}\text{Cl} \] became extinct. The \[ ^{35}\text{Cl}/^{34}\text{S} \] bulk ratio was estimated as 1145±400 by averaging 30 raster analyses. The \[ ^{36}\text{Cl}/^{35}\text{Cl} \] ratio in the bulk of the Curious Marie CAI is estimated as \((1.5\pm0.6)\times10^{-3} \).

The \[ ^{26}\text{Al}/^{27}\text{Mg} \] systematics has been analyzed in the secondary phases (sodalite and nepheline) of the Curious Marie CAI, giving an elevated and uniform \[ ^{26}\text{Mg} \] excess of...

-43% and implying a canonical 26Al/27Al ratio of (6.2±0.9)×10^{-5} for the bulk inclusion [13]. To explain this result, an early aqueous alteration event (probably on a small icy body) must have occurred while 26Al was still at the canonical abundance in the ESS (≤0.15 Myr) [15]. Introduction of 36Cl into Curious Marie likely took place during this event, as any open-system alteration occurring later on would have resulted in a lower than canonical model 26Al/27Al ratio for this sample. If so, 36Cl and 26Al must have coexisted early in the solar nebula, and the calculated 36Cl/35Cl model ratio in Curious Marie (1.5±0.6)×10^{-5} represents the 36Cl/35Cl ratio at the time of the early aqueous alteration, thus giving the initial 36Cl/35Cl ratio in the ESS to be 1-3×10^{-5}. This ratio is lower than the upper limit in the ESS inferred in previous studies on sodalites in other CAIs by a factor of ~10 [6,7].

36Cl can be produced by local irradiation or inherited from stellar sources. The volatile nature of this radionuclide and the need for volatile target nuclides (Cl and K) pose a serious challenge to early in-situ irradiation models [6]. One interpretation is that intense local irradiation could have occurred in a volatile-rich reservoir adjacent to chondrite-accreting regions [9]. Subsequently, 36Cl was incorporated into secondary, chlorine-rich minerals during parent body alteration. However, this scenario requires an optically thin protoplanetary disk while the Sun was a weak T Tauri star (Class III, t ≥ 1 Myr after CAI condensation) and would thus require late aqueous alteration (> 1 Myr). Such late, open-system alteration would remove radiogenic Mg from the inclusion resulting in a lower bulk 26Al/27Al ratio (26Al/27Al ≤ 2 × 10^{-5}), contrary to our results in Curious Marie. Hence, we propose that 36Cl in Curious Marie was derived from an external stellar source (e.g., inheritance from the molecular cloud, or a specific stellar source; [3]) along with 26Al, and accreted into a pre-accretionary icy body. Early aqueous alteration then took place before 26Al had decayed significantly, and formed 36Cl-bearing sodalite. The isotopic characteristics of Curious Marie indeed suggest that 36Cl and 26Al could have been co-incorporated into secondary minerals. However, our observation does not rule out the presence of 36Cl due to late spallation as inferred in the secondary minerals from other CAIs and chondrules. 26Al-26Mg in situ analyses in the secondary phases of AL10S1, 4332-CG-1, and 4321-FG-1 will be done in the near future to quantify the timescale of aqueous alteration in these objects.


Figure 1. 36Cl/35Cl systematics in Allende CAIs. In Curious Marie, red dash line reflects the model 36Cl/35Cl ratio based on the average δ34S vs. and bulk 35Cl/34S ratio.
THE ISOTOPIC FRACTIONATION OF TITANIUM IN IGNEOUS SYSTEMS: IMPLICATIONS FOR STUDIES OF EARLY DIFFERENTIATED ASTEROIDS. M. P. Ptáček¹, N. D. Greber¹, T. Pettke², L. Gfeller³, and N. Dauphas⁴, ¹Origins Lab, University of Chicago, 5734 S Ellis Ave, Chicago IL 60637-1468, mptacek@uchicago.edu, ²Institut für Geologie, Universität Bern, Baltzerstrasse 1+3, CH-3012 Bern, Switzerland. ³TrES Gruppe, Geographisches Institut, Universität Bern, Hallerstrasse 12, CH-3012 Bern, Switzerland.

Introduction: The existence of highly differentiated asteroids in the early Solar System has long been hypothesised, and many instances of basaltic achondrites have been catalogued. However, the corresponding discovery of andesitic meteorites has taken much longer, and their petrogenetic studies are complicated by alteration and sulphite melt processes [1], which make it difficult to determine exactly how much partial melting a given sample has undergone. Herein we illustrate how the Ti isotope composition can be used to constrain the degree of partial melting, and thus shed some light on early Solar System processes.

The published literature contains very little work on mass-dependent Ti isotope systematics. In addition to being refractory and lithophile, Ti is also highly immobile, and is present (in terrestrial redox conditions) only in the Ti⁴⁺ valence state. Hence, Ti isotopic fractionation should be resistant to alteration, and affected predominantly by magmatic processes.

Significant variation in the Ti isotopic composition (δ⁴⁹Ti) of terrestrial rocks has been observed, with values ranging from -0.07 to +0.55 ‰, and a well-defined correlation between δ⁴⁹Ti and the SiO₂ bulk concentration [2]. Calculations have also shown that in intermediate compositions (SiO₂ < 65 wt.%), the positive trend between δ⁴⁹Ti and silica content can be explained via the fractionation of light Ti isotopes into Fe-Ti oxides, which leaves behind a melt enriched in heavy isotopes [2]. However, this simple model begins to diverge from reality when applied to more evolved melts.

We present new Ti isotope measurements of samples from the Kos Plateau Tuff (KPT) in eastern Greece, where Mediterranean seafloor is subducted beneath the Aegean plate. Xenoliths from protracted calc-alkaline magmatic activity can be found among the eruptive products of the KPT [3]. Petrological studies have indicated that this magmatic system evolved predominantly by crystal fractionation with no or only very minor assimilation of sedimentary rocks [4], making it an ideal candidate for studies of Ti isotope fractionation in magmatic systems. Within the course of this study we measured the Ti isotope composition of two rhyolites (SiO₂ > 73 wt.%), two andesites, an olivine basalt, and a hornblende cumulate. The latter is a solid residue from an early-stage basaltic melt, measured in order to verify our hypothesis that as the fractionating melt becomes isotopically heavy, the cumulate should also become correspondingly lighter.

Measurement Methods: The samples were digested using flux fusion carried out in a graphite crucible, with a sample to LiBO₂ ratio of 1:6. A clean fragment of the resultant quenched glass was selected, mixed with a ⁴⁷Ti-⁴⁹Ti double spike, and then digested in 3M HNO₃ acid. Titanium was extracted from the sample through two stages of ion-exchange chromatography, using the TODGA and AG1-X8 resins respectively. The resulting purified sample was dissolved in 0.3M HNO₃ + 0.005M HF and analysed in a Neptune ICPMS. Results are reported in the δ notation relative to the Origins Lab OL-Ti standard, the isotopic signature of which is within measurement error of the bulk silicate Earth [2]. The 2σ uncertainty for the KPT samples was calculated as ±0.035‰ [5].

Fig. 1: Bulk rock isotopic fractionation data from Millet & al. (blue diamonds) and new measurements from the Kos Plateau Tuff (red crosses), alongside the best-fitting distillation model (green line). Whilst the fit to intermediate rocks is acceptable, highly evolved samples consistently plot above expected values. The measurement on the far left represents the hornblende cumulate, which is the solid residue of early fractional crystallisation, and shows significant depletion in the heavy Ti isotope. Errors are 95% confidence intervals.

Results: A trend of increasing isotopic fractionation with silicate content has been observed in the KPT samples, ranging from -0.06±0.035‰ in the magmatic hornblende cumulate to +0.66±0.035‰ in the heavily differentiated rhyolites. This trend is in general agreement with previously published terrestrial data [2], as shown in Fig. 1.

To our knowledge, the δ⁴⁹Ti signatures of the two rhyolites are the heaviest igneous Ti isotope compositions recorded to date. The measurement of the cumulate is consistent with our earlier prediction. Further-
more, the new data also confirm that at high values of SiO$_2$, we observe isotopic values in excess of what was expected from an extrapolation of earlier data.

**Fractionation Model:** We have chosen to model isotopic fractionation through a simple Rayleigh distillation equation [5], of the form:

$$\delta_i = \delta_0 + 1000(\alpha - 1) \cdot \left( \ln \frac{c_i}{c_0} + \ln F \right)$$

where $\delta_i$ and $c_i$ represent the isotopic composition & Ti concentration of a partially-fractionated liquid, $\delta_0$ and $c_0$ the original values of the bulk liquid, $\alpha$ the isotopic fractionation factor, and $F$ the remaining melt fraction. This model requires the knowledge of the Ti concentration in the melt as a function of $F$. We have chosen to parameterise this via a second distillation equation, of the form:

$$c_i = c_0 \cdot F^{(K_d - 1)}$$

where $K_d$ is the bulk solid-melt partition coefficient for Ti. Although the values generated by this model can be used to create a good fit to the isotopic data, the model cannot fully reproduce the measured TiO$_2$ concentrations of the data set, especially in the case of the non-intermediate samples (c.f. Fig. 2).

![Fig. 2: Results from the first-order distillation model show a rough fit with Ti concentration outside intermediate SiO$_2$ compositions, suggesting a more complex chemical model might be necessary. Point on far left is the hornblende cumulate, which is not part of the fractionation trend. See Fig. 1 for legend.](Image)

**Discussion:** We observe there exists no single value for the isotopic fractionation factor that can adequately fit data from both intermediate and evolved samples, especially in the case of the new KPT data. This suggests the underlying mechanisms are more complex than assumed by our model.

One possibility is to consider other magma chamber processes aside from pure fractional crystallisation. For instance, petrological studies show that an evolved melt crystallising in a magma chamber often mixes with a freshly injected basaltic melt [6], and exactly such an event is thought to have triggered the KPT eruption [4]. Since highly evolved melts have lower Ti concentrations than basaltic melts (Fig. 2), even a minimal amount of mixing could significantly alter their isotopic composition. However, since the isotopic trend caused by the mixing of basaltic and silicic endmembers should be very different from the fractionation trend, $\delta_{\text{Ti}}$ could also provide insights into the mixing history of a given sample, in addition to its fractionation history. To disentangle the effects of mixing & fractionation with greater reliability, the amount of mixing could also be independently constrained with another geochemical system, for instance one of the high field strength elements.

Furthermore, as fractionation progresses, the liquid will be precipitating different mineral phases, each of which could have a different isotopic fractionation factor. For instance, evolved calc-alkaline systems have been known to precipitate biotite containing up to 5.8 wt.% TiO$_2$ [7]. In this case, our model will have to incorporate several mineral-specific fractionation factors, instead of a single bulk value. Should mineralogy prove significant, it will also be important to better identify when particular Ti-bearing phases stabilise during fractional crystallisation, and to fully integrate these results with the isotopic model.

**Further Work:** Mineral separates from the Kos Plateau Tuff will be analysed to determine whether the isotopic partition coefficient varies significantly across mineralogies. Furthermore, the rhyoliteMELTS software package will be used to constrain the evolution of the TiO$_2$ content and mineralogy better than a simple one-parameter distillation model.

**Summary:** Due to the immobility of Ti in the presence of fluids, the Ti isotopic system should prove a superior approach for investigating the fractional crystallisation history of heavily altered rocks and meteorites, compared to more traditional geochemical inversion methods. This technique has numerous applications – for instance, an isotopic study of the Graves Nunataks (GRA) 06128 and GRA 06129 differentiated meteorites, alongside brachinite samples, could help to confirm or reject the hypothesis that the latter represent the melt residues of the former [8][9].

MARS ALLUVIAL FAN FORMATION DURING THE AMAZONIAN AND LATE HESPERIAN SPANNED >10 MYR. Edwin S. Kite¹, Jonathan Sneed¹, David P. Mayer¹, Sharon Wilson². ¹University of Chicago (kite@uchicago.edu) ²Smithsonian Institution.

Summary: Large alluvial fan deposits on Mars record the most recent undisputed window of Mars surface habitability (the end of this interval has previously been dated to ~2.5 Ga) [1]. We find net sedimentation rate <10 µm/yr in the alluvial-fan deposits, using the frequency of craters that are visibly interbedded with alluvial-fan deposits. Assuming steady aggradation, this sets a lower bound of >100 Myr on the total interval spanned by alluvial-fan aggradation. This estimate would rise further if the Sadler effect operates on Mars. Despite the possible addition of pre-existing interbedded craters, such that the only interbedded craters are the ones that are visibly outcropping today (which is very improbable), fan formation still spanned >10 Myr. Several factors not included in our calculations would further increase the lower bound. Our lower bound rules out fan-formation by a single catastrophic episode, such as a single impact-induced water–vapor greenhouse [2], or localized impact-triggered warming [3]. During the Late Hesperian/Amazonian, persistent or repeated processes permitted habitable surface conditions.

Fig. 1. A large synfluvial impact crater within Holden crater (previously noted by R.P. Irwin). Alluvial fan deposits sourced from the NW were cratered; the largest crater was then overlain by additional alluvial fan deposits sourced from the NE.

Introduction: Large alluvial fans on Mars correspond to the youngest undisputed evidence for a global river-supporting climate on Mars. This climate permitted run-off production of >0.1 mm/hr that fed rivers with discharge up to 60 m³/s [4]. Because of the large fluxes of fluid required to form the broad rivers that fed these alluvial fans, these streams probably had a water activity that would permit life. The duration of the habitable conditions recorded by the alluvial fans is not known.

Figure 1. Top: Time span of alluvial fan formation, considering only the observed embedded-crater population. Crater counts are cumulative. Blue line shows best fit; blue error bars show the corresponding Poisson-statistics error. The gray area shows the 5%-95% uncertainty range in the lower limit from a Monte Carlo method including uncertainty in fan age, cratering rate, and paleo-atmospheric pressure. The ‘Excluded’ region is excluded at the 95% level. The asterisks correspond to the median output of the Monte Carlo method. Bottom: As above, but for best-fit fan aggradation rate. The gray area shows the 5%-95% uncertainty range in the upper limit.

Previous estimates used geomorphic methods, which produce estimates of the time over which sediment transport occurred (e.g., Ref. 5). However, these methods rely heavily on Earth analogy both in terms of seasonal sediment transport and any time gaps (intermittency) in
fan build-up (aggradation). In particular, they assume either zero intermittency, or Earth-like intermittency, neither of which should necessarily hold for Mars. To get a more accurate estimate of the interval over which alluvial fans formed, we used interbedded craters [6].

Crater density on a quiescent planetary surface is proportional to exposure duration. This method may be extrapolated to three dimensions: the total number of craters interbedded within a deposit depends on the time spanned by active sedimentation as well as interdepositional periods [6]. Naturally, this approach is complicated by the fact that interbedded craters may be completely buried: a comprehensive count via orbital photography is not feasible. However, if an impact occurs near the end of active sedimentation (by volume), then its crater may be only partially buried. Smaller craters are more readily buried, and larger craters require more sediment to be completely obscured. If the distribution of crater diameters in visibly interbedded craters is compared to some known impact frequency, then the past burial rate can be inferred. These “synfluvial” craters are distinguishable from pre-fan “prefluvial” craters that are overlain by alluvial fan deposits, but which formed before the start of fluvial activity [7]. The principle is straightforward and was first implemented by Hartmann (Ref. 8). See Ref. 6 for a detailed discussion.

Methods: In order to establish a lower bound on the length of time over which alluvial fans formed, we manually investigated the deposits catalogued by Ref. 9. 6m-pixel CTX images were used to produce an initial list of candidate craters showing possible evidence of interbedding with paleochannels or other fluvial features. Each candidate was then reviewed by a three-person panel for final classification, where 25cm-per-pixel HiRISE images and stereopairs were used (when available) to supplement the initial CTX search. We constrain the sedimentation rate of surveyed alluvial fans following the method of [6]. Importantly, different crater diameters probe different depth ranges and thus aggradation rate over different timescales. From Earth data (e.g. Ref. 10), we might expect aggradation rate to decrease over larger timescales, and this is in fact consistent with our data. All craters were classed as “synfluvial,” “prefluvial,” or “uncertain.” This distinction is needed because alluvial fan activity might have started well after the formation of the larger craters (e.g. Holden, Saeheki, Ostrov) that host the alluvial fans [7].

The contribution of false positives to our catalog is likely negligible. Although polygonal faulting in Earth marine sediments can produce crater-like concentric layering structures [11], this is unlikely for Mars alluvial-fan deposits and many of our craters retain rims. On the other hand, there are certainly false negatives in our survey area: re-survey of a crater of interest found several additional embedded craters not found on the first pass. Therefore, our counts represent lower limits.

Monte Carlo analysis. The usual procedure for assaying crater-counting error is to use Poisson statistics [12]. The results of this procedure are shown by the blue error bars in Fig. 2. However, this ignores (1) uncertainty in the true crater flux, (2) filtering by a potentially thicker past atmosphere, and (3) variations in target strength. To determine past alluvial fan aggradation rates we must also consider (4) the time of formation of the alluvial fans, and (5) the amount of burial or erosion – expressed as a fraction of the crater’s diameter – that is needed to prevent the crater from being detected at CTX resolution. We adopted conservative priors on parameters (1), (2), (4), and (5) in a Monte Carlo simulation of our lower bound that also includes Poisson error. Specifically, we assumed a log-uniform uncertainty between 0.5× and 2× the Hartmann crater flux; a log-uniform prior between 6 mbar and 1000 mbar for atmospheric filtering (the “Popova correction” of Ref. 13); a uniform uncertainty between fan formation 2.0 Ga (low-end crater retenage) and 3.6 Ga (age of the large craters which host alluvial fans); and a log-uniform prior between 0.05 (rim burial; Ref. 14) and 0.2 (original crater depth; Ref. 15) for the obliteration depth fraction (relative diameter). Results are shown by the gray error bars in Fig. 2. The effects of varying target strength (parameter 3) will be discussed at the conference. The results are lower limits because of survey incompleteness.

>100 Myr span of fan formation assuming steady aggradation: We measured alluvial fan thicknesses by comparing CTX DTM profiles across fans to analogous profiles across parts of the same craters that lacked fans. We found maximum fan thickness 1.1 km, with thicknesses ~1 km common. If steady aggradation is assumed, then our <10 μm/yr aggradation rate bound corresponds to a >100 Myr span of (perhaps intermittent) surface habitability.

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Introduction: On Earth, biologically mediated reactions enable the occurrence of minerals in geochemical environments which should pose a significant kinetic barrier to their formation. Abundant jarosite and haematite on Meridiani Planum, Mars recorded by Mars Exploration Rover Opportunity indicated that iron oxidation occurred in low pH (~2-3) waters [1-5]; but O₂-mediated oxidation of iron is extremely slow in acidic conditions [6-8] and on Earth it is only made viable by iron-oxidizing acidophiles [9]. There are strong mineralogical and geochemical similarities between Meridiani Planum and terrestrial acid mine drainage environments, where acidophiles using Fe²⁺ oxidation as a source of metabolic energy accelerate the reaction kinetics by a factor of ~10⁵ [6,9-12]. Use of this analogue depends on whether a) compelling evidence for ancient life is discovered on Mars, or b) a viable abiotic pathway for iron oxidation can be demonstrated. One possible mechanism is UV photooxidation [7,8,13]. Experiments have shown UV photo-oxidation is a viable process for forming the precursor minerals to banded iron formations on Earth before the rise of atmospheric O₂ [8,14,15]. However, photooxidation in small Martian water bodies faces the obstructions of weaker solar radiation; unbuffered acidification, which slows the rate of UV absorption; and rapid evaporation of standing water. We have constructed a model for photo-oxidation on Mars which incorporates the caveats above, and a more realistic UV radiation spectrum for the Martian surface. We find that the viability of photo-oxidation at Meridiani Planum is dependent upon the evaporation rate and initial water depth, and the potential for a water body to fully oxidize improves with increasing initial water depth. Evaporation has little direct effect on photooxidation until the late stages of desiccation, where it can slow photo-oxidation by accelerating acidification.

The Model: We calculate the rate of photo-oxidation of Fe(II) in mol sec⁻¹ cm⁻² over a water column of depth z, following the equation of [14]:

\[ \frac{d[Fe^{II}]}{dt} = \frac{\Phi}{N_A} \int_0^{450\text{nm}} \int_{180\text{nm}}^{1000\text{nm}} D_{\lambda}(\lambda) \epsilon_{\lambda}(\lambda) F(\lambda, z) \, d\lambda \, dz \]

Where \( \epsilon_{Fe^{II}}(\lambda) \) and \( \Phi_{Fe^{II}}(\lambda) \) are the molar absorptivity and quantum efficiency (atoms oxidized per photon absorbed) of Fe(II) species, and \( F(\lambda, z) \) is the surface radiation attenuated through the water column. We use an experimentally determined \( \Phi_{Fe^{II}}(\lambda) \) [8], and a ~3.9 Ga, 0.1 bar CO₂ atmosphere surface radiation model adapted from [16] to Martian orbital distance (Figure 1). Photo-oxidation in water columns with initial conditions of [17] was modelled by removing Fe(III) and SO₄²⁻ and releasing H⁺ in the stoichiometric proportions for schwertmannite; and re-equilibrating after each time step [7,8]. We run models with upper- and lower-limit evaporation rates (0.1-1 m yr⁻¹) for early Mars [18], and performed control runs at fixed depth for comparison with [8].

Results and Discussion: The time required for 90% oxidation [4] in non-evaporating water is shown as a function of depth in Figure 2. Photo-oxidation times are longer in our model are because we utilize a photon flux which is cut off below 200 nm by atmospheric absorption, however our data agree with [8] to better than a factor of 2. At depths <~10 cm, even lower limit evaporation rates outpace photo-oxidation, so that Fe(II) concentrations rise to levels where ferrous minerals would precipitate before most Fe(II) is
oxidized [17]. Therefore scenarios where ferric mineral deposition on Meridiani Planum occurred through repeated small scale effusions of groundwater to the surface appear unlikely, because very shallow (<10 cm) water bodies always dry out before significant photo-oxidation occurs. However, at shallow depths, photo-oxidation times increase only slightly with increasing depth, so that at ~10 cm depth, the timescales for total oxidation and evaporation at 0.1 m yr\(^{-1}\) are similar. Figures 3 and 4 show photo-oxidation scenarios for 10 cm water depth with fast, slow, and no evaporation. In the fast evaporation scenario, only 20% oxidation occurs before total desiccation. Fe(II) concentrations rise sharply to >0.1 mol L\(^{-1}\), around which point ferrous iron minerals would precipitate [17] (Figure 3). In the slow evaporation scenario, the eventual result is again sharply climbing Fe(II) concentrations, however over 90% photo-oxidation occurs prior to evaporative concentration, so the Fe(III)/Fe\(_{\text{Total}}\) of the deposits would satisfy Opportunity data [4] (Figure 4). Figure 4 shows that despite rising concentrations of Fe(II), photo-oxidation rates (normalized to the initial depth) remain unaffected by evaporation until its very latest stages. Therefore, the proportion of Fe(II) oxidized evolves with time in the same way in all scenarios whilst sufficient water remains. We suggest that photo-oxidation rates may fall in the late stages of desiccation because H\(^+\) becomes extremely concentrated in solution, which favours speciation of FeOH\(^+\) to the less absorptive Fe\(^{2+}\) ion. At greater depths (>1 m), the relationship between photo-oxidation time and depth becomes more linear (Figure 2). There should be an effective depth of UV photon penetration due to attenuation of UV radiation through the water column, so essentially all photo-oxidation will occur within a shallow region. For deeper water bodies, the time required for total oxidation should scale proportionally to the relative depth of the ‘UV photic zone’ to the total water column. Our model results indicate that if even small-scale (>10 cm) ephemeral lakes [19] were able to persist on the order of years to decades, photo-oxidation appears to be a viable solution to the oxidation of iron under acid conditions on Meridiani Planum.

**Conclusions:** Haematite-jarosite deposition requires iron oxidation to occur at low pH, which on Earth is made possible by the influence of iron-oxidizing microbes. On Mars, an alternative pathway is UV photo-oxidation, which we have modelled here with evaporation and a more realistic radiation flux. Photo-oxidation appears to still be an effective mechanism for Fe(III) mineral formation at Meridiani Planum, provided that initial water depths are at least tens of cm and/or evaporation rates lie close to lower limits provided by geomorphological constraints.

**References:**


**Acknowledgements:** Nicole Nie and Edwin Kite are gratefully acknowledged for discussions which were useful in the construction of the model.
Introduction: The Mars Exploration Rover mission revealed the presence of rocks and minerals indicative of water-rock interactions on Mars. A range of mineralogies have been identified, including hematite spherules (i.e., blueberries), jarosite, Mg-, Ca-sulfates, silica-rich materials and silicate relics from basaltic rocks. The mineral assemblages have been interpreted to be derived from acid-sulfate alteration of basaltic materials [1, 2]. Indeed, the chemical compositions of rocks and soils at Home Plate in Gusev Crater follow the trends expected for acid-sulfate alteration [3, 4].

While concretions from the Navajo sandstone in Utah provide a good field analogue to Martian blueberries, they formed in very different conditions [5, 6]. Hematite spherules and altered basaltic tephra from Hawaii volcanoes provide a very good terrestrial analogue to Martian sulfur-rich deposits, meaning that the chemical pathways responsible for the formation of those spherules may have been similar [7, 8]. They were formed by acid-sulfate alteration of basaltic materials from volcanoes. Their mineral assemblages including hematite, jarosite, alunite and other sulfates, and basaltic precursors are comparable to the source rocks on Mars. We performed a detailed Fe isotope study of Hawaii tephra and hematite spherules to understand the formation of hematite and sulfate deposits on Mars. This study will also provide an interpretive framework to iron isotope analyses of Martian blueberries if some samples are ever returned to Earth.

Samples and Methods: Samples are from two localities in Hawaii: Sulfur Bank (HWSB) and Mauna Kea volcano (HWMK). The Sulfur Bank sample HWSB820 [9] is a tholeiitic basalt sampled in the vicinity of an active fumarole that has led to acid-sulfate alteration of the rock. However, since the rock was partially buried in the ground, acid-sulfate alteration affected more its exposed top part but not much the bottom part, producing a color gradation from white to grey to black (top to bottom). The rock was sliced to 9 rock slabs with ~1 cm thickness. Each of the slabs has been measured for Fe isotopes.

The HWMK samples include both tephra samples and hematite spherules. Tephra consists of unaltered tephras, acid-sulfate altered tephras (including jarosite-bearing tephra and sulfate- and phyllosilicate-bearing tephra), and tephras that experienced other types of alteration (such as low-T palagonitic alteration or high-T dry oxidation). A hematite spherule concentrate was extracted from a sulfated tephra HWMK745R [8] by grinding a spherule-rich portion, dry sieving and centrifugation. Fifteen individual spherules ranging in diameter from 25 to 50 µm were hand-picked from the concentrate in water under a binocular microscope with a 10 µL pipette.

Iron isotopic analyses of the samples were conducted at the Origins Lab of the University of Chicago, following methods described in [10]. For HWSB820 slabs and HWMK tephras, approximately 10-20 mg of each sample was digested with HF-HNO$_3$-HClO$_4$ method. The spherule concentrate has a high Fe content (~36 wt %), therefore about 1 mg aliquot was digested. Iron was separated from matrix elements and purified with AG1-X8 resin twice, and then measured for isotopes using a Thermo Scientific Neptune MC-ICPMS. Individual spherules were digested and measured individually without any purification, as the chemistry blank would have represented a significant fraction of the analyzed iron.

Results: The nine slabs of HWSB820 show a range of δ$^{56}$Fe values ([56/54]Fe ratio relative to IRMM-014) from +0.22 to +0.94 ‰, correlated with their Fe/Ti ratios (Fig. 1). HWMK tephra samples also show variable Fe isotopic compositions, depending on the alteration type. Unaltered tephras have Fe isotopic compositions similar to other OIBs, with δ$^{56}$Fe=+0.15 ‰ on average. Acid-sulfate altered tephras have variable δ$^{56}$Fe, from +0.11 to +0.49 ‰. Samples that experienced other alteration processes than acid-sulfate alteration have values similar to unaltered tephras, with an average of +0.12 ‰.

The hematite spherule concentrate has a heavy δ$^{56}$Fe value of +0.42 ‰. All individual spherules appear to have identical Fe isotopic compositions to the spherule concentrate. Since each spherule contain only very small amount of Fe (tens to hundreds nanogram), their δ$^{56}$Fe values have bigger uncertainties, which decrease as the Fe quantity increases.

Discussion: Tephra that is associated with acid-sulfate alteration show variable and in general heavier Fe isotopic compositions compared to unaltered tephras and tephras altered by other processes. Therefore, acid-sulfate alteration process should drive the liquid to have a lighter Fe isotope signature than the alteration residue. The 9 slabs from the single rock HWSB820 show a very good Rayleigh-type fractionation (Fig. 1). The slab least affected by acid-sulfate
alteration (highest Fe/Ti ratio) has δ^{56}Fe value (+0.22 ‰) similar to the unaltered tephas (+0.15 ‰), while the most altered slab has the lowest Fe/Ti ratio and the highest δ^{56}Fe value of +0.94 ‰. Rayleigh fractionation simulation suggests that the Fe isotope fractionation between liquid and solid is -0.24 ‰.

The individual spherules show identical δ^{56}Fe values, regardless of their sizes, suggesting that they are co-genetic, probably derived from the same Fe source. It has been suggested that the spherules could form either by 1) direct precipitation from the liquid produced by dissolution of basaltic material, or by 2) a two-step process involving precipitation of jarosite and other sulfates in a first step and hydrolysis of jarosite to form hematite in a second step [8]. Direct precipitation of hematite from a liquid would most likely produce rather heterogeneous Fe isotope compositions. This is because the precipitated solid would presumably be unable to exchange isotopically with the liquid to maintain isotope equilibrium at all stages. Therefore a Rayleigh-type Fe isotope fractionation during precipitation is expected. Hematite spherules measured here seem to have identical δ^{56}Fe values (due to small Fe amount, uncertainties are big, but no correlation between Fe quantity and δ^{56}Fe values was found). Most likely, the δ^{56}Fe homogeneity of the spherules reflects isotope re-equilibrium during the formation of hematite through jarosite hydrolysis.

To produce the +0.4 ‰ isotopic composition of the hematite spherules through jarosite hydrolysis, jarosite should either have a similar isotopic composition, if its conversion to hematite is quantitative, or have a δ^{56}Fe value close to ~+0.9 ‰, assuming equilibrium fractionation between the two minerals and a fractionation factor of ~0.5 ‰ [11, 12]. The isotopic fractionation between jarosite and the fluid it precipitated from should thus be ~+0.5 ‰ or ~+1 ‰. Iron isotope fractionation during precipitation of jarosite from Fe(II)aq solution has not been investigated. However, experiments studying precipitation of Fe(III) oxide-hydroxide from Fe(II)aq solutions have shown that precipitates are always enriched in heavier Fe isotopes, by ~+1 ‰, regardless of oxidation paths (biotic, O2-mediated or photo-oxidation) [13-15]. Jarosite precipitation could record similar isotope fractionation. If this is the case, the two-step process can readily produce the isotope signature measured in the hematite spherules.

The two-step process is applicable to the formation of hematite spherules and sulfate deposits on Mars. Thermodynamic modelling shows that jarosite and other sulfates on Mars could be produced by evaporation of acidic fluids produced by acid-sulfate alteration of basalts. After this, a pH-raising fluid recharge event could convert jarosite to hematite [2]. Therefore, hematite spherules and sulfates from Hawaii and from Mars appear to have formed in similar ways. This study provides some interpretative framework for iron isotope studies of future Mars sample return missions.

**Conclusion:** Iron isotope analyses of acid-sulfate alteration products from Hawaii show that acid-sulfate alteration process tends to enrich the fluid phase in light Fe isotopes compared to the solid phase, by -0.24 ‰ in terms of δ^{56}Fe values. The hematite spherules from Hawaii have δ^{56}Fe values consistent with a two-step formation process, that is, jarosite precipitation from fluids produced by acid-sulfate alteration of basalts followed by hydrolysis of jarosite to form hematite. This two-step formation scenario is similar to the formation of Martian hematite spherules, making further study of Hawaii analogue a very promising approach to understand Martian surface processes.

![Fig. 1: Iron isotope fractionation in the slabs of HWSB820 is consistent with Rayleigh fractionation, with a factor of -0.24 ‰ between fluid and solid in acid-sulfate alteration.](2802.pdf)

EXPERIMENTAL STUDY OF REE AND URANIUM FRACTIONATION IN HYDROGEN-RICH GASES: IMPLICATIONS FOR FORMATION OF FUN CAIs. R. A. Mendybaev1,2 and A. M. Davis1,2,3, 1Department of the Geophysical Sciences, 2Chicago Center for Cosmochemistry, 3Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (ramendyb@uchicago.edu).

Introduction: Enrichments of REE in CAIs compared to CI chondrites are an indicator of volatility-controlled processes that occurred during formation and/or later thermal processing of CAI precursors (e.g., [1–3]). Depletion in Ce observed in some CAIs, such as in Allende FUN CAIs HAL, C1 and STP-1 (e.g. [2, 4, 5]), is usually considered as an indicator of their formation/processing under “oxidizing” conditions when volatile Ce⁴⁺ becomes thermodynamically stable. On the other hand, some CAIs, such as in Allende B30 [4], are depleted in Eu (and Yb) which is considered as indicators of “reducing” conditions when volatile Eu²⁺ becomes stable.

FUN and FUN-like CAIs are also depleted in U by ~100× compared to “normal” (non-FUN) CAIs, which has prevented so far the use of the Pb-Pb chronometer for measurement of the absolute ages of FUN CAIs [5–7]. The U depletions also suggest “oxidizing” conditions of their formation/processing. Petaev et al. [8] argued that both Ce and U depletions could occur under reducing conditions.

How “oxidizing” or “reducing” conditions must be to produce Ce and/or Eu/Yb anomalies still remains unclear. Ce depletion was observed when solar composition melt was evaporated to a high degree (mass loss of ~20% or higher) at 1800°C in vacuum (e.g., [9]). No REE fractionation was observed in experiments when Type B composition melt was evaporated in a low-pressure hydrogen furnace at 1500°C [10], although ~50% of mass was lost in these experiments.

Here we present preliminary results from our experiments in which CMAS melt doped with trace elements was evaporated in flowing H₂-CO₂ gas mixtures with different fO₂s at 1600°C.

Experimental: The experiments were conducted at 1600°C in a vertical 1-atm furnace equipped with a gas-mixing apparatus. The fO₂ of the flowing gas (linear flow rate ~1.1 cm/s) in the furnace hot spot varied from IW–3 to a nominally pure H₂ by mixing H₂ and CO₂ in various proportions. As starting material we used a CMAS mixture containing 18.4 wt% MgO, 14.3% Al₂O₃, 43.4% SiO₂ and 23.9% CaO doped with ~400 ppm of trace elements. Run durations varied from few minutes to an hour in H₂ and up to 16 hours in oxidized gas mixtures to produce significant mass loss. The material was also evaporated in the vacuum furnace (P~10⁻⁶ torr) at the same temperature. REE and U concentration in run products was measured by laser-ablation ICPMS at the Field Museum, Chicago.

Results: Typical REE profiles in the experimental charges are shown in Fig. 1a. No Ce depletion was observed in any experiments conducted in the 1-atm furnace within the range of fO₂ studied. Even samples exposed to H₂-CO₂ gas with log fO₂ =IW–3.2 (~ 3 log units more oxidizing than the solar nebula gas) for ~16 hours which lost ~50 % of mass (MgO and SiO₂), exhibit flat REE patterns (green squares in Fig.1a). A sample produced by evaporation of the melt in the vacuum furnace for 6 hours was strongly depleted in Ce (solid red circles in Fig.1a). Although fO₂ in the vacuum experiments is poorly constrained, the redox condi-
tions in the furnace should be more reducing than $fO_2$ of the WWO buffer (~IW+1) in order to keep the tungsten heater and tungsten heat shields stable during even more extended and higher temperature runs.

Evaporation of the CMAS melt in nominally pure H$_2$ for 60 minutes resulted in ~90% mass loss and strong Eu depletion (blue diamonds in Fig. 1) in agreement with expectations.

No U depletion was observed in experiments conducted in the 1-atm furnace within the range of $fO_2$ studied, but it was strongly depleted in the vacuum evaporation residues.

**Discussion:** The experimental data on evaporation of CMAS melt in H$_2$-CO$_2$ gas are in agreement with results of calculations on distribution of REEs between CMAS melt and gas as function of $fO_2$ in a flowing H$_2$-CO$_2$ gas (Fig. 1b). In these calculations, we assumed that CMAS melt with a typical mass 50 mg was in equilibrium with 1 liter of H$_2$-CO$_2$ gas at 1600°C, and that concentration of Ca sites, that can be occupied by REEs, is 10$^{-7}$ moles/l which allows Eu depletion at log $fO_2$ of IW–6. This number of Ca sites is much lower than the value calculated from the mass of the sample and Ca concentration in the starting material (2×10$^{-4}$), but the volume of gas interacting with the melt could also be much less than 1 liter. We also assumed ideal solution of REE into the CMAS melt. Fig. 1b shows that change in $fO_2$ of the flowing gas only affects the distribution of Ce, Eu and Yb between the melt (small symbols) and gas (large symbols), while all other elements are expected to remain in the melt. As gas becomes more reducing, Eu and Yb evaporate from the melt thus increasing their fractions in the vapor which is then removed from the vicinity of the sample by a flowing gas. Based on Fig. 1b, noticeable Ce depletion in the melt is expected at $fO_2$ values close to ~IW, but not at ~IW–3.2 of our experiments. We have conducted a set of experiments under conditions more oxidizing than IW–3.2 and will report the results after we analyze the run products. Fig. 1b also shows that only Eu depletion (no Yb depletion) is expected in samples produced by evaporation in highly reducing gases at 1600°C, which is in agreement with our experiments.

Our experimental data (Fig. 1a) and thermodynamic calculations (Fig. 1b) clearly indicate that evaporation of a CMAS melt does not result in depletion of both Ce and Eu/Yb. The coexistence of negative Ce anomaly, along with Eu and Yb anomalies observed in some CAIs (e.g. [11]), thus could be explained by several episodes of melting in solar nebula with different redox conditions (due to different dust/gas ratios, for example). The reason why both Ce and Eu/Yb depletions were observed by Nagasawa and Onuma [12] when CAI composition melt was evaporated in vacuum and in low-pressure H$_2$-H$_2$O mixtures (H$_2$O/H$_2$ <100), but not in our experiments as well as in vacuum [9] and in low-pressure hydrogen furnaces [10] remains unclear. We should note, however, that experimental conditions in [12] appear to be much less controlled than in [9] and [10]. Concomitant Ce and Eu depletions observed by Floss et al. [13] in some experimental run products, when CAI composition melt was evaporated in vacuum, is due to extremely high degree of evaporation (>97% mass loss) produced at 1900–2250°C. Ce and Eu loss was also observed when CaTiO$_3$ melts were evaporated in vacuum at 2000°C [14] and 2150°C [15]. We believe that due to slow evaporation kinetics of major oxides under oxidizing conditions in our 1-atm experiments at 1600°C (e.g., ~10% mass loss after 2.5 hours and ~50% mass loss after 16 hours at log $fO_2$ =IW–3.2), the oxygen fugacity at the melt-gas interface in these experiments is controlled by $fO_2$ of the flowing gas rather than by oxygen released from the melt due to evaporation of MgO and SiO$_2$ as might be the case in very high-temperature vacuum runs.

Similar to Ce, strong U depletion was observed in our vacuum evaporation experiment at 1600°C, but not in 1 atm H$_2$-CO$_2$ even at log $fO_2$ =W–3.2. Possible correlation between Ce and U depletions will be tested in our future experiments.

**Conclusions:** No Ce or U depletions were observed in experiments at 1600°C when CMAS melt was exposed to a flowing H$_2$-CO$_2$ gas mixture with $fO_2$ values from ~IW–3 to a nominally pure hydrogen, but they were highly depleted in run products from vacuum evaporation experiments. Strong Eu depletion was observed when the melt was evaporated in 1 atm H$_2$. The result suggest that a negative Ce anomaly and U depletion, along with Eu and Yb anomalies observed in some CAIs could only be explained by several episodes of heating and cooling in solar nebula with different redox conditions.

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**References:**

THE TITANIUM ISOTOPE COMPOSITIONS OF CHONDRITES, AUBRITES AND THE MOON

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Introduction: Many non-traditional stable isotope systems are used to study the evolution of the Earth and other solar system bodies [1]. However, mass-dependent Ti isotope variations have seldom been measured. A previous study observed that terrestrial rocks exhibit significant variations in their Ti isotope composition (δ49Ti), with values ranging between -0.07 and +0.55 ‰, whereby the δ48Ti correlates positively with the SiO2 concentration [2]. The systematic shift towards a heavier Ti isotope composition with magmatic differentiation was interpreted to result from preferential incorporation of light Ti isotopes in Fe-Ti oxides during fractional crystallization, leaving behind a melt that is enriched in heavy Ti isotopes. In terrestrial mafic and ultramafic igneous rocks, Ti isotopes show little variations and their composition has been used to estimate the bulk Earth δ49Ti value relative to the OL-Ti standard to be +0.005 ± 0.005 ‰ [2].

We will present new δ49Ti data for a range of ordinary (H, L, LL), enstatite (EH, EL) and carbonaceous chondrites (CO, CM, CI, CV), six aubrites and a lunar KREEP-rich impact melt breccia (Sayh al Uhaymir (SaU) 169), with the objectives to determine the Ti isotopic composition of the major groups of chondrites and to investage two mafic systems where Ti and Ti-bearing minerals had a more pronounced role during magmatic differentiation processes than in mafic terrestrial systems.

Aubrites are unusual achondrites, likely due to the fact that core-mantle differentiation and magmatic evolution on their parent-body occurred under highly reducing conditions. In contrast to terrestrial systems, Ti3+ and Ti4+ co-exist and Ti exhibits chalcophile behavior [3].

Model calculations predict that in the latest stages of the lunar magma ocean solidification, extensive ilmenite crystallization occurred [4]. Sayh al Uhaymir 169 is a KREEP-rich lunar impact melt breccia, a rock enriched in incompatible trace elements and thought to represent leftover melt after major ilmenite crystallization in the lunar magma ocean [5]. Thus, if ilmenite crystallization affected the Ti isotope composition, one should observe a strongly fractionated δ49Ti in KREEP-rich lunar rocks.

Methods: Samples analyzed in this study have been digested using the LiBO2 fusion technique, which, unlike the more conventional acid digestion technique, leads to complete dissolution of refractory accessory minerals and it avoids the creation of insoluble Ti-bearing fluoride. A further advantage of flux fusion is, that the boron in the flux prevents fluorine in laboratory fumes from complexing with Ti during column chemistry, a matter that can lead to erratic behavior of Ti during chromatography. Chemical purification and Ti isotope measurements using a 47Ti-49Ti double spiking procedure were done following the methodology of [6].

Chondrite and aubrite data were corrected for the presence of 45Ti and 47Ti isotopic anomalies (δ69Ti is not used for isotope reduction procedure) based on previously published values [7]. The Ti isotope composition is expressed in the delta notation (i.e. δ49Ti) relative to the 49Ti/47Ti isotope ratio of the Origins-Lab Ti standard (OL-Ti). Measurement uncertainty expressed as 95% c.i. is around 0.03‰ [8].

Recommended data presentation of titanium isotope compositions: To facilitate inter-laboratory comparison of Ti isotope data, we recommend that δ49Ti data is published normalized to the OL-Ti standard, which is distributed by SARM (Service d’Analyses des Roches et des Minéraux, Nancy, France). The OL-Ti standard fulfills the guidelines for a suitable reference material as put forward by [1]. It also has an ideal Ti isotope composition, which is within current measurement precision identical to the bulk silicate Earth and chondrites [2, 8]. The δ49Ti value of NIST SRM 3162a is +1.056 ± 0.026 ‰ and is not suitable for expressing Ti isotope variations. In case other in-house Ti reference materials are used than the OL-Ti standard, it is suggested to calibrate them against the OL-Ti standard and to subsequently correct the δ49Ti data for the offset between the two Ti reference materials. For example, δ49Ti data measured relative to standard reference material 3162a from NIST can be recalculated to the OL-Ti standard with δ49TiOL-Ti = δ49TiSRM3162a + 1.054‰.

Results and Discussion: No major variations are found in the Ti isotopic composition of chondrites, except for a slightly heavier δ49Ti value in the Allende (Fig.1). Without this sample, chondrites average at a δ49Ti value of +0.004 ± 0.010 ‰, in good agreement with the proposed composition of the bulk silicate Earth [2]. The homogenous δ49Ti observed among all investigated chondrite groups contrasts the published Ca isotope pattern of the similarly refractory and lithophile Ca, where carbonaceous chondrites have lighter δ44Ca compared to enstatite and ordinary chondrites [9, 10].

It was suggested that the Ca isotope composition among chondrites could be linked to the amount of incorporated calcium-aluminum rich inclusions (CAI) and refractory dust [11, 12]. CAIs carry a very light Ca
isotope signature, reaching -11% (e.g. [12, 13]). Thus, the high Ca concentration and light $\delta^{44}\text{Ca}$ of refractory dust can influence the Ca budget and isotope composition of chondrites.

Conclusions and Outlook: The Ti isotope composition of ordinary, enstatite, and carbonaceous chondrites is very homogeneous averaging at $+0.004 \pm 0.010\%$, a value identical to the published estimate for the bulk silicate Earth. This isotope pattern contrasts with that of Ca isotope. The decoupling of the Ti and Ca isotope systems probably originated from differences in behaviors between Ca and Ti during condensation in the solar nebula.

Further data of aubrites and KREEP-rich lunar impact melt breccia SaU 169 will be presented at the conference, to evaluate the potential of Ti isotope systematic in constraining the igneous history of differentiated planetary objects.


![Figure 1: Mean Ti isotope composition versus Ca isotope composition of different chondrites and the bulk silicate Earth (BSE), recalculated to 1 amu mass difference. Ca isotope data from [10]. Dotted line with circles is a mixing curve between an ordinary chondrite and increasing addition of refractory dust.](image-url)
**Introduction:** Hibonite is a primary refractory phase occurring in many Ca-Al-rich inclusions (CAIs), typically with spinel and perovskite [1]. Previous microstructural studies of hibonite in CAIs revealed the presence of numerous stacking defects along the (001) plane and correlated non-stoichiometry in hibonite [2,3]. These features are interpreted as complex intergrowths of stoichiometric and Ca-deficient hibonites, as shown by experimental studies of reaction-sintered CaO-Al2O3 compounds [4]. Here, we extend our transmission electron microscope (TEM) studies to hibonite-bearing CAIs in CM chondrites that have been well characterized isotopically [5–7].

In addition, we have undertaken a series of annealing experiments to explore the effect of minor elements (Mg and Ti) on the microstructure of hibonite [8,9, this study]. The results of these experiments are being applied to hibonite in CAIs in order to better understand its formation conditions.

**Samples and Methods:** Building on our earlier annealing studies [8,9], a new experiment was prepared by allowing a 2CaO-Al2O3 eutectic melt containing 5 wt% MgO and CaTiO3 to react with a pure alumina crucible at 1,530°C for ~5 days, followed by air quenching. Two TEM sections were extracted from hibonite in the reaction zone of the run product using a FEI Quanta 3D field emission gun SEM/FIB instrument at NASA JSC.

A spinel-hibonite inclusion (SHIB) 1-9-5 and two platy hibonite crystals (PLACs) 2-7-1 and 2-8-2, recovered by freeze-thaw disaggregation and density separation from the Murchison CM2 chondrite, were also studied using TEM. Hibonite in these two CAI types is compositionally and isotopically distinct [5,6]; SHIB 1-9-5 hibonite contains 2.0–3.1 wt% MgO, whereas hibonite in PLACs 2-7-1 and 2-8-2 contains <1 wt% MgO with no resolvable radiogenic 26Mg excess. PLAC 2-7-1 is unusual in that spinel occurs at its margin [6,10]. The TEM sections of hibonite from the three CAIs were prepared using a Tescan LYRA3 SEM/FIB instrument at University of Chicago [10].

The FIB sections were then examined for structural and chemical characteristic by a JEOL 2500SE field emission scanning TEM equipped with a ThermoNoran thin window energy dispersive X-ray (EDX) spectrometer at NASA JSC.

**Results: Hibonite in the Reaction Zone.** The new annealing experiment produced a reaction zone similar to that observed in our previous experiments [8,9]. Adjacent to the alumina is a hibonite layer, followed by a grossite layer, and finally a zone of krotite and Ti-bearing residual melt (Fig. 1a). While corundum occurs as numerous inclusions in hibonite, no spinel intergrown with or in contact with hibonite is observed. Instead, abundant euhedral spinel crystals occur as inclusions in both grossite and krotite + melt.

![Figure 1. (a) BSE image of the reaction zone from experiment (4) showing a sequence of corundum (cor), hibonite (hib), grossite (grs), and krotite (kr) + melt. (b) BF STEM image of FIB 4-2. Hibonite crystals contain stacking defects indicated by red arrows.](image)

In FIB 4-1 prepared from the middle of the hibonite layer, hibonite is defect-free and pure CaAl12O19. Both electron diffraction patterns and lattice fringe images of hibonite show uniform d spacings and 2.2 nm wide (001) spacing. Hibonite in FIB 4-1 represents well ordered, stoichiometric hibonite.

FIB 4-2 cut near the hibonite-grossite interface consists of compact intergrowths of randomly-oriented hibonite laths (Fig. 1b). Hibonite crystals show i) a low density of stacking defects parallel to their elongation direction, ii) weak streaking along the c axis in electron diffraction patterns, and iii) random variations in lattice fringe spacing along the c axis (e.g., random intergrowths of 2.6 nm (001) spacing within prominent 2.2 nm (001) spacing). Our EDX analyses show that hibonite contains Mg and Ti (<1 wt% MgO and <0.5 wt% TiO2) and that the stacking defects are clearly linked to an increase in the MgO contents with constant Al2O3 and CaO contents. However, defect-rich regions in hibonite appear to be uncorrelated with their TiO2 content compared to its defect-free regions. Hibonite in FIB 4-2 thus consists of complex, disordered intergrowths of stoichiometric and MgO-enriched hibonites.

**Murchison CAIs.** Hibonite crystals in both PLACs 2-7-1 and 2-8-2 are free of stacking defects, and show uniform 2.2 nm wide (001) spacing in lattice fringe...
images. However, PLAC 2-7-1 contains numerous rounded, strained regions (Fig. 2a) that have slightly distorted, narrower lattice fringes in their center compared to the surrounding hibonite. These structural disturbances accommodate a very minor Al$_2$O$_3$ enrichment and correlated CaO and TiO$_2$ depletions relative to the host hibonite. Additionally, hibonite in PLAC 2-7-1 is partially embayed by intergrowths of spinel and perovskite [10], but has a crystallographic orientation relationship of (001)$_{hib} // (111)_{sp}$ with only spinel.

![BF STEM images of CAIs 2-7-1 (a) and 1-9-5 (b). In (a), the rounded, strained regions in hibonite are shown in black. In (b), stacking defects in hibonite are indicated by red arrows, and an inset shows a refractory metal nugget (RMN) embedded in spinel.](image)

In contrast, in SHIB 1-9-5, hibonite crystals contain a low density of stacking defects (Fig. 2b). Their microstructural and compositional characteristics are very similar to those observed in FIB 4-2. In addition, spinel is crystallographically oriented to hibonite with (001)$_{hib} // (111)_{sp}$. A refractory metal nugget embedded in spinel [10] has a uniform composition of (in wt%) 2 Re, 25 Os, 4 W, 15 Ir, 10 Mo, 17 Ru, 12 Pt, 3 Rh, 2 Ni, and 10 Fe. These elements show approximately a flat pattern with enrichment factors of $\sim1-5 \times 10^5$ on a CI-normalized diagram.

**Discussion:** Our new experiment produced hibonite that contains a range of stacking defect densities and correlated compositional variations, consistent with the results of our previous experiments [8,9]. The similar characteristics are also observed in hibonite from the Murchison CAIs. These characteristics of hibonite can be explained by the rearrangement of two basic spinel and Ca-containing blocks [3,4] and the preferential substitution of Mg and Ti in hibonite [11]. The MgO enrichments along stacking defects in hibonite are therefore direct evidence that the substitution of Mg with Al in the spinel blocks stabilized the formation of wider spinel blocks in hibonite, hence forming complex intergrowths of stoichiometric and disordered, Mg-enriched hibonite [3]. The lack of a correlation between the presence of stacking defects and the TiO$_2$ contents may suggest that the substitution of Ti with Al in the Ca-containing blocks is not an important mechanism to form stacking disorder (e.g., wider Ca-containing blocks) in hibonite. However, a much lower density of stacking defects in Mg,Ti-bearing hibonite in our new experiment compared to only Mg-bearing hibonite in our previous experiments [8,9] suggests that the introduction of Ti during the formation of hibonite appears to have inhibited the substitution of Mg with Al in the spinel blocks. An additional TEM study of synthetic and meteoritic hibonites is underway to investigate in more detail the effect of Ti on the formation of stacking disorder in hibonite.

Hibonite in PLACs 2-8-2 and 2-7-1 appears to have condensed stoichiometrically before $^{26}$Al arrival in the solar nebula [6]. The strained regions in PLAC 2-7-1 hibonite may represent regions where Al$_2$O$_3$-rich spinel nucleated metastably at the very early stages of the formation of wider spinel blocks (i.e., stacking defects) in hibonite. Later, spinel nucleated epitaxially and grew onto hibonite by reaction of hibonite and gaseous Mg, as indicated by their crystallographic orientation relationship, during condensation of perovskite.

The lack of the original textural context of SHIB 1-9-5 makes it difficult to infer its origin. Thus, defect-structured hibonite in this inclusion may have formed metastably by direct condensation or by melting of an early-condensed refractory assemblage as Mg was incorporated into hibonite as extra spinel blocks (i.e., stacking defects). Spinel nucleated and grew in a crystallographic continuity with hibonite and then coninuted to form into larger crystals.

**Conclusions:** Our TEM study shows a microstructural difference between Muchison PLAC and SHIB hibonites, consistent with their different formation conditions, as inferred by their isotope compositions [5,6]. Combined with the results of our annealing experiments [8,9, this study], this difference can be interpreted as the result of the accommodation of non-stoichiometry in hibonite by altering stacking sequence of spinel and Ca-containing blocks in the ideal hibonite structure [3,4].

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Introduction: Silicates are pervasive not only in our solar system, but have also been detected in a multitude of other environments such as protostars, protoplanetary disks, AGB stars, and the diffuse interstellar medium. Cosmic silicates are therefore integral in understanding the life cycle of matter. A lineage between various silicate components in primitive material has yet to be established, but may potentially display a gradient of properties outlining the lives of silicate grains from the time they leave their parent stars until they are incorporated into a protoplanetary disk.

Circumstellar silicates that originated in the winds of dying stars have been positively identified by their highly anomalous oxygen isotopic compositions using NanoSIMS [see 1 for review]. Unfortunately, isotopic studies of other elements in presolar silicates are limited due to their small size (~250 nm on average) and analytical limitations. Interstellar grains refer to circumstellar grains that were partially destroyed, modified, and isotopically homogenized by irradiation, supernova shocks, or grain-grain collisions in the interstellar medium (ISM). Glass with embedded metal and sulfides (GEMS) are argued to be these interstellar grains [2]. A competing hypothesis argues that GEMS formed in the solar nebula by late-stage, nonequilibrium condensation [3]. In either case, GEMS may also be the precursors to amorphous silicates in primitive meteorites prior to parent body processing. Presolar (circumstellar) silicates, GEMS, and primitive matrix grains may therefore represent related and consecutive stages in the lifetime of cosmic silicates. We have begun a thorough isotopic study of presolar silicates, GEMS, and Acfer 094 matrix grains with the unparalleled analytical capabilities afforded by the Chicago Instrument for Laser Ionization (CHILI) in order to reveal the ancestral connections, or lack thereof, between them.

Our first focus is on the Fe and Ni isotopic composition of presolar silicates. Iron is highly abundant in presolar silicates, reaching as high as 40 at% in some samples [e.g. 4]. The high abundance of iron makes it analytically favorable for analysis, but is also a puzzle of its own: spectral observations of silicates around various stellar sources and in the ISM as well as thermodynamic calculations of silicate condensation predict Mg-rich/Fe-poor compositions. While secondary alteration may seem like an obvious explanation for this discrepancy, many presolar silicates with high Fe abundances show little evidence for secondary alteration.

Iron and Ni isotopic measurements can also help refine nucleosynthesis or galactic chemical evolution (GCE) models. The parent stars influence the neutron-rich nuclides but have little effect on the neutron-poor nuclides, which can then serve as proxies for GCE ($^{56}$Fe/$^{52}$Fe; $^{60}$Ni/$^{60}$Ni). This has been studied in presolar SiC grains [5]. In neutron-rich Fe isotopes, the largest compositional changes take place during the asymptotic giant branch (AGB) phase where the $^{57}$Fe/$^{56}$Fe ratios can become elevated by as much as 700‰ by the late dredge-up episodes. Silicates are predicted to form in earlier episodes before large $^{57}$Fe/$^{56}$Fe excesses develop. Precise measurements of presolar silicates should probe this earlier stage of AGB evolution. While stellar models predict small to large excesses in $^{57}$Fe/$^{56}$Fe, many presolar silicates and presolar SiC grains show large depletions in this ratio [4, 9]. Iron-58 has never been measured in presolar silicates due to isobaric interferences, but presolar SiC can have significant $^{58}$Fe/$^{56}$Fe enrichments of up to 500‰ [5].

CHILI is a resonance ionization mass spectrometer designed to achieve an unprecedented lateral resolution of 10 nm and a useful yield of ~40% [6]. Because of its high spatial resolution, improved sensitivity, and ability to eliminate isobaric interferences, CHILI is far better equipped than current SIMS instruments to resolve the true isotopic composition of nanometer-sized grains. The anticipated ~10 nm lateral resolution will be achieved using a Ga ion gun that is currently still in development. The isotopic composition of presolar SiC grains have instead been successfully analyzed by applying Nd:YLF desorption laser beam, frequency-tripled to 351 nm, focused to ~1 µm [6]. However, presolar SiC grains are much larger than presolar silicates and can be extracted from their host meteorite using chemical treatments. The desorption laser’s large beam size compared to the size of presolar silicates would lead to significant overlap of surrounding material. To avoid this issue, we have developed a method to fully isolate sub-µm grains for study with the desorption laser.

Methods: Ten presolar silicates were previously identified using NanoSIMS by O isotopic imaging of grain size separates from Acfer 094 dispersed onto Au foil. Acfer 094 is an ungrouped carbonaceous chondrite
with a high abundance of presolar silicates considered to be one of the most primitive meteorites [7]. The elemental compositions of the presolar silicates were also characterized by Auger Nanoprobe. Using a TESCAN LYRA3 FIB-SEM equipped with an OmniGIS II gas injector, we isolated two of the presolar silicates using FIB milling. FIB milling has been used previously to isolate presolar silicates for NanoSIMS analysis [8, 9]. First, a cap of Pt is electron deposited over the grain to protect it from further milling and redeposition. Second, an annulus with an outer diameter of ~4 µm around the grain is milled away using a low current (~50 pA) Ga⁺ ion beam (Figure 1). The Fe and Ni isotopic compositions were then measured in the two isolated presolar silicates using CHILI.

Our analyses of Acfer 094 matrix material as well as silicate standards (meteoritic olivine and pyroxene) show that these materials can be efficiently desorbed with the desorption laser. The laser power needed to desorb Fe and Ni from Pt and Au was found to be higher than the power needed to desorb from silicates. Thus, to avoid possible contamination from the Pt and Au, we maintained the laser power below that needed for Pt or Au desorption. Nevertheless, subsequent electron imaging showed that material outside of the milled region was also desorbed. During analysis, it also appeared the spoke holding the grain was immediately lost while still showing a signal.

Figure 1. SEM images of grain isolation. (Left) untilted and (middle) tilted views of Pt deposit over grain. (Right) tilted view of FIB isolated grain.

For the remaining presolar silicates, we developed a method for fully lifting out and sequestering the grains from the surrounding material (Figure 2). After FIB milling around the grains, a W needle is attached to the Pt cap with another layer of Pt via ion deposition using an Oxford OmniProbe 400 micromanipulator. An area of the Au foil is “cleaned” by ion milling. The needle with exposed grain is then affixed to the surface with another Pt deposit to avoid loss of the sample.

One matrix grain has been successfully lifted out and analyzed with CHILI. The Fe and Ni isotopic compositions of this grain as well as the two (failed) presolar silicates are shown in Figure 3. While the presolar grains appear distinct in $^{54}$Fe, more measurements are needed to assess any systematic errors. The other isotopes are within uncertainties. Due to aforementioned reasons, it is likely the presolar grains actually reflect separate matrix measurements.

**Outlook:** We are now prepared to analyze the Fe and Ni isotopic composition of the remaining presolar silicates. The entire presolar silicate grain will be consumed during Fe and Ni analysis, impeding an isotopic study of other elements; however, more isotopic data on the matrix of Acfer 094 is needed and there is ample material for a multi-element study. Once the Ga ion gun is available for use, we will begin measurements on GEMS as described in [10].

Figure 2. (Left) FIB image of W needle prior to attachment to Pt cap. (Right) SEM image of lifted out and detached grain.

Figure 3. Fe and Ni isotopic composition in presolar silicates (red) and lifted out matrix grain (blue), normalized to meteoritic pyroxene measured in Ornans. 2σ error bars.