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**DAY 1 — Feb. 13, 2017**8:30–8:50 **Opening and Logistics****SESSION 1: Ice and Organics under Irradiation in Space**

8:50–9:15 am H. Sugahara

Nitrogen Isotopic Evolution of Organic Molecules in Interstellar Ice Analogues by UV Irradiation

9:15–9:40 am F. R. Orthous-Daunay

Effect of UV Irradiation on the Soluble Organic Matter Extract from the Murchison Chondrite

9:40–10:05 am M. Roskosz

Deuteration of Insoluble Organic Matter and Silicates by Ionizing Irradiation in the Solar Nebula

10:05–10:30 am E. Quirico

Origin of Cometary and Chondritic Refractory Organics: Ion Irradiation Experiments

10:30–10:55 am J. Duprat

On the Origin of Interplanetary Organics at the Surface of Icy Bodies

10:55–11:20 am F. Robert

Alive  $^{14}\text{C}^*$  at the Formation of an Organic Grain from Comet 81P/Wild 2?**Lunch and Free Discussion**

4:30–4:55 pm S. Tachibana

Low-Temperature Liquid Formed from UV-Irradiated Amorphous Ice

**SESSION 2: Sample Return Missions and Instrumentation to Open Up a New Era for Cosmochemistry**

4:55–5:20 pm K. Bajo

High Spatial Resolution Imaging of Helium Isotope by TOF-SNMS

5:20–5:45 pm F. S. Anderson

In-Situ Dating State of the Art: Context and Concordance Using CODEX

5:45–6:10 pm H. C. Connolly, Jr.

Status Reports on OSIRIS-REx and Hayabusa2 Asteroidal Sample Return Missions

6:10–6:40 pm **Summary of Sessions 1 & 2**6:40 pm– **Dinner and Discussion****DAY 2 — Feb. 14, 2017****SESSION 3: Water and Organics in Small Bodies**

8:30–8:55 am Z. Peeters

Big Individuals or Big Collections of Small Inclusions — Two Approaches to Looking for Organic Matter in Meteorites

8:55–9:20 am V. E. Hamilton

Mapping the Distribution of Water in Carbonaceous Chondrites

9:20–9:45 am E. Quirico (for L. Bonal)

Antarctic Micrometeorites vs. Carbonaceous Chondrites: The Organic Point of View

9:45–10:10 am T. Koga

The 10 New Amino Acids Identified in the Murchison Meteorite: A Suggestion of New Formation Pathways of Meteoritic Amino Acids

10:10–10:35 am L. Piani

Origin and Evolution of Water and Organic Compounds in the CM Carbonaceous Chondrites

10:35–11:00 am **Summary of Session 3****Group Photo, Lunch and Free Discussion****SESSION 4: Organic Evolution in the Solar System (Invited Lecture)**

4:30–5:30 pm J. Dworkin

Organic Evolution in the Solar System

**POSTER SESSION**

5:30–6:30 pm

A. Takigawa Condensation Experiments in the Mg-Si-O System

N. Sakamoto Solar Component Survey from Carbonaceous Chondrite

H. Naraoka Introduction to the Research Center for Planetary Trace Organic Compounds

M. Hashiguchi High-Resolution Mass Imaging for Organic Species in the Murchison Meteorite using Desorption Electrospray Ionization with an Orbitrap Mass Spectrometer

Y. Isono Molecular Diversity of Soluble Organic Matter Synthesized through the Formose-like Reaction

J. Bayron A Fluid Flow Model for Chondritic Parent Bodies

J. Song Development of Cryogenic SIMS  
Technique for Isotopic Analysis of Individual Fluid  
Inclusions

A. Tonomi Detection of CME Components of  
Solar Wind Noble Gas from DOS Sample of  
Genesis

K. Yoshinari Development for In-Situ Radiogenic  
 $^4\text{He}$  Analysis in Zircon for U-Th-He Dating

T. H. S. Harris Suborbital Ballistic Emplacement

### **Banquet**

## **DAY 3 – Feb. 15, 2017**

### **SESSION 5: Refractory Materials in the Evolving Protosolar Disk**

8:30–8:55 am K. Kobayashi  
Water Vapor Pressure-Dependent Crystallization  
of Amorphous Enstatite

8:55–9:20 am D. Yamamoto  
Oxygen Isotope Exchange between Amorphous  
Silicates and Water Vapor: Implication for  
Survivability for Presolar Amorphous Silicates in  
the Solar Nebula

9:20–9:45 am M. Schönbacher  
Nucleosynthetic Isotope Variations in Refractory  
Inclusions: Records of Protoplanetary Disk  
Evolution

9:45–10:10 am N. Kawasaki  
Crystal Growth and Disequilibrium Distribution of  
O isotopes in an Igneous CAI from Allende

10:10–10:35 am T. J. Fagan  
Rapid Formation of  $^{16}\text{O}$ -poor Rim on a  $^{16}\text{O}$ -rich CAI  
in the Nebular Setting

10:35–11:00 am A. N. Krot  
Oxygen- and Magnesium-Isotope Compositions  
of Grossite-bearing CAIs from DOM 08004  
(CO3.1) and DOM 08006 (CO3.0) Chondrites

11:00–11:25 am M. Bizzarro  
Early Formation of Planetary Building Blocks  
Inferred from Pb Isotopic Ages of Chondrules

### **Lunch and Free Discussion**

### **SESSION 6: Delivery of Volatiles to Terrestrial Planets**

4:30–4:55 pm H. Busemann  
Noble Gases in Various Chondrite Classes – Clues  
to Parent Body Processing and the Origin of the  
Terrestrial Volatiles

4:55–5:20 pm J. P. Greenwood  
A Cometary Source for Water on Mars from D/H  
of Allan Hills 84001

5:20–5:45 pm B. Marty  
Cometary Noble Gases Measured by the Rosetta  
Orbiter Spectrometer for Ion and Neutral Analysis  
(ROSINA): Planetary Implications

5:45–6:10 pm R. Brasser  
Late Veneer and Late Accretion to the Terrestrial  
Planets

6:10–6:40 pm **Summary of the Symposium  
Dinner and Discussion**

6:40 pm– **Closing Remarks**

# Nitrogen Isotopic Evolution of Organic Molecules in Interstellar Ice Analogues by UV Irradiation

H. SUGAHARA<sup>1</sup>, Y. TAKANO<sup>1</sup>, S. TACHIBANA<sup>2</sup>, I. SUGAWARA<sup>2</sup>, N. O. OGAWA<sup>1</sup>, Y. CHIKARAISHI<sup>3</sup>, N. OHKOUCHI<sup>1</sup>, H. YURIMOTO<sup>2</sup>, AND A. KOUCHI<sup>3</sup>

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## SESSION 1

### Ice and Organics under Irradiation in Space

DAY 1 – Feb.13, 2017

8:30 am – 11:20 am

4:30 pm – 4:55 pm

Nitrogen isotopic composition ( $\delta^{15}\text{N}$ , relative to terrestrial air) of pristine solar system materials (e.g., comets and chondrites) show elevated  $\delta^{15}\text{N}$  values such as +1500‰ as bulk [e.g., 2], compared to the Sun ( $-407\pm 7\%$ ) [1]. They also have extreme  $^{15}\text{N}$ -enrichment up to +5000‰ in microscale domains [3]. The formation mechanisms of the  $^{15}\text{N}$ -enrichment have not been fully understood, whereas photodissociation of  $\text{N}_2$  in cold interstellar medium (ISM) is considered to be a plausible candidate [4]. Previous studies focused mostly on simple, gaseous N-containing molecules, but complex organic molecules in interstellar grains have not been investigated from the aspect of nitrogen isotopic composition.

We conducted laboratory experiments to examine nitrogen isotopic fractionation caused by UV irradiation to interstellar ice analogues. The experiments were designed to focus on the effects of UV irradiation during the formation of interstellar ice analogues at 12 K (Run-1) and of the further UV irradiation in a warm environment (room temperature) after ice evaporation (Run-2). An apparatus called PICACHU (Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido Univ.) was used for the experiments. The typical ISM gas ( $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 2:1:1$ ) was introduced into the highly vacuumed chamber and deposited onto the surface of sapphire substrates at  $\sim 12$  K. During the experiments, UV photons ( $\sim 10^{14}$  photons  $\text{cm}^{-2}\text{s}^{-1}$ ) were simultaneously irradiated for 71 h. For the Run-2, UV photons were further irradiated for 232.5 h after warmed up to room temperature.

The nitrogen isotopic composition of organic residue was analyzed as bulk sample by nano-EA/IRMS technique [5] and also in individual amino acids: a representative of N-containing complex organic molecule by GC/C/IRMS [6]. A significant nitrogen isotopic fractionation observed for Run-2 suggests that the UV photodissociation of organic matter is important for the isotopic fractionation. In addition, the degree of the isotopic fractionation was large in bulk sample, but it was small in amino acids.

**References:** [1] Marty B. et al. (2011) *Science* 332, 1533. [2] Manfroid J. et al. (2009) *A&A* 503, 613. [3] Briani G. et al. (2009) *PNAS* 106, 105222. [4] Chakraborty S. et al. (2014) *PNAS* 111, 14704 [5] Ogawa N. O. et al. (2010) in *Earth, Life, and Isotopes*. pp.339. [6] Chikaraishi Y. et al. (2010) in *Earth, Life, and Isotopes*. pp.367.

**Effect of UV Irradiation on the Soluble Organic Matter extract from the Murchison Chondrite.** F. R. Orthous-Daunay<sup>1</sup>, L. Flandinet<sup>1</sup>, R. Thissen<sup>1</sup>, V. Vuitton<sup>1</sup>, F. Moynier<sup>2</sup>, L. Piani<sup>3</sup>, S. Tachibana<sup>3</sup>. frod@ujf-grenoble.fr. <sup>1</sup>IPAG, CNRS Univ. Grenoble Alpes, IPAG, F-38000 Grenoble, France, <sup>2</sup>Institut de Physique du Globe de Paris, France <sup>3</sup>Department of Natural History Sciences, Hokkaido University, Japan.

**Introduction:** The Soluble Organic Matter (SOM) consists of thousands of compounds varying in mass up to 2000 Da [1], [2]. These compounds size is in-between the molecules detected in space environments (tens of atoms) and larger macromolecules found only in meteorites. Their size distribution can be related to their synthesis process with the help of high resolution mass spectrometry [3], [4]. The carbonaceous chains have kept track of molecular growth as well as cyclization and photolytic contribution in their size distributions. This is consistent with an interstellar origin as recent studies reported efficient aliphatic chains growth in hot corinos [5] and simulated photolysis occurring in Photon Dominated Regions [6]. An experimental test of this origin hypothesis for the SOM would be to expose it to photolytic condition and to monitor any chemical change with high resolution MS.

**Method:** Sixty-five g of Murchison were washed with water and freeze-thaw disaggregated before being macerated in methanol and toluene (1:2) for 1 week in a dark room. Extracts were recovered after centrifugation and stored in glass tubes. Thin films of extract were deposited on sapphire glasses and exposed to UV (115 to 165 nm) deuterium lamps under  $\sim 10^{-6}$  Pa vacuum inside the PICACHU apparatus at Hokkaido University. Samples received various fluencies of photons, reaching  $10^{20}$  photons/cm<sup>2</sup> in 500 hours of exposure. Photolytic outgassing was monitored by unity-resolved (quadrupole) mass spectrometry. Chemical modification of the whole mixture was checked by measuring high resolution mass spectra before and after exposure with a Thermo LTQ Orbitrap XL coupled with an Electrospray ionization (ESI) source, at Univ. Grenoble Alpes.

**Results and discussion:** Concerning the high-resolution spectrometry, detected ions are in the 150-750 Da range. In particular, cations have an average mass of  $\sim 350$  Da. In this mass range, the Orbitrap resolution is high enough not to compromise stoichiometry computation for each exact mass. Each mass detected bears at least NH, consistently with the ESI ionization bias for amines in positive polarity. We interpret the periodicity in mass as a repetition of stoichiometric patterns. CH<sub>2</sub> is one of the most frequent patterns. Molecules varying only by a given number of CH<sub>2</sub> all exhibit a lognormal distribution. This is characteristic of the molecular growth depending on chains transfer polymerization. After exposure, we still observe a lognormal distribution but with a slightly smaller width than for the experiment without exposure. Our observations may help to understand the survivability of such large molecules in both space and on planetary surfaces.

**References:** [1]Schmitt-Kopplin P. et al. (2010) *Proc. Natl. Acad. Sci. U. S. A.*, 107, 7 pp. 2763–8.[2]Yamashita Y. and Naraoka H. (2014) *Geochem. J.*, 48 pp. 519–525.[3]Wesslau H. (1956) *Makromol. Chem.*, 20 p. 111.[4]Somogyi Á. et al. (2016) *Int. J. Mol. Sci.*, 17, 439.[5]Belloche A. et al. (2014) *Science (80-. )*, 345, 6204 p. 15841587.[6]Alata I. et al. (2015) *Astron. Astrophys.*, 123 pp. 1–9.

**DEUTERATION OF INSOLUBLE ORGANIC MATTER AND SILICATES BY IONIZING IRRADIATION IN THE SOLAR NEBULA.** M. ROSKOSZ<sup>1</sup>, B. LAURENT<sup>2</sup>, L. GAVILAN<sup>3</sup>, L. REMUSAT<sup>1</sup>, N. CARRASCO<sup>3</sup>, H. LEROUX<sup>4</sup>, <sup>1</sup>IMPMC, UMR CNRS 7590, SORBONNE UNIVERSITÉ, UPMC, IRD, MNHN, PARIS, FRANCE (MATHIEU.ROSKOSZ@MNHN.FR). <sup>2</sup>DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES, UNIVERSITY OF ST. ANDREWS, ST. ANDREWS. <sup>3</sup>LATMOS, UNIVERSITÉ VERSAILLES ST-QUENTIN, FRANCE. <sup>4</sup>UMET, UNIVERSITÉ LILLE 1, FRANCE.

**Introduction:** Organic matter found in carbonaceous chondrites is highly enriched in deuterium, relative to H<sub>2</sub> in the protosolar nebula (PSN) and compared to the bulk “chondritic water” mainly adsorbed on or dissolved in silicate and oxide grains. Ion-molecule or gas-grain reactions could lead to such D-enrichment of organics. The ionizing irradiations in the PSN potentially enhanced these mechanisms. In this context, we conducted electron and X-ray irradiation experiments on a large array of well-characterized analogues of the IOM and of hydrous silicates.

**Results:** These irradiations affect the structures of organic precursors. A strong correlation between the structural, compositional and isotopic evolutions is observed. As the dose increases, the  $\delta D$  of each precursor increases until it reaches a plateau value that depends on the nature of the sample. This is a consequence of the nature and the relative proportions of the different CH groups present in the starting material. Concerning silicates, a large deviation from the initial isotopic signature was found. The magnitude of this fractionation is highly correlated to the drop of the water content.

**Discussion:** Concerning organics, intramolecular fractionation factors were derived and found remarkably consistent with factors determined from the IOM of the Orgueil meteorite. Data collected on silicates can be modeled by a Rayleigh-type distillation equation. The fit to the data is consistent with a pure kinetic effect. A quantitative model is derived, that accounts for both structural and isotopic evolutions of the IOM and silicates. Starting from a similar D/H signature, the deuteration of silicate grains larger than about 100 nm is very limited. Conversely, the deuteration of micron-size particles of IOM is very efficient for a comparable irradiation dose. This new fractionating process could explain the systematic D-enrichment measured in the IOM relative to the water present in carbonaceous chondrites.

## Origin of cometary and chondritic refractory organics: Ion irradiation experiments

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Refractory organic matter (ROM) – termed Insoluble Organic Matter (IOM) in chondrites – is a polyaromatic carbonaceous solid ubiquitous in cometary dust and primitive chondrites. The origin of this material is still a debated issue. While the high D/H fractionation points to a formation step in low-T conditions, the polyaromatic structure might require an energetic input as thermal processing and/or ions irradiation [1-4]. We report here experimental simulations in order to test both these processes for producing kerogen-like materials from various precursors: polyethylene glycol (PEG1450), sucrose, lignine, cellulose and a Me-OH soluble extract of lignite. Thermal degradation experiment were run at IPAG with a tubular furnace maintained under secondary vacuum, over the range 300-1000 °C. Low-energy (LE-) irradiations were performed on the IRMA beamline at CSNSM (Orsay-France) with fluences up to  $4.10^{14}$  ions/cm<sup>2</sup> [C 40 keV, Ne 170 keV], and high-energy (HE-) irradiation at GANIL (Caen-France) [Zn 590 MeV, C 12 MeV, Ni 12 MeV]. Infrared spectra were collected *in situ* during irradiation. Raman spectroscopy (514 and 244 nm) was performed *ex situ* to characterize the polyaromatic structure of the samples. These experiments provide new insights into the origin of IOM and cometary ROM. Heating processes provide fair IOM-like polyaromatic solids, and kinetics and precursor effects might even improve these analogs. In contrast, LE-irradiation leads to almost amorphous carbonaceous materials, irrelevant to IOM/ROM. HE-irradiation appears as a possible chemical root to transform simple species into an insoluble solid, but with final structure and composition dissimilar from IOM. Nebular heating might then appear as an essential process. However, the contribution of HE-ionic irradiation cannot be excluded at this point, for instance in the first step of precursors formation.

**References:** [1] Kerridge. et al. (1999) *Space Sci. Rev.* 90, 275-288 . [2] Alexander et al. (1998) *Meteorit. Planet. Sci.* 33, 603-622. [3] Quirico, E. et al. (2014) *Geochim. Cosmo. Acta* 136, 80-99. [4] Brunetto R. et al. (2009) *Icarus* 200, 323-337. [5] Costantini J-M et al. (2002) *Nucl. Inst. Met. Phys. Res. B* 194, 132-140. 19, 292-311.

## On the origin of interplanetary organics at the surface of icy bodies

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**Introduction:** The origin of interplanetary organic matter (OM) is still debated considering either a direct heritage from the parent molecular cloud or processes in the solar protoplanetary disk itself. However, formation of organics at later stages of the solar system evolution, when small bodies such as asteroids or comets were already formed, should be considered to explain the formation of organics components observed in interplanetary dust.

**Irradiation of N-rich ices:** It is possible to recover from Antarctic ice and snow ultracarbonaceous micrometeorites (UCAMMs) that exhibit exceptional OM concentrations [1, 2]. This OM is N-rich and show extreme Deuterium excesses [3, 4]. The OM components observed in UCAMMs are substantially different from that of insoluble OM extracted from chondrites, requiring an alternative synthesis. Large reservoirs of N<sub>2</sub>-CH<sub>4</sub> rich ices occur at the surface of trans-Neptunian icy objects, as recently imaged by the New-Horizon space probe [5]. These ices endure substantial irradiation by Galactic cosmic rays [6]. Recent experiments demonstrated that irradiation of N<sub>2</sub>-CH<sub>4</sub> ices by high-energy ions produce an N-rich refractory organic residue that can be the precursor of the OM observed in UCAMMs [7]. We will review the results obtained by analyzing primitive OM in interplanetary dust and Antarctic micrometeorites and compare it to the recent results of the Rosetta mission that confirmed the presence of abundant OM at the surface of comet 67P/Churyumov-Gerasimenko [8, 9].

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**References:** [1] Nakamura, T., et al., *M&PS Suppl.* 2005. **40**: p. 5046. [2] Duprat, J., et al., *Science*, 2010. **328**: p. 742-745 [3] Yabuta, H., et al., *M&PS Suppl.*, 2012. **75**: p. 5196. [4] Dartois, E., et al., *Icarus*, 2013. **224**: p. 243-252. [5] Grundy, W.M., et al., *Science*, 2016. **351**. [6] Cooper, J.F., et al., *Earth Moon and Planets*, 2003. **92**: p. 261-277. [7] Augé, B., et al., *A&A*, 2016. **592**. [8] Capaccioni, F., et al., *Science*, 2015. **347**. [9] Fray, N., et al., *Nature*, 2016.

# Alive $^{14}\text{C}^*$ at the formation of an organic grain from comet 81P/Wild 2 ?

F. ROBERT<sup>(1)</sup> AND A. THOMEN<sup>(2)</sup>

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In 2006, thanks to the Stardust Space Mission, solid particles constituting the core of a comet (81P/Wild 2) were collected in situ and returned to Earth for laboratory examinations. The capture medium for these particles was a low density aerogel. Previous analyses of these samples have shown some mineralogical similarities between comets and carbonaceous meteorites [1], demonstrating that the protosolar nebula was thoroughly mixed in space and time through the intense turbulence of the protosolar disk. Here we will report NanoSims data of the carbon and nitrogen isotope ratios [2] of carbon-rich particles isolated in the explosion cavity and located close to the aerogel surface.

Most of the grains exhibit typical chondritic values indicating that the comet is not an aggregate of presolar materials. However, a pure organic particle (4  $\mu\text{m}$  in size) exhibits non solar isotopic compositions with extreme enrichments in  $^{13}\text{C}$  and  $^{15}\text{N}$ . An isochron like correlation between  $^{12}\text{C}/^{15}\text{N}$  vs.  $^{14}\text{N}/^{15}\text{N}$  suggests the *in situ* decay of  $^{14}\text{C}^*$ . Theoretically, a single event of irradiation by neutrons accounts for the measured isotopic ratios, namely: the initial  $^{14}\text{N}/^{15}\text{N}$  ( $\approx 5$ ), the  $^{14}\text{C}^*/^{12}\text{C}$  ( $\approx 8 \times 10^{-3}$ ) and the  $^{13}\text{C}/^{12}\text{C}$  ( $\approx 5.5 \times 10^{-2}$ ) ratios. This irradiation would have taken place in the gas phase, the decay of  $^{14}\text{C}^*$  taking place after the formation of the grain.

Excluding a supernovae contribution from the fact that the D/H ratio of this grain is typically chondritic ( $\text{D}/\text{H} \approx 1.7 \times 10^{-4}$ ), secondary neutrons resulting from spallation reactions seems the only possible explanation for the production of  $^{14}\text{C}^*$  from  $^{14}\text{N}$  [3]. However, the origin of the required flux of protons that would yield such an enormous flux of neutrons remains a puzzling question.

**References:** [1] Brownlee et al., (2006) *Science*, 314, 1711–1717 [2] Thomen A. (2012) PhD Thesis. *Museum Nat. Hist. Naturelle Paris*. [3] Leya I. et al. (2000), *Meteoritics & Planet. Sci.* 35, 287-318

# Low-Temperature Liquid Formed from UV-Irradiated Amorphous Ice

S. TACHIBANA<sup>1</sup>, A. KOUCHI<sup>2</sup>, T. HAMA<sup>2</sup>, P. LAURETTE<sup>1</sup>, AND I. SUGAWARA<sup>1</sup>

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**Introduction:** Ultraviolet photon irradiation to ice in molecular clouds and in the outer part of protoplanetary disks may play a key role in synthesizing organic matter prior to the formation of building blocks of planets. However, the formation and evolution processes of ice and organic matter and their material properties have not yet been fully understood.

**Experiments:** A mixture of  $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3$  gas ( $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 5:1:1$ ) was deposited on a gold-coated copper substrate at  $\sim 10$  K with simultaneous UV photon irradiation (a photon/molecule flux ratio  $\sim 1$ ) in an experimental apparatus (PICACHU; *Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University*) [1]. After the deposition of several- $\mu\text{m}$ -thick ice, gas deposition, UV irradiation, and cooling of the substrate were stopped, and in-situ optical microscopic observation of the ice deposit during warm-up was made from a glass window of the vacuum chamber. Gas molecules sublimated from the deposited ice during temperature increase were also analyzed with a quadrupole mass spectrometer.

**Results and Discussion:** The ice deposit cracked at  $\sim 60$  K, and started bubbling at  $\sim 70$  K. A typical bubble size was several to several-tens  $\mu\text{m}$  in diameter. The bubbling continued up to  $\sim 140$  K, where the ice crystallized. This observation suggests that the photo-irradiated amorphous ice liquefied at temperatures below its crystallization temperature (70–140 K), within which amorphous ice has been thought to be solid. The dominant gas species sublimated from the ice deposit during bubbling was  $\text{H}_2$ , and the abrupt increase of  $\text{H}_2$  signal was observed during the bubbling-phase. These observations indicate that bubbling was caused by hydrogen molecules, which is most likely to be formed by photo-dissociation of deposited molecules ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{NH}_3$ ). Similar bubbling behavior was also reported for proton-irradiated  $\text{H}_2\text{O}-\text{NH}_3$  ice at 120 K [2]. Liquefaction of photo-irradiated ice at 70–140 K may be caused by the presence of abundant radicals formed by photo-dissociation in the ice structure, as in the case of less viscous silicate melts with higher abundance of non-bridging oxygen.

The low-temperature liquid formed from photo-irradiated amorphous ice could be an effective reaction media for organic synthesis [e.g., 3] and could have promoted aggregation of ice-coated particles in the outer Solar System.

**References:** [1] Piani L. et al. *Astrophys. J.* in revision. [2] Loeffler M. J. and Baragiola R. A. (2012) *Astrophys. J.* 744, 102–108. [3] Meinert C. et al. (2016) *Science* 352, 208–212.

## High spatial resolution imaging of helium isotope by TOF-SNMS

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## SESSION 2

### Sample Return Missions and Instrumentation to Open Up a New Era for Cosmochemistry

DAY 1 – Feb.13, 2017

4:55 pm – 6:40 pm

**Introduction:** Solar wind (SW) has average energy of  $\sim 1 \text{ keV u}^{-1}$  corresponding the SW plasma stream of  $400 \text{ km s}^{-1}$ . Some extra-terrestrial materials contain noble gases of SW composition [1, 2] because the surface of the materials was directly irradiated by SW. The typical penetration range of SW into rocky materials is less than 100 nm. The depth distribution of an implanted ions reflects an energy distribution of SW which corresponds to an activity of the Sun at a time of SW-irradiation. Here, we test a performance of LIMAS [3] of lateral resolution for He imaging using a <sup>4</sup>He-implanted Si substrate [4].

**Experimental:** The Ga<sup>+</sup> primary beam of LIMAS set to 30 keV in energy and 1 nA in current was used for the measurement, of which probe diameter was  $\sim 90 \text{ nm}$ . The primary beam was pulsed with 200 ns width. The aberration corrector equipped on the primary beam column works to form primary beam having sharp edge, which is useful to improve lateral resolution of two-dimensional He images with high probe current [4].

An edge of rectangle crater of <sup>4</sup>He-implanted Si wafer sputtered by Ga ion beam was prepared for the sample. The total fluence of implanted <sup>4</sup>He was  $2 \times 10^{16} \text{ cm}^{-2}$ , and the implantation energy was 27 keV. The crater edge is a flat plane and the slope is  $14^\circ$ . Therefore, a layer of 10 nm thick parallel to the wafer surface exposed as 40 nm width on the crater edge plane. The primary beam scanned  $20 \times 100$  pixels on the edge slope with  $40 \text{ nm} \times 50 \text{ nm}$  step (total area of  $0.8 \times 5 \mu\text{m}^2$ ).

**Results:** A depth profile of implanted He obtained by the 2D-He-image for the edge slope is identical to that from the conventional depth profiling, indicating that the He imaging using crater depth has a spatial resolution of tens nm in depth direction. The depth resolution obtained is consistent with geometric derivation between edge slope and beam diameter for  $\sim 20 \text{ nm}$ . The detection limit is  $\sim 10^{19} \text{ atoms cm}^{-3}$ .

**References:** [1] Goswami J. N. et al. (1984) SSRv., 37, 111-159. [2] Wieler R. et al. (1980) Proc. LPSC 11th, 1369-1393. [3] Ebata S. et al. (2012) SIA, 44, 635-640. [4] Bajo K. et al. (2016) SIA, 48, 1190-1193.



## In-Situ Dating State of the Art: Context and Concordance Using CODEX

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**Introduction:** During the first 1.5 Ga of solar system history, many important events occurred that define the planets as we know them today. However, the timing and duration of many of these processes remain uncertain, and in some cases, have dramatic implications for the history of the solar-system [1, 2]. State-of-the-art in-situ dating approaches such as the Chemistry, Organics, and Dating EXperiment (CODEX), can provide context and concordance measurements useful for assessing events exceeding 50-100 Ma duration.

Two years ago we published results for Rb-Sr dating with accuracy and precision to  $\pm 200$  Ma [1, 2]. Since then, we have continued to develop the CODEX instrument, enabling colocated raster images of elemental abundance and organics detection, and we have now added the capability to provide Pb-Pb dating, with precision and accuracy as good as  $\pm 50$  Ma.

**Method and Results:** CODEX uses laser-ablation (LA) to remove atoms at each of hundreds of analytical spots on a  $\sim 1$  cm<sup>2</sup> sample and resonance ionization (RI) to selectively ionize atoms of Rb and Sr, thereby mitigating isobaric interferences, followed by time of flight mass spectrometry (MS; or, in total, LARIMS) to determine the abundance of individual isotopes. By adding two lasers to the CODEX system, we can use the LARIMS approach to obtain  $\sim 10$  ppb sensitivity in isobar-free measurements of <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb. Our initial studies used wavelengths of 283.3 nm and 600.2 nm for resonance excitation, followed by IR photoionization. These, in turn, can be used to assess the Pb-Pb isochron age of samples. We tested our approach on the Kuehl Lake 91500 zircon and MIL 05035. The results were in excellent agreement with the known ages, being respectively within 50 and 80 Ma of previous results [3, 4].

**Conclusion:** We have previously demonstrated that we can measure elemental and organic abundance using simpler CODEX modes of, respectively, laser ablation mass spectrometry (LAMS), and two-step laser mass spectrometry (L2MS) [e.g., 5]. Using LAMS in conjunction with LARIMS, we have been able to assess samples with a complex history, separating mineralogies that have been altered from those still containing true dating information [6]. Furthermore, using LARIMS to produce both Pb-Pb and Rb-Sr data allows us to date a wider range of samples, provides an independent test of concordance, permits new insight into potential sample contamination, facilitates understanding of initial Th/U and <sup>87</sup>Sr/<sup>86</sup>Sr reservoirs [e.g., 7], and enables confirmation of the presence of previously unidentified but geologically meaningful isotopic contributions [e.g., 8]. We are currently testing other isotope dating systems using our approach, such as Sm-Nd, and in the future, expect our accuracy and precision will continue to improve.

**References:** [1] Anderson F.S. et al (2015), *RCMS* 29, 1-8. [2] Anderson F.S. et al (2015), *RCMS* 29(2), 191-204. [3] Schoene B. et al (2006) *GCA* 70(2), 426-445. [4] Zhang A. et al (2010) *Science China Earth Sciences* 53(3), 327-334. [5] Anderson F.S. et al (2014) *IPM Conf. 2014*, 2p. [6] Foster S. et al (2016) *LPSC*, 47 abs. #2070. [7] Bouvier A. et al (2009) *EPSL* 280(1), 285-295. [8] Bellucci J. et al (2016) *EPSL* 433, 241-248.

## Status Reports on OSIRIS-REx and Hayabusa2 Asteroidal Sample Return Missions

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**OSIRIS-REx:** OSIRIS-REx is NASA's New Frontiers 3 sample return mission that will visit study and collect sample from asteroid (101955) Bennu. The spacecraft launched flawlessly 180 ms after  $t = 0$  on 8 September 2016. On 28 December 2016 the first Deep Space Maneuver was executed and the spacecraft is now on course for a Earth gravity-assist course correction on 22 September 2017. The payload science instruments, OCAMS, OVIRS, OTES, OLA, and REXIS have completed post-launch aliveness checkouts and all instruments are healthy. First images taken with OCAMS instruments were released to the general public in September 2016. In February 2017, the OSIRIS-REx spacecraft will turn on OCAMS to search for Trojan asteroids. OSIRIS-REx will arrive at Bennu in August 2018 and return sample to Earth in September 2023. The initial analysis will consist of 6 subteams (Pre-Solar, Protoplanetary Disk, Geologic Activity, Regolith Evolution, Dynamical History and the OSIRIS-REx Epochs) with a thematic focus on testing specific hypotheses.

**Hayabusa2:** Hayabusa2 is a JAXA's sample return mission from asteroid (162173) Ryugu. The spacecraft launched in December 2014, and the Earth gravity assist a year later transferred the spacecraft into the Ryugu-rendezvous orbit. The spacecraft is healthy and the operations team is taking advantage of lessons learned from the original Hayabusa mission. Astronomical observations suggest that Ryugu has an effective diameter of 850–880 m, a geometric albedo of 0.044–0.050 and a thermal inertia of 150–300 J m<sup>-2</sup> s<sup>-0.5</sup> K<sup>-1</sup> and that it rotates retrograde with an obliquity of 136° with respect to Ryugu's orbital plane normal [1]. Hayabusa2 will get to Ryugu in mid 2018, make three touchdowns for sampling during its 18-month stay, and bring back  $\sim 100$ -mg of samples in late 2020 [2, 3]. The initial analysis of Ryugu samples will be made in 2021 after preliminary examination at JAXA. The international initial analysis team will consist of six sub-teams (chemistry, petrology and mineralogy of coarse and fine grains, volatiles, insoluble and soluble organic matter) to fulfill the scientific goals of the mission.

**References:** [1] Müller T. G. et al. (2016) *A&A* doi:10.1051/0004-6361/201629134. [2] Tachibana S. et al. (2014) *Geochem. J.* 48, 571-587. [3] Okazaki R. et al. (2016) *Space Sci. Rev.* doi: 10.1007/s11214-016-0289-5.

## **Big individuals or big collections of small inclusions — two approaches to looking for organic matter in meteorites.**

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### **SESSION 3**

#### **Water and Organics in Small Bodies**

DAY 2 – Feb.14, 2017

8:30 am – 11:00 am

Meteoritic organic matter has in the past been extensively studied in its extracted form. After dissolving away the surrounding meteoritic material (metals, silicates, sulfides) in strong acids, the insoluble organic matter (IOM) can be extracted. This was used to measure the elemental and isotopic composition, chemical information, and the degree of alteration of the IOM. The results, however, can only describe the bulk average of the IOM. By extracting the IOM, all spatial information and any sign of heterogeneity within the meteorite is lost.

In our experiments, we focus on measuring the composition of meteoritic OM in situ, without destroying the surrounding matrix. We have used our nanoSIMS (nanometer-scale secondary-ion mass spectrometer) to map the carbon and nitrogen content of a large area (typically 300 x 600  $\mu\text{m}$ ) of Murchison (CM2), QUE 99177 (CR3), GRA 95229 (CR2), and SaU 290 (CH3) meteorites. Meteoritic OM usually occurs as a fine-grained, sub- $\mu\text{m}$  material dispersed within the matrix. We found, however, that it can also occur as large (up to 10  $\mu\text{m}$ ) veins of pure organic matter. We used a range of analytical tools (FIB, TEM, XANES, and again nanoSIMS) to investigate the morphology, elemental, chemical, and isotopic compositions of these veins.

In parallel with the search for large veins, we developed a technique to automatically detect all carbon-rich inclusions in the large number of nanoSIMS images (~250 per map) that were collected for the four meteorites. The output from the automated detection (coordinates, counts, area, ellipticity, etc. of each detected inclusion, 1,000–10,000 inclusions per meteorite) was post-processed to perform statistical analysis.

The results show that there is a lot of heterogeneity amongst the various inclusions within one meteorite and distinct trends in various properties of the organic inclusions between meteorites from different classes.

# Mapping the Distribution of Water in Carbonaceous Chondrites

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**Motivation:** Carbonaceous chondrites (CCs) record the different types of alteration (aqueous vs. thermal metamorphism vs. impact) these materials have experienced and their locations (nebular vs. parent body). Understanding alteration also drives petrologic classification approaches. Abundant mineralogical evidence for the aqueous alteration of chondritic materials early in solar system history is present across nearly all major chondrite groups in the form of hydrated or other secondary phases. Nominally anhydrous phases typically are associated with a lack of aqueous alteration or with thermal metamorphism. Unfortunately, the distribution, speciation, and abundance of water have proven notoriously difficult to measure and integrate into meteorite studies because water is not measured directly by techniques such as mass spectroscopy of bulk materials or electron microprobe and X-ray mapping of thin sections; rather, its presence is inferred from major element chemical data and it is generally assumed to be present in the nominally hydrous phases as water and/or (oxy-)hydroxyl. However, nominally anhydrous phases can host small amounts of OH<sup>-</sup> and H<sub>2</sub>O, and knowledge of the distribution and speciation of water among meteoritic components could contribute greatly to understanding meteorites' alteration histories. Fortunately, infrared (IR) spectroscopy is sensitive to the presence and speciation of water through vibrational modes in the ~3- $\mu$ m region; combined with diagnostic fundamental absorptions in the ~6 – 25  $\mu$ m region, these features indicate mineralogy and solid solution composition. Used at microscopic scales (25-300  $\mu$ m) to map thin sections, IR spectroscopy can provide valuable information about the spatial distribution and speciation of water in petrologic context, e.g., between clasts, as well as in discrete components such as matrix, chondrules, and dark inclusions. Finally, IR spectroscopy is a commonly used remote sensing tool, and individual phase spectra are important for the correct interpretation of such data.

**Preliminary Analysis:** Our IR reflectance micro-spectroscopy of 25 meteorites representing virtually all CC groups reveals differences in the spatial distribution of water across meteorites representing petrologic types 1 – 6 [1]. Our examination of individual map spectra has enabled us to identify OH<sup>-</sup> and H<sub>2</sub>O, as well as the host phases. We are now in the process of evaluating whether spectral feature strength and band area can be used to determine the quantitative abundance of water using methods developed by [2-4] for transmission and reflectance spectra of powders.

**References:** [1] Hamilton, V. E. et al. (2016) *LPS XLVII* 1793–1794. [2] Milliken, R. E. and Mustard, J. F. (2005) *JGR 110*, doi: 10.1029/2005JE002534. [3] Osawa, T. et al. (2005) *MAPS 40*, 71-86. [4] Beck, P. et al. (2010) *GCA 74*, 4881-4892.

# ANTARCTIC MICROMETEORITES vs. CARBONACEOUS CHONDRITES: the organic point of view

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**Introduction:** Primitive small bodies of the Solar System might be much more diverse than revealed by the few chondrite groups we have in hands. The present work is focused on CONCORDIA Antarctic micrometeorites (AMMs) [1] in comparison to primitive carbonaceous chondrites (CCs): one of the objectives is to constrain the nature and diversity of the parent body(ies) sampled by AMMs in comparison to CCs. We are based on combined Raman at 514 nm (to characterize the structure of polyaromatic organic matter (OM)) and InfraRed (IR) (functional analysis of OM and bulk mineralogy) spectroscopies.

**Samples and experiments:** 10 fine-grained (Fgs), 1 scoriaceous (Sc) and 1 intermediate particle (Fg-Sc) are considered here. Fgs did not experienced significant heating through atmospheric entry, in contrast to Sc and Fg-Sc that are partially melted [2, 3]. For measurements, each AMM was pressed on a diamond or on a germanium window. To remove adsorbed terrestrial water, IR spectra were acquired under heated (T=80°C) vacuum (P=10<sup>-6</sup> mbar) [4].

**Results:** Raman spectra of the considered AMMs attest the presence of polyaromatic organic matter, whose structure reflects the thermal history of the samples: a range of atmospheric flash heating and absence of significant thermal metamorphism on their respective parent body(ies). Five (out of 10) Fg-AMMs have mostly escaped flash heating: (i) their Raman spectral parameters are indicative of comparable or even lower structural order than in CCs [3,5]; (ii) they are systematically enriched in organics in comparison to CCs and other AMMs; (iii) they have the lowest CH<sub>2</sub>/CH<sub>3</sub> among the considered AMMs, slightly higher than in CCs; and (iv) they are hydrated, in contrast to other AMMs. Last, recent NanoSIMS measurements reveal bulk <sup>15</sup>N-enrichments higher in these Fg-AMMs than in the other ones.

**Discussion:** Raman and IR spectroscopy allows for the identification of AMMs the least modified by their atmospheric entry. The poorly structured OM, hydration signatures, high organic abundance and <sup>15</sup>N-enrichments are interpreted as primordial signatures and point to the sampling of parent bodies distinct from CCs. This confirms that studying AMMs in laboratory offer the opportunity to get a more complete sampling of small primitive bodies than chondrites. These results will be complemented with 244-nm Raman measurements, to seek other chemical groups (e.g. –CN) and further insights into the polyaromatic structure.

**References:** [1] Duprat et al. (2007) *Advances in Space Research* **39**, 605 [2] Genge et al. (2008) *MAPS 43*, 497 [3] Dobrica et al. (2011) *MAPS 46*, 1363 [4] Beck et al. (2010) *GCA 74*, 4881 [5] Quirico et al. (2014) *GCA 136*, 80

# The 10 new amino acids identified in the Murchison meteorite: A suggestion of new formation pathways of meteoritic amino acids

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**Introduction:** Carbonaceous chondrites contain a diverse suite of extraterrestrial amino acids [1]. The amino acid distribution (e.g.  $\alpha$ -aminoisobutyric acid and  $\beta$ -alanine [2]) and L-enantiomeric excess (Lee) of isovaline [3] could be correlated with the degree of aqueous alteration. Although these results suggest that aqueous alteration has influence on amino acid synthesis on the meteorite parent body, the detailed formation mechanisms remain unclear. In this work, we revisited amino acid analysis of the Murchison meteorite to pursue their formation pathways and performed the amino acid synthesis experiments simulating the condition of meteorite parent body: the aqueous solution (300  $\mu$ L) containing ammonia/formaldehyde/acetaldehyde and/or glycolaldehyde (100/10/1/1 by mol) with  $\text{NH}_3/\text{H}_2\text{O}$  (1/100) was heated at 60 °C for 6 days in a  $\text{N}_2$ -purged glass ampoule with or without olivine powder (San Carlos, 27.0 mg).

**Results and Discussion:** Totally 29 amino acids between  $\text{C}_2$  and  $\text{C}_6$  were identified in the extract of Murchison, in which glycine was the most abundant (up to approximately 3.0 ppm). In addition to the amino acids reported previously, the nine  $\text{C}_3$  and  $\text{C}_4$  hydroxy amino acids (isoserine, homoserine,  $\gamma$ -amino- $\alpha$ -hydroxybutyric acid,  $\gamma$ -amino- $\alpha$ -(hydroxymethyl)propionic acid,  $\beta$ -homoserine,  $\beta$ -amino- $\alpha$ -hydroxybutyric acid,  $\alpha$ -methylserine, isothreonine and allo-isothreonine, ranged from ~20 to ~140 ppb) have been newly identified from the Murchison extract. A new dicarboxy amino acid,  $\beta$ -(aminomethyl)succinic acid, was also detected as a relatively large peak (~90 ppb). The discovery of 10 new amino acids is striking after numerous surveys of meteoritic amino acids since the half century ago.

The simulation experiments gave various amino acids including the hydroxy amino acids with the most abundant of glycine as identified in the Murchison extract. The hydroxy amino acids were identified using glycolaldehyde in addition to formaldehyde, acetaldehyde and ammonia. Moreover,  $\beta$ -(aminomethyl)succinic acid was produced using formaldehyde, acetaldehyde and ammonia in the presence of olivine, but not detected in the absence of olivine. These results indicate that formose reaction with ammonia in the presence of minerals is an important formation pathway to produce meteoritic amino acids during aqueous alteration on the meteorite parent body.

**References:** [1] Burton A. S. et al. (2012) *Chem. Soc. Rev.*, 41, 5459-5472. [2] Glavin D.P. et al. (2006) *Meteor. Planet. Sci.*, 41, 889-902. [3] Glavin D. P. and Dworkin J. P. (2009) *Proc. Natl. Acad. Sci. USA*, 106, 5487-5492.

# Origin and evolution of water and organic compounds in the CM carbonaceous chondrites.

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**Introduction:** Organic matter (OM) and hydrated minerals found in chondrites are the remnants of primordial reservoirs present in the protoplanetary disk 4.6 billion years ago. Nevertheless, it is unclear how their primordial chemical and isotopic signatures might have been modified by chemical reactions occurring on asteroidal parent bodies [e.g. 1]. The CM-type carbonaceous chondrites constitute a well-identified chemical group of chondrites that presents a wide range of hydrothermal alteration degrees on their parent body and may be one of the dominant sources of meteoritic material fallen on Earth [2]. CM chondrites are thus valuable samples to study the origin and evolution of the primordial signatures of OM and water in the Solar System.

In this study, we analysed the D/H and C/H ratios in the fine-grained matrices of different CM chondrites at the scale of some micrometers to trace the interactions between OM and water on the CM- carbonaceous chondrite parent body.

**Experimental:** Sub-millimeter pieces of 6 CM chondrites (from the most altered to the least altered: Sayama, Cold-Bokkeveld, Murray, Mighei, Murchison, Paris) were pressed in indium foils. Fine-grained matrix areas were selected under optical and electron microscopes. The SIMS IMS1280-HR at Hokkaido University was used to measure their D/H and C/H ratios on areas of 10 x 10  $\mu\text{m}^2$  with a  $\text{Cs}^+$  primary beam.

**Results and discussion:** Depending on the position of the primary beam on the matrix, the D/H and C/H ratios vary as a function of the relative amount of OM to hydrated minerals. Positive correlations between these ratios are found in all the CM matrices. For all CMs but Paris, the positive correlations indicate that their H isotopic compositions can be explained by a mixing between a D-rich OM and a D-poor water having an isotopic composition of  $\delta\text{D} = -350 \text{‰}$ . For Paris, the least altered lithologies show a clear D-enrichment comparing to other CMs, while the more altered lithologies tend so have a H isotopic distribution closer to the other CMs. These results indicate that no significant isotope exchange occurred between OM and water, as it should have enhanced the D/H ratio of water in the more altered meteorites. The D-rich points of Paris could be explained by the presence of a third mixing component, a D-rich water, that could originate from low temperature regions. The presence of two sources of water in the Paris chondrite is consistent with recent carbonate oxygen isotope measurements [3].

**References:** [1] Alexander et al. (2012) *Science* 337, 721-3. [2] Gounelle et al. (2005) *GCA* 69, 3431-3443. [3] Vacher et al. (2016) *ApJ* 827:L1.

# Organic Evolution in the Solar System

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## SESSION 4

### Organic Evolution in the Solar System

#### *Invited Lecture*

DAY 2 – Feb.14, 2017

4:30 pm – 5:30 pm

**Introduction:** The astrochemical cycles that spawn nebulae and stars also produce and deliver organic compounds and their precursors in the solar system. These organic species can further evolve as the solar system condenses into small bodies and planets where geochemical processes interreact with cosmochemistry. On Earth (and possibly elsewhere), this interface between geochemistry and cosmochemistry lead to life. On Earth, biochemistry has dominated and subsumed organic geochemistry and cosmochemistry. Thus, to understand the journey of organics before life, we must look to spectroscopy of the interstellar medium, the examination of samples, and tests with models and experiments to tie them together.

**Observations and Analyses:** The 1930s saw the spectroscopic detection of small organic ions and neutral gas molecules in the interstellar medium and isotopic studies followed over 40 years later. The inventory and distribution of simple molecules in gas, grains, and ices was further advanced by ground and space-based observatories, such as ISO, Spitzer, ALMA, and soon JWST. These observations provide context for studies of samples generated in models, laboratory experiments, and the analysis of meteorites.

Though studies of the organic content of meteorites date to Berzelius in 1834, it did not accelerate until the 1970s. Until recently, most of these focused on a few carbonaceous chondrites. Meteorite analyses today show a complex and highly diverse suite of organics, including hydrocarbons, carboxylic acids, aromatics, hydroxy acids, polyols, amino acids, and more. Antarctic and other systematic meteorite collection campaigns now provide an astounding wealth of samples to study. The study of one suite of compounds across meteorite types is now beginning to provide insight into the early solar system. Though the study of prebiotic chemistry in the laboratory from the 1950s and 60s helped interpret the complex mix of compounds in samples, it was preparation for the study of moon rocks that catalyzed the study of extraterrestrial organics.

**Sample Return:** Apollo 11 returned the first samples from space for laboratory organic analysis. Human and robotic lunar sample return was followed by the capture of IDPs from the edge of space, then samples from a comet and asteroid by Stardust and Hayabusa. Today the Hayabusa2 and OSIRIS-REx spacecraft are traveling to different asteroids to collect and return samples for the next frontier in the study of primitive solar system organics. The addition of pristine samples in context will bring new depth to our increasingly sophisticated understanding of solar system organics.

# Condensation Experiments in the Mg-Si-O System

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## POSTER SESSION

DAY 2 – Feb.14, 2017

5:30 pm – 6:30 pm

**Introduction:** Enstatite whiskers elongated to the [001] axis were identified in chondritic porous interplanetary dust particles (CP-IDPs), Antarctica Micrometeorite (AMM), and samples from a comet Wild 2, while those elongated to the [001] axis are common in minerals occurred in the Earth and meteorites [1-4]. The difference in the morphology of enstatite whiskers reflects their different condensation conditions in the early solar system [5-7]. In order to constrain on the formation conditions of enstatite whiskers with different crystal habits, we performed condensation experiments of enstatite at low super saturation ratios.

**Experiments:** Experiments were performed in a stainless-steel vacuum chamber with a W-mesh heater. MgO and SiO<sub>2</sub> powders were used as a gas source. Each powder was put in a small cell with a hole on the lid. The cells were placed in a cylindrical Ir-crucible and a Pt or Ir-wire was hung at the center of the crucible as a substrate for condensation. Temperature gradient inside the crucible was measured by a thermocouple. Gas temperatures were (a) 1650 and (b) 1580 °C. Condensates were observed with FE-SEM (JEOL 7001F). Chemical compositions and crystal structures were analyzed with EDS and EBSD.

**Results:** (a) *Gas temperature of 1650 °C:* No condensate was observed at 1650-1600°C. Forsterite covered the substrate at ~1600°C. Grain size of forsterite is about 10-20 μm. Roundish clino-enstatite appears at <1580°C. Faceted grains of 15 μm in size condensed at <1440°C and a small amount of Pt was detected at their grain surfaces and boundaries, which may affect the grain shape. (b) *Gas temperature of 1580 °C:* No condensate was observed at 1580-1520°C. Ortho- or proto-enstatite appeared at very small temperature region of ~1520°C. Those grains are rounded and 5-10 μm in size. At lower temperature regions between 1520-1380°C, platy shaped clino-enstatite covered the substrate.

**References:** [1] Bradley J. P., Brownlee D. E., Veblen D. R. (1983) *Nature* 301, 473. [2] Noguchi T. et al. (2008) *MAPS*, Abst# 5129. [3] Ishii H. A. et al. (2008) *Science* 319, 447-450. [4] Nakamura-Messenger, K. et al. (2009) *MAPS*, Abst# 5330. [5] Mysen B. O. & Kushiro I. (1988) *AmMin* 73, 1-19. [6] Tsuchiyama A. et al. (1988) Proc. NIPR Symp. Antarct. Meteorites 1, 185-196. [7] Yamada (2002), Master Thesis (Tohoku University)

## Solar Component Survey From Carbonaceous Chondrite

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**Introduction:** Oxygen in the solar system is believed to be formed by mixing of <sup>17,18</sup>O-rich and <sup>16</sup>O-rich reservoirs [1]. One candidate of <sup>17,18</sup>O-rich end member was proposed from the magnetite in cosmic symplectite ( $\delta^{17,18}\text{O} \approx +180\text{‰}$ ) ubiquitously distributed in the matrix of Acfer 094 carbonaceous chondrites [2]. Some potential candidates of <sup>16</sup>O-rich end member are reported from 1 chondrule [3], 5 CAIs [4,5] and the Sun [6]. However, the characteristics of <sup>16</sup>O-rich candidates are unclear. Therefore, we are investigating the <sup>16</sup>O-rich component in carbonaceous chondrites using an automatic isotope ratio mapping technique.

**Automated Isotope Microscope:** The automated isotope microscope system consists of a stigmatic SIMS and an ion imager SCAPS controlled by LabVIEW software packages including customized CIPS software for SIMS, SUSHI-VIEW for SCAPS and integration software CHAIN. This system allows us to obtain oxygen isotope ratio images of 1 x 1mm region having sub-micron resolution and permil precision within 2 days. Figure shows combined X-ray elemental map of solar component candidate found from the Acfer 214 CH chondrite. The candidate has similar oxygen isotopic composition of previous reports. Future survey would clarify the characteristics of a distinct solar component.

**References:** [1] Yurimoto et al. (2008) *Reviews in Mineralogy and Geochemistry* 68, 141–186. [2] Sakamoto et al. (2007) *Science* 317, 231–233. [3] Kobayashi et al. (2003) *Geochemical J.* 37, 663–669. [4] Gounell et al. (2009) *ApJ* 698, L18–L22. [5] Krot et al. (2017) *GCA in press*. [6] McKeegan et al. (2011) *Science* 332, 1528–1532.

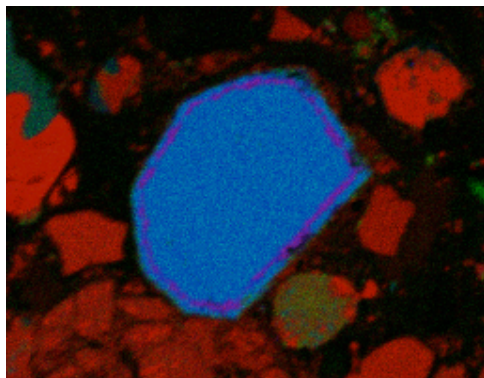


Figure Combined X-ray elemental map of solar component candidate from the Acfer 214 CH chondrite with Mg (red), Al (green), and Ca (blue).

## Introduction to the Research Center for Planetary Trace Organic Compounds

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**Introduction:** Extraterrestrial organic compounds are essential components to understand chemical evolution in the universe. They are present in primitive meteorites in trace amounts as complex mixtures. The research center for Planetary Trace Organic Compounds (PTOC center) was founded in 2016 to develop analytical techniques of trace organic compounds under clean conditions.

**High-resolution mass spectrometry:** Recent high-resolution mass spectral (HRMS) analysis detected tens of thousands of different mass peaks consisting of C, H, N, O, and/or S from the Murchison meteorite [1]. Considering the structural and optical isomers, the current organic contents identified in the meteorite correspond to only approximately 1% of the total compounds present. Recently we found > 600 compounds consisting of  $\text{C}_n\text{H}_m\text{N}$ ,  $\text{C}_n\text{H}_m\text{N}_2$  and  $\text{C}_n\text{H}_m\text{N}_4$  in elemental composition using Orbitrap HRMS coupled with HPLC [2].

**High-resolution chromatography:** Meteoritic organic compounds usually have suites of homologues with various functional groups. They have many structural isomers (including stereoisomers), in which the isomer distribution reflects physical and chemical conditions of the extraterrestrial environment. High-resolution chromatography analysis will be achieved to identify many isomers using a long silica capillary column using nanoLC coupled with an Orbitrap HRMS. The nanoLC and nanoESI techniques can enhance the detection sensitivity by three orders of magnitudes (*vs.* conventional HPLC).

**Organic compound imaging by in-situ analysis:** Trace organic compounds have been generally analyzed using the solvent extracts of powdered samples. The molecular imaging on meteorite surface has been performed using desorption electrospray ionization (DESI) coupled with an Orbitrap MS. Alkylated N-containing cyclic compounds including alkyipyridines ( $\text{C}_n\text{H}_{2n-4}\text{N}^+$ ) and alkylimidazoles ( $\text{C}_n\text{H}_{2n-1}\text{N}_2^+$ ) were identified on the surfaces of the Murray meteorite by in situ analysis using DESI/Orbitrap HRMS [3]. The distribution of alkylimidazoles and alkyipyridines appeared different on the surface, suggesting different their source regions or asteroidal chromatographic effect on the parent body.

**Summary:** The technical development will allow for the improved identification of organic compounds to study the formation pathways and origins of asteroidal organic compounds. Furthermore, the new analytical techniques will allow for the definitive identification of organic compounds in greatly reduced sample sizes (using ~[g of sample *vs.* current ~mg requirement), thereby contributing to the successful analysis for future sample-return missions (e.g. Hayabusa 2 and OSIRIS-REx).

**References:** [1] Schmitt-Kopplin P. *et al.* (2010). *Proc. Natl Acad. Sci.*, **107**, 2763. [2] Yamashita Y. & Naraoka H. (2014) *Geochem. J.*, **48**, 519. [3] Naraoka H. & Hashiguchi M. (2016) *79<sup>th</sup> Ann. Meeting, Met. Soc.* #6169.

## High-resolution mass imaging for organic species in the Murchison meteorite using desorption electrospray ionization with an Orbitrap mass spectrometer

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**[INTRODUCTION]** Primitive meteorites contain a wide variety of organic molecules, which are identified using mass spectrometry (MS) with gas or liquid chromatography (GC or LC). Recent high-mass resolution chemical analyses for the solvent extracts revealed presence of various CHO, CHNO, CHNOS [1] and CHN species [2]. Furthermore, in-situ chemical analyses with MS have been performed on primitive meteorites using two-step laser desorption/ photoionization mass spectrometry [3] or matrix assisted laser desorption ionization [4]. Such investigations of spatial distribution of the organic species are necessary to understand evolution of organics in extraterrestrial materials.

Now, we are trying to apply the high mass resolution imaging using two dimensional (2D) desorption electrospray ionization (DESI) [5], which is a spray based ionization technique, with Orbitrap-MS to surface of carbonaceous chondrites [6].

**[EXPERIMENTAL]** The DESI-MS analysis was performed in a clean room at the Research Center for Planetary Trace Organic Compounds of Kyushu University. Fragments of Murchison (CM2) (~ a few mm) were obtained by chipping and a fragment with flat surface was embedded in Indium or alloy with low melting point. To comparison of analyzed area of sample surface and obtained DESI imaging data, a few points (~100  $\mu\text{m}$ ) on metal around the fragments were marked by rhodamine B ( $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ ). The imaging was performed ~10x10 mm area of the sample surface using a DESI ion source (Omni Spray Source 2-D, Prosolia) equipped with a hybrid quadrupole-Orbitrap mass spectrometer (Q-Exactive Plus, Thermo Scientific). Methanol (100%) was sprayed on the sample surface with 1  $\mu\text{l}/\text{min}$  flow rate. The nebulizer  $\text{N}_2$  gas pressure was 100 psi. Electrospray voltage were set at 3 kV. The positive ions were obtained with mass resolution of 140,000 ( $m/z$  200) from sample surface in full scan mode motorized x-y stage.

**[RESULTS AND DISCUSSION]** Numerous ion peaks with  $m/z$  70-700 were detected from sample surface. The signal of rhodamine B ( $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3^+$ ) were clearly detected from marked region of the sample surface. Then, we carefully compared with DESI images and stereoscope image of the sample. Alkylated imidazole homologs ( $\text{C}_n\text{H}_{2n-1}\text{N}_2$ ) ( $n=4-10$ ) were detected from surface of Murchison distinguishing from surrounding metal. The identification of the alkylated imidazole homologs was consistent with bulk chemical analysis for the methanol extract of the Murchison sample using high-performance LC-MS [2]. Our results suggest usefulness of the DESI-MS analysis for understanding of spatial distribution of polar organic species in primitive meteorites. Further investigations (e.g. comparison of mineralogy) are needed and they will provide us important sights of the evolution of the extraterrestrial organic materials.

[1] Schmitt-Kopplin P. *et al.* 2010. *PNAS*, 107:2763. [2] Yamashita Y. and Naraoka H. 2014. *Geochem. J.*, 48: 519. [3] Clemett S. J. *et al.* 1993. *Science*, 262:721. [4] Ito M. *et al.* 2016, *Goldschmidt Conference*, 2016. #1297. [5] Takáts. Z. *et al.* 2004. *Science*, 306: 471. [6] Naraoka H. and Hashiguchi M. 2016, 79<sup>th</sup> *Ann. Meeting, Met. Soc.* #6169.

## Molecular Diversity of Soluble Organic Matter Synthesized through the Formose-like Reaction

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**Introduction:** Several formation pathways have been proposed for extraterrestrial organic matter (e.g., photochemical reaction in a cold molecular cloud or outer solar system environment [1] and hydrothermal reaction in planetesimals [2]). Cody *et al.* [2] and Kebukawa *et al.* [3] reported that chondritic insoluble organic matter could be produced by the formose-like reaction in planetesimals. The formose-like reaction also produces soluble organic molecules (SOMs). In this study, we applied the high mass resolution mass spectrometer (HRMS) to identify a series of SOMs formed by the formose-like reaction and their possible formation pathway.

**Methods:** Organic synthesis experiments were carried out as follow [3]. A mixture of paraformaldehyde, glycolaldehyde,  $\text{Ca}(\text{OH})_2$ , ammonium hydroxide and ultra-pure water was sealed in pyrex glass tubes and heated at 90°C for 72 hours. Experiments on the mixture without  $\text{NH}_3$  were also performed for comparison. Supernatant liquids of run products were diluted with solvents and analyzed with a positive ion mode by HPLC-ESI-HRMS (EASY nLC-Orbitrap Elite, Thermo Fisher Scientific) at Hokkaido University. The obtained mass spectra were analyzed with the software ATTRIBUTOR [4] to identify molecular formulas.

**Results and Discussion:** Molecules synthesized with and without  $\text{NH}_3$  had the same retention time in liquid chromatography, and similar peak abundance distributions from  $m/z$ -50 to ~600 on the mass spectra. Considering the presence of doubly-charged ions, molecules with masses up to ~1200 were synthesized irrespective of the presence of  $\text{NH}_3$ . The most frequent mass difference between molecules synthesized either with and without  $\text{NH}_3$  corresponds to the mass of  $\text{C}_2\text{H}_2\text{O}$ . More detailed analysis of molecular distribution indicates that addition of 2  $\text{CH}_2\text{O}$  accompanied by dehydration of 1  $\text{H}_2\text{O}$  occurred to synthesize the SOMs which resulted in the mass difference of  $\text{C}_2\text{H}_2\text{O}$ . A characteristic mass difference observed in molecules synthesized with  $\text{NH}_3$  was the mass of CHN. However, the number of nitrogen in one molecule is limited, and the N-bearing molecules are expressed as  $[\text{CHN}]_m[\text{C}_x\text{H}_y\text{O}_z]$  ( $m = 1, 2$ ) which were possibly formed by a reaction between  $\text{NH}_3$  and products of the formose-like reaction.-

**References:** [1] Greenberg J. M. *et al.* (1995) *Astrophys. J.* 455, L177. [2] Cody G. D. *et al.* (2011) *PNAS*, 108, 19171. [3] Kebukawa Y. *et al.* (2013) *Astrophys. J.* 771, 19. [4] Orthous-Daunay F. -R. *et al.* (2014) *LPSC abstract* #2575.



## A Fluid Flow Model for Chondritic Parent Bodies

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Some carbonaceous chondrites (CC) preserve evidence of geologic activity in the life of their parent bodies (PBs), specifically aqueous alteration. The nature of alteration can constrain characteristics of both the porosity and permeability of the host rock, the composition of the fluid itself, initial <sup>26</sup>Al concentration, and the size of the PB. Oxygen isotopes may be a proxy for water-dominated or rock-dominated types of water-rock interactions[1][2][3].

Thermodynamic models have been used to predict thermal evolution, isotopic composition and abundance in chondritic PBs. Most of the models consider rock properties that are based on CV3 chondrite material, which include the presence of interstitial fluids. Assumptions about the rate of flow in these models are crucial to the analysis of geological processes that led to aqueously altered chondrite material. The “vapor piston model” is one such model that assumes that fluid from melting ice is flowing radially outward from the PB interior toward the vacuum of space, albeit slowly enough to engage in chemical reactions with would-be anhydrous minerals. An opposing hypothesis suggests a scenario in which the PB was in fact not permeable enough for fluid to flow at a rate that would cause phyllosilicates to form[4][5]. A third, less likely hypothesis posits that the fluid would be able to flow freely enough throughout the PB to convect beneath the surface, with high Al abundance providing plenty of internal heat. [5]

We present our initial results on the modeling of the evolution of oxygen isotopes in CC PBs under the assumptions of the “vapor piston model”[2][5]. We assess the robustness of this model’s ability to produce isotopic compositions that are indeed found in aqueously altered meteorites, and the validity of the underlying assumptions that produce the scenarios stated above.

**References:**[1] Young, E. D., Ash, R. D., England, P., & Rumble, D. (1999). *Science*, 286(5443), 1331-1335.[2] Young, E. D. (2001) *Phil. Trans. of the Royal Soc. of Lond. A: Math., Phys. and Eng.Sci.*, 359(1787), 2095-2110.[3] MacPherson, G.J. (2007), Oxford, Pages 1-47.[4] Corrigan, C. M., Zolensky, M. E., Dahl, J., Long, M., Weir, J., Sapp, C. and Burkett, P. J. (1997). *Met. & Plan. Sci.*, 32: 509-515.[5] Young, E. D., Zhang, K. K., & Schubert, G. (2003). *Earth and Planetary Science Letters*, 213(3), 249-259.

## Development of Cryogenic SIMS Technique for Isotopic Analysis of Individual Fluid Inclusions

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**Introduction:** Fluid inclusions found in halite crystals from meteorites can potentially provide direct information of extraterrestrial liquid water, and the cold-stage system equipped by SIMS realized in-situ isotope analysis of fluid inclusions[1, 2]. However, the fluid inclusions should be unexposed in previous system because there was no sample introducing system under low temperature. We are developing cryogenic apparatus for SIMS in order to overcome several difficulties for accurate analysis of fluid inclusions, such as targeting, long presputtering and charging.

**Cryogenic SIMS:** The major components of cryogenic SIMS technique are cryo-polisher, cryo-holder, cryo-coating, cryo-transfer vessel, cryo-loadlock chamber and cryo-stage.

Cryo-polisher is equipped with liquid nitrogen recirculating cooling system placed inside of glove-box purged with dry nitrogen gas. Temperature controller controls the influx of liquid nitrogen to achieve a temperature range (173K ~ 193K) of cryo-polisher. Frozen samples are polished by the polishing sheet on the stage of cryo-polisher to expose fluid inclusions. Polished samples are mounted into cryo-holder which is integrally molded to prevent deformation caused by temperature change. The cryo-holder containing polished sample is coated by gold to avoid charging caused by ion beam. We investigated gold-coating method under low temperature and found that the frost on sample surface prevented making a well-conductive gold-coating. When temperature of sample surface is higher than ~213K, we got good coating. The temperature is consistent with the dew point of the dry nitrogen gas. Coated cryo-holder is set into liquid nitrogen fulfilled cryo-transfer vessel by VAT-valve equipped cryo-loadlock chamber. This cryo-loadlock chamber can be attached to the storage chamber of SIMS directly. Cryo-stage can keep the cryo-holder at ~77K during analysis. All processes should be performed under low temperature enough to keep the fluid inclusions as solid state.



Fig. photo of exposed fluid inclusions in halite crystal

**References:** [1] M. Zolensky et al.(1998) *Sci.* 285, 1377-1379. [2] H.Yurimoto et al. (2014) *Sci.* 48, 549-560

## Detection of CME components of solar wind noble gas from DOS sample of *Genesis*

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**Introduction:** Solar wind (SW) noble gases can be utilized as a tracer to investigate solar activity from the SW irradiated materials. Recently, depth profiling of solar wind He was firstly observed from diamond-like carbon layer on Si substrate (DOS) from NASA's *Genesis* mission [1], which is a sample return mission of SW [2]. They analyzed interstream and coronal hole components, but not coronal mass ejection (CME) components because the detection limit was limited by residual noble gases in the sample chamber vacuum. We have exchanged sputter ion pumps and added getter pumps to improve the chamber vacuum of LIMAS.

**Experimental:** A DOS sample of *Genesis* was prepared in this study. Laser ionization mass nanoscope (LIMAS) [3] was used to measure depth profile of SW noble gases implanted in the DOS.

A pulsed primary beam of 1.5  $\mu\text{m}$  in diameter with  $\sim 50$  nA was used. Sputtered neutrals were ionized by the newly installed fs-laser (Astrella, Coherent) with a pulse energy of 5.6 mJ at the repetition rate of 1 kHz and a power density of  $\sim 10^{20}$  W m<sup>-2</sup>. Mass spectrometer setting of LIMAS was adjusted according to [4]. Multi-turning of <sup>4</sup>He<sup>+</sup> ions was set to 100 cycles and ion gates were used for elimination of interfering ion such as <sup>12</sup>C<sup>3+</sup>. After depth profiling, atomic force microscope was used for measurement of crater shapes.

**Results and discussion:** <sup>4</sup>He background in this study was reduced to  $\sim 4 \times 10^{17}$  atoms cm<sup>-3</sup> for DOS sample, which is one order of magnitude lower than that of [1] ( $3 \times 10^{18}$  atoms cm<sup>-3</sup>). As a result, Depth profile of SW He was traced to the depth of 300 nm from surface. The profile deeper than 100 nm corresponds to CME components. Moreover, depth profile for SW Ne was determined from the DOS sample.

**References:** [1] Bajo K. et al. (2015) *Geochem. J.* 49, 559-566. [2] Burnett, D. S. (2013) *MaPS* 48, 2351-2370. [3] Ebata S. et al. (2012) *SIA* 44, 635-640. [4] Tonotani A. et al. (2016) *SIA*. 49, 559-566.

## Development for in-situ radiogenic <sup>4</sup>He analysis in zircon for U-Th-He dating

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**Introduction:** Zircon has been used for U-Th-He dating of various rocks because zircon contains relatively large amounts of U, Th, and radiogenic <sup>4</sup>He which is produced by  $\alpha$ -decay of U and Th [e.g., 1]. The closure temperature of U-Th-He dating of zircon is  $\sim 180^\circ\text{C}$ . Therefore, a low-temperature thermal history of rocks, e.g. the process of uplift and denudation of mountains, are revealed by using the U-Th-He dating of zircon [e.g., 2]. Radiogenic He atoms close to zircon crystal surface produced by the  $\alpha$ -decays escape from the crystal because a typical range of the  $\alpha$ -decay is  $\sim 20$   $\mu\text{m}$ . Conventional measurements, of which spatial resolutions were tens of  $\mu\text{m}$  [e.g., 3] are difficult to identify the He escaped region. If the He distribution can be observed with micro-meter resolution, we can trace a track of the  $\alpha$ -particle by  $\alpha$ -decay from U and Th, and evaluate radiogenic <sup>4</sup>He loss from the crystal. LIMAS (Laser Ionization Mass nAnoScope) is an analytical system developed for analyzing noble gases in submicro-meter resolution on sample surfaces, which should be a key instrument to realize the analysis.[4]. LIMAS would be analyze spatial distribution of the <sup>4</sup>He concentration in a zircon crystal. Moreover, the analysis may be clarified <sup>4</sup>He re-distribution during low-temperature thermal history. Here, we apply LIMAS to measure <sup>4</sup>He in Jack Hills zircon crystals.

**Analysis for Jack Hills zircon:** Jack Hills (JH) zircon crystals are collected from Jack Hills sedimentary belt, Western Australia, Australia. Ages of JH zircon range from 4.4 to 1.2 Ga by U-Pb dating [5]. We carried out quantitative analysis of <sup>4</sup>He in a JH zircon by LIMAS. The <sup>4</sup>He intensities are calibrated by an ion-implanted silicon standard. We implanted <sup>4</sup>He of 4 keV with a fluence of  $1 \times 10^{15}$  cm<sup>-2</sup> into silicon wafer. A single crystal of JH zircon homogeneously contained radiogenic <sup>4</sup>He about 150 ppm, but a <sup>4</sup>He-rich area of 10  $\mu\text{m}$  across was observed. The concentration was  $\sim 700$  ppm, which was 5 times larger than surrounding. We will carry out line profiles of zircon crystals to obtain distribution of radiogenic <sup>4</sup>He.

**References:** [1] Reiners et al. (2004) *GCA*, 68, 1857-1887. [2] Sueoka et al. (2011) *J. Geograp.* 120, 1003-1012. [3] Horn et al. (2016) *CA*, 178, 106-123. [4] Bajo et al. (2015) *GJ*, 49, 559-566. [5] Wilde et al. (2001) *Nature*. 409, 175-178.

# Suborbital Ballistic Emplacement

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**Introduction:** A large, enigmatic North America (N.A.) sand blanket bears signatures of secondary partitioning from an oblique cosmic impact. Recent lunar data, tektite source composition analysis, high resolution LiDAR, Suborbital Analysis and impact modeling are reviewed and considered.

**Discussion:** Indication of large recent impacts in the terrestrial neighborhood include lunar swirls [1], volatiles H<sub>2</sub>O & CO<sub>2</sub>, light hydrocarbons and sulfur-bearing species on the moon [2]. Tagel et al. suggest traces of chondrite within the Australasian (AA) tektites [3], but that Cr/Ir mix line is not from Upper Continental Crust (UCC), rather from a more mafic CC source shown in Ni/Ir and Cr/Ir ratios per Shirai et al. [4]. Overall, the 786 ka Australasian (AA) tektite REE signature compares to UCC. The recent AA tektite event has no known impact structure [3], possibly due to an unusual imprint from oblique impact into a low impedance layered target, per Stickle and Schultz [5] and others.

**Analytical Methods:** Ongoing LiDAR Survey analysis by M. E. Davias [6-9], continuing Suborbital Analysis by T.H.S. Harris [10-14] and Harris & Davias [15,16] characterize an implied ejecta blanket from a large, low density oblique bolide impact into the continental ice sheet over the N.A. Great Lakes region at MIS 20, at once creating the 400,000 sq. km. Carolina bays depositional blanket and the nearly antipodal AA tektite strewn field with laterite bed.

**Question:** Is Michigan's "lost interval" [17] actually impact excavation, with ice sheet shocked to steam plasma as the motive engine for the AA tektites, their highly acidic Indochina laterite bed and the Carolina bays? The latter expresses 45,000+ suborbital ballistic emplacements of only 6 archetype shapes in a blanket of highly fractured angular depositional sand having no biotic detritus, no local source, and seeping H<sub>2</sub> [18]. AA zircons match Michigan [15]....

**References:** [1] M.B. Syal & P.H. Schultz (2015) *Icarus* v257, 194–206. [2] A. Colaprete et al. (2010) *Science* v330, 463. [3] Tagel et al. (2014) *LPSC XLV*, 2222. [4] N. Shirai et al. (2016), *LPSC XLVII*, 1847. [5] Stickle and Schultz (2011), *LPSC XLII*, 2698. [6] M. Davias (2011), *GSA Ann. Mtg.*, P#165-9 [7] M. Davias (2012), *GSA Annual Mtg.*, S28 P#14 [8] M. E. Davias (2013), *GSA Annual Mtg.*, S314 P#2 [9] M. Davias (2015), *GSA Annual Mtg.*, P214-1 [10] T.H.S. Harris and H. Povenmire (2015), *LPSC XLVI*, 1291 [11] T.H.S. Harris (2015), Bridging the Gap III, 1021 [12] T.H.S. Harris (2015), Bridging the Gap III, 1042 [13] T.H.S. Harris (2015), *LPSC XLVII*, S305 P#90 abs. 1214 [14] T.H.S. Harris (2016), *LPSC XLVII*, S306 P#119, abs. 1033 [15] M. Davias and T.H.S. Harris (2015), *GSA N. Central Section Mtg.*, S3 P#1 [16] T.H.S. Harris and M. Davias (2015), *AGU Fall Mtg.*, ED31C-0906 [17] Dorr & Eschman 1970, *U Michigan Press* [18] V. Zgonnik et al. (2015), *Progress in Earth Sci.*

# Water Vapor Pressure-Dependent Crystallization of Amorphous Enstatite

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## SESSION 5

### Refractory Materials in the Evolving Protosolar Disk

DAY 3 – Feb.15, 2017

8:30 am – 11:25 am

**Introduction:** Infrared spectroscopic observations show that both crystalline and amorphous silicate dust is present in protoplanetary disks, while silicate dust in the interstellar medium is mostly amorphous [1, 2]. This indicates that amorphous silicates transform into crystalline silicates due to thermal annealing in protoplanetary disks. Crystallization of amorphous silicates has been investigated experimentally [e.g., 3], but the effect of disk gas, especially water vapor, has not yet been fully understood except for amorphous forsterite that crystallizes efficiently in the presence of water vapor [4]. Here we performed crystallization experiments of amorphous enstatite at various water vapor pressures.

**Experiments:** Amorphous enstatite powder synthesized by an induced thermal plasma method was annealed at 780-850°C in air ( $P_{\text{H}_2\text{O}} \sim 10^{-3}$  bar), in vacuum ( $P_{\text{H}_2\text{O}} \sim 10^{-10}$ - $10^{-9}$  bar) and at  $P_{\text{H}_2\text{O}} \sim 10^{-5}$  bar. Run products were examined with FT-IR, XRD, and TEM.

**Results and Discussion:** Quantitative analysis of crystallization degree was made by infrared spectral fitting of the 10- $\mu\text{m}$  infrared absorption feature. The time evolution of the fraction of crystalline enstatite was fitted with the Johnson-Mehl-Avrami equation. The obtained Avrami parameter (a parameter related to the reaction mechanism)  $n$  in air was  $\sim 2.5$ , suggesting the 3-dimensional diffusion-controlled growth with heterogeneous nucleation. This is consistent with previous crystallization experiments of amorphous enstatite in air [5, 6]. The crystallization rate was larger than that in air in vacuum, and  $n$  of  $\sim 1.5$  was obtained, which suggests that three-dimensional diffusion-controlled growth of crystalline enstatite after heterogeneous nucleation. This was supported by TEM observations, where crystalline enstatite was only identified at the surface of the grains in the sample heated at 800°C in vacuum for a short duration. Selective evaporation of Mg and O from the grain might promote to form  $\text{SiO}_4$  chain structures at the surface, leading to heterogeneous nucleation of crystalline enstatite at the grain surface. We also found that crystallization of amorphous enstatite at  $P_{\text{H}_2\text{O}} \sim 10^{-5}$  bar occurs more rapidly than that in vacuum, indicating that water molecules diffusing into the amorphous structure cut atomic bonds and promotes the crystallization as in the case of amorphous forsterite [4].

**References:** [1] Waelkens, C. et al. (1996) *A&A* 315, L245. [2] Kemper, F. et al. (2004) *ApJ* 609, 826. [3] Hallenbeck, S. L. et al. (1989) *Icarus* 131, 198-209. [4] Yamamoto, D. (2016) *Master thesis*. [5] Murata, K. et al. (2009) *ApJ* 697, 836-837. [6] Imai, Y. (2012) *PhD thesis*.

# Oxygen Isotope Exchange between Amorphous Silicates and Water Vapor: Implication for Survivability for Presolar Amorphous Silicates in the Solar Nebula

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**Introduction:** Presolar silicate grains exhibiting large oxygen isotope anomalies are the most abundant type of presolar material [e.g. 1]. Floss & Stadermann [2] proposed a possibility of nebular thermal destruction of presolar silicate/oxide grains in an ungrouped carbonaceous chondrite Adelaide. However, the susceptibility and/or survivability of presolar silicate in the Solar nebula have not yet been investigated in detail. We experimentally showed that water molecules diffuse into amorphous forsterite under nebula-like low water vapor pressure ( $P_{\text{H}_2\text{O}}$ ) conditions to promote crystallization [3], implying that water molecule reacts with presolar amorphous silicates to change their oxygen isotopic compositions in the Solar nebula.

**Experiments:** Oxygen-isotope exchange reaction experiments between sub- $\mu\text{m}$ -sized amorphous forsterite and  $\text{H}_2^{18}\text{O}$  vapor were conducted at 803–1073 K and  $P_{\text{H}_2\text{O}} \sim 1$  Pa in a gold-image furnace equipped with a gas injection system.

**Results & Discussion:** Crystallization did not proceed in samples heated at 803–883 K and  $P_{\text{H}_2^{18}\text{O}} \sim 1$  Pa, but the 10- $\mu\text{m}$  infrared absorption peak shifted to higher wavelength with time. This indicates that the isotopic exchange between amorphous forsterite and  $^{18}\text{O}$ -enriched water occurred without accompanying crystallization. At 953 K, amorphous forsterite crystallized and its infrared absorption peak positions shifted to higher wavelengths than those of isotopically normal crystalline forsterite. Moreover, these peaks were broader than crystalline forsterite heated at the same condition with normal  $\text{H}_2\text{O}$  vapor. These can be interpreted as simultaneous oxygen isotope exchange and crystallization. At 1073K, an infrared spectrum of a run product heated for 2 hr showed sharp features, consistent with isotopically normal crystalline forsterite, suggesting that crystallization proceeded without the aid of water molecules and no isotopic exchange occurred between crystalline forsterite and  $^{18}\text{O}$ -enriched water vapor.

These results imply that there would be nebular conditions, where oxygen isotope signatures of presolar amorphous silicates were erased by isotopic exchange with nebular water vapor.

**References:** [1] Floss, C. & Haenecour, P. (2016) *Geochem. J.* 50, 3–25. [2] Floss, C. & Stadermann, F. J. (2012) *MAPS* 47, 992–1009. [3] Yamamoto, D. (2016) *Master thesis*.

## NUCLEOSYNTHETIC ISOTOPE VARIATIONS IN REFRACTORY INCLUSIONS: RECORDS OF PROTOPLANETARY DISK EVOLUTION.

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Calcium-aluminum-rich inclusions (CAIs) are the oldest known solids that formed in our solar system. They condensed during the earliest evolution stages in a hot region of the cooling protoplanetary disk. Many CAIs were subsequently re-heated and melted before they were transported into cooler disk regions and accreted onto their respective chondrite parent body. CAIs preserved characteristic isotope fingerprints from the region of the disk where they formed and thereby provide vital clues about the conditions prevailing in the hot region of the disk where they formed and evolved.

Our previous results showed that common CAIs (non-FUN) can be divided into two groups based on their nucleosynthetic variations in Zr, Ti, Ni and Hf isotopes [1, 2]. For the majority of the analyzed CAIs (main group),  $^{96}\text{Zr}$  excesses positively correlate with excesses in the neutron-rich  $^{50}\text{Ti}$ , and surprisingly s-process excesses (= r-process deficits) in Hf isotopes. The other rarer group exhibits lower  $^{96}\text{Zr}$  and  $^{50}\text{Ti}$  excesses coupled with s-process depletions in Hf isotopes. Our preferred interpretation for these data is a decoupling of the nucleosynthetic sources that produced the heavy ( $A > 130$ ) neutron-rich isotopes compared to the lighter isotopes. In the context of our model, the light isotopes (e.g.,  $^{96}\text{Zr}$ ) were mainly produced in Type II supernovae by charged-particle reactions. These took place in a high entropy wind environment, in which Hf isotopes cannot be synthesized.

Here, we have extended our study to 15 new CAIs from the CV chondrites Allende and Mokoia. The CAIs were classified as type A, B or C. Rare earth element concentrations and high precision Zr, Sr and Ti isotope data were also determined. The new data are consistent with our previous results [1, 2], which showed a relatively limited spread in isotopic composition with e.g.,  $\epsilon^{96}\text{Zr}$  around 0.8 (rare group) or 2.0 (main group). This indicates that these CAIs (fine-grained and coarse-grained) formed from a relatively well-homogenized gas-rich reservoir, potentially close to the Sun in the protoplanetary disk.

However, in contrast to the previous work [1, 2], we also analyzed fine-grained, spinel-rich inclusions with group II rare earth element patterns. These patterns suggest that these inclusions formed by condensation [3]. The nucleosynthetic isotope data of these CAIs display a much larger and more variable isotopic spread in particular for Zr isotopes ( $\epsilon^{96}\text{Zr}$  from -0.3 to + 5.0). This indicates that these inclusions formed from a less well-homogenized reservoir that was separated from the reservoir of the other CAIs either in time and/or space.

Therefore, common CAIs can be divided into different groups that likely sampled an evolving reservoir in the protoplanetary disk close to the Sun. They reflect condensates and re-melting on one hand, but potentially also record the survival of extremely refractory minerals in a hot environment.

**References:** [1] Akram et al. (2013) *ApJ* 777, 169. [2] Leya et al. (2009) *ApJ* 702, 1118. [3] Aléon et al. (2005) *MAPS* 40, 1043.

# Crystal growth and disequilibrium distribution of O isotopes in an igneous CAI from Allende

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Coarse-grained Ca-Al-rich inclusions (CAIs) in meteorites, the oldest objects in the Solar System [1], exhibit unequilibrated O isotope distributions among/within minerals [e.g., 2]; however, the origin of the disequilibrium distribution of O isotopes remains controversial. We propose O isotope disequilibrium among minerals in an Allende Type B1 CAI TS34 was formed by change of O isotopic composition of melt during crystallization, based on petrography and in-situ O isotope measurements. TS34 mainly consists of melilite, Ti-Al-rich clinopyroxene (fassaite), and spinel in addition to minor anorthite, in igneous textures, and O isotopic compositions of the constituent minerals plot along the carbonaceous chondrite anhydrous mineral line. The spinel is uniformly <sup>16</sup>O-rich ( $\Delta^{17}\text{O} = -22.7 \pm 1.7\text{‰}$ ), while the melilite is uniformly <sup>16</sup>O-poor ( $\Delta^{17}\text{O} = -2.8 \pm 1.8\text{‰}$ ). The fassaite crystals exhibit growth zoning overprinting poorly-developed sector zoning: they generally grow from Ti-rich to Ti-poor compositions. The fassaite crystals show continuous variations in  $\Delta^{17}\text{O}$  along the inferred directions of crystal growth, from <sup>16</sup>O-poor ( $\Delta^{17}\text{O} \sim -3\text{‰}$ ) to <sup>16</sup>O-rich ( $\Delta^{17}\text{O} \sim -23\text{‰}$ ), which covers a full range of O isotope variations of the minerals in TS34. The early crystallized <sup>16</sup>O-poor fassaite and the melilite are in O isotope equilibrium. The O isotope variations in the fassaite likely correlate with the O isotope evolution of CAI melt during the fassaite crystallization, from <sup>16</sup>O-poor to <sup>16</sup>O-rich, which plausibly originated from O isotope exchange with surrounding <sup>16</sup>O-rich nebular gas. The <sup>16</sup>O-poor fassaite could have crystallized after <sup>16</sup>O-poor melilite, while the <sup>16</sup>O-rich spinel was a relict at the melilite crystallization from <sup>16</sup>O-poor melt. These crystallization sequences are consistent with phase diagram of CAI melt crystallization. Therefore, O isotope variations of intra- and inter-minerals recorded in the CAI trace crystallization sequences of the CAI melt. The melilite and fassaite show an <sup>26</sup>Al-<sup>26</sup>Mg mineral isochron proving an initial value of  $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.003 \pm 0.075) \times 10^{-5}$ , corresponding to a relative age of  $0.05 \pm 0.02$  Myr from the canonical [3]. These data demonstrate that both <sup>16</sup>O-rich and <sup>16</sup>O-poor reservoirs had been existed in the solar nebula at least  $\sim 0.05$  Myr after the birth of the Solar System.

**References:** [1] Connelly et al. (2012) *Science* **338**, 651–655. [2] Clayton et al. (1977) *Earth Planet. Sci. Lett.* **34**, 209–224. [3] Larsen et al. (2011) *Astrophys. J. Lett.* **735**, L37–L43.

# Rapid Formation of <sup>16</sup>O-poor Rim on a <sup>16</sup>O-rich CAI in the Nebular Setting

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## Oxygen Isotopes of Ca-Al-rich Inclusions (CAIs):

Since the work reported in 1973 by Clayton and co-workers [1], <sup>16</sup>O-rich compositions ( $\delta^{17,18}\text{O} \sim -40$  to  $-50\text{‰}$ ) have proven to be characteristic of many primary minerals in both CAIs and amoeboid olivine aggregates (AOAs) (reviewed by [2]). However, <sup>16</sup>O-poor compositions have been reported for some CAI minerals and have been attributed in some cases to isotopic exchange during fluid-enhanced parent body metamorphism [3,4] and in other cases to re-setting in the solar nebula [5,6]. Distinguishing parent body vs. nebular effects is essential for interpreting crystallization histories of CAIs, particularly for evaluating flows of materials between <sup>16</sup>O-rich and <sup>16</sup>O-poor settings in the solar nebula [7].

In this project, we describe a CAI with a <sup>16</sup>O-poor diopside-rich rim from the primitive carbonaceous chondrite Acfer 094 [8–10]. The rim formed on the <sup>16</sup>O-rich core of the CAI in the nebular setting, suggesting material transfer between isotopically distinct regions of the solar nebula. Furthermore, the sharp isotopic boundary between rim and core indicates rapid cooling after rim formation.

**Acfer 094 and CAI with Diopside-rich Rim:** Like many CAIs from Acfer 094 [9,10], CAI RO-64 has a concentric texture: grossite-rich core with spinel and hibonite mantled by an anorthite±melilite layer and an outer rim of diopside with tiny grains of Fe,Ni-rich metal. SIMS spot analyses and isotope imaging (SCAPS, see [11]) indicate that the anorthite-rich layer and core are fairly <sup>16</sup>O-rich ( $\delta^{17,18}\text{O} \sim -30\text{‰}$ ), whereas the diopside-rich outer rim is <sup>16</sup>O-poor ( $\delta^{17,18}\text{O} \sim -2\text{‰}$ ). The isotopic boundary between the outer rim and CAI interior appears to be a discontinuity. Our models of O-diffusion across this boundary suggest that the duration of time at elevated temperature during and after rim formation was less than one year at 1400K or less than six months at 1450K, necessitating a rapidly cooling environment in the solar nebula.

**References:** [1] Clayton R.N. et al. (1973) *Science* **182**, 485–488. [2] Yurimoto H. et al. (2008) *Reviews Mineral. Geoch.* **68**: 141–186. [3] Wasson J.T. et al. (2001) *GCA* **65**: 4539–4549. [4] Imai H. and Yurimoto H. (2003) *GCA* **65**: 765–772. [5] Fagan T.J. et al. (2004) *MaPS* **39**: 1257–1272. [6] Aleon J. (2016) *EPSL* **440**: 62–70. [7] Simon J.I. et al. (2016) *GCA* **186**: 242–276. [8] Greshake A. (1997) *GCA* **65**: 765–772. [9] Krot A.N. et al. (2004) *GCA* **68**: 2167–2184. [10] Simon S.B. and Grossman L. (2011) *MaPS* **46**: 1197–1216. [11] Park C. et al. (2012) *MaPS* **47**: 2071–2083.

# Oxygen- and Magnesium-Isotope Compositions of Grossite-bearing CAIs from DOM 08004 (CO3.1) and DOM 08006 (CO3.0) Chondrites

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<sup>2</sup>The University of Chicago, USA

**Introduction:** Ca,Al-rich inclusions (CAIs) in chondrites of petrologic types 2–3 show a bimodal distribution of the initial  $^{26}\text{Al}/^{27}\text{Al}$  ratios [ $(^{26}\text{Al}/^{27}\text{Al})_0$ ] with peaks at  $\sim 0$  and  $\sim 5 \times 10^{-5}$ , most likely indicating heterogeneous distribution of  $^{26}\text{Al}$  in the solar nebula during an apparently a brief epoch of CAI formation. Most of these CAIs are uniformly  $^{16}\text{O}$ -rich ( $\Delta^{17}\text{O} \sim -24\text{‰}$ ) suggesting formation in a gas of  $\sim$ solar composition. The important exceptions are isotopically anomalous  $^{26}\text{Al}$ -poor FUN (fractionation and unidentified nuclear effects) CAIs and PLACs (platy hibonite crystals), and  $^{26}\text{Al}$ -poor grossite-rich CAIs in CH chondrites showing a range of  $\Delta^{17}\text{O}$ , from  $\sim -35\text{‰}$  to  $\sim -10\text{‰}$ . Grossite,  $\text{CaAl}_4\text{O}_7$ , is one of the most refractory minerals predicted to condense from a cooling gas of solar composition. 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. Here, we report on oxygen and Al-Mg isotope systematics of grossite-bearing CAIs in DOM 08004 (CO3.1) measured *in situ* with the UH Cameca ims-1280. Isotopic compositions of grossite-bearing CAIs in DOM 08006 (CO3.0) will be reported at the meeting.

**Oxygen isotopes:** On a three-isotope oxygen diagram ( $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$ ), compositions of the DOM 08004 grossite-bearing CAIs plot along  $\sim$ slope-1 line. All CAIs are isotopically heterogeneous with grossite ( $\Delta^{17}\text{O} = -11\text{‰}$  to  $0\text{‰}$ ), and, in most cases, melilite ( $\Delta^{17}\text{O} = -15\text{‰}$  to  $-1\text{‰}$ ) being  $^{16}\text{O}$ -depleted relative to hibonite, spinel, and Al,Ti-diopside ( $\Delta^{17}\text{O} \sim -24\text{‰}$ ).

**Magnesium isotopes:** Hibonite and grossite in two CAIs show no resolvable excess of  $^{26}\text{Mg}^*$ ,  $(^{26}\text{Al}/^{27}\text{Al})_0 < 5.7 \times 10^{-7}$  and  $< 6.8 \times 10^{-7}$ , respectively.  $(^{26}\text{Al}/^{27}\text{Al})_0$  in four other CAIs are  $(4.4 \pm 0.3) \times 10^{-5}$ ,  $(4.0 \pm 0.3) \times 10^{-5}$ ,  $(4.5 \pm 0.3) \times 10^{-5}$  and  $(4.3 \pm 0.3) \times 10^{-5}$ . The lower than the canonical  $(^{26}\text{Al}/^{27}\text{Al})_0$  is probably due to improper sensitivity factor used for grossite that was assumed to be the same as for hibonite.

**Conclusions:** DOM 08004 experienced hydrothermal alteration resulting in formation of magnetite, fayalite, Fe,Ni-sulfides, Ni-rich metal, and phyllosilicates. The  $^{16}\text{O}$ -depleted compositions of grossite and melilite in DOM 08004 CAIs could have resulted from postcrystallization exchange during fluid-rock interaction on the CO chondrite parent body. The alteration appears to not have unaffected Al-Mg systematics of the CAIs. Therefore, the inferred  $(^{26}\text{Al}/^{27}\text{Al})_0$  must reflect the primordial, heterogeneous distribution of  $^{26}\text{Al}$  in the CAI-forming region. The  $^{26}\text{Al}$ -poor CAIs could have formed prior to addition of  $^{26}\text{Al}$  to the protoplanetary disk.

# Early Formation of Planetary Building Blocks Inferred from Pb Isotopic Ages of Chondrules

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The most abundant component of chondrite meteorites are millimetre-sized chondrules that formed as free-floating molten droplets in the early Solar System. In addition to providing insights into the thermal and physical evolution of the protoplanetary disk, chondrules may have promoted the rapid growth of planetary bodies [1]. Thus, acquiring a statistically-meaningful age distribution of individual chondrules is critical for understanding the early dynamics of the protoplanetary disk, including the thermal history of the material precursor to terrestrial planets.

Our data-set of U-corrected Pb-Pb dates of 22 chondrules define ages ranging from  $4567.61 \pm 0.54$  to  $4563.24 \pm 0.62$  Ma, with  $\sim 50\%$  of chondrules having formed  $< 1$  Myr after Solar System formation at  $4567.30 \pm 0.16$  Ma [2]. An abundance of chondrules with ages within 1 Myr of Solar System formation suggest that the production of chondrules may have been more efficient at early times. The chondrule ages are correlated to their their initial Pb isotope compositions, with younger chondrules recording evolved compositions indicative of a complex thermal pre-history relative to older chondrules. We infer that primary chondrule production was restricted to the first million years of disk evolution whereas the younger chondrules reflect remelting and recycling of first generation chondrules for  $\sim 3$  Myr. This is consistent with astronomical observations indicating that replenishment of fresh dust to the disk is limited to the embedded stage of star formation lasting  $< 1$  Myr [3]. The energy responsible for chondrule production and subsequent recycling may have shifted from shocks associated with spiral arms in a young gravitationally unstable disk to planetary bow shocks and collisions at later times. Our new chronological framework is in keeping with chondrules being a key ingredient driving the efficient and early formation of planetary objects.

**References:** [1] Johansen, A. *et al.* (2015) *Science Advance* **1**, 1500109. [2] Connelly, J.N. *et al.* (2012) *Science* **338**, 651. [3] Evans, N.J. *et al.* (2009) *Astrophys J Supp* **18**, 321

# Noble Gases in Various Chondrite Classes – Clues to Parent Body Processing and the Origin of the Terrestrial Volatiles

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## SESSION 6

### Delivery of Volatiles to Terrestrial Planets

DAY 3 – Feb.15, 2017

4:30 pm – 6:40 pm

**Background:** A fundamental goal in cosmochemistry is to understand the origin of water and volatile elements in Earth-like planets and evolution of their atmospheres. Noble gas considerations can complement other evidence, e.g., from diagnostic H and N isotopes [1-3]. (Giant) impacts likely erased most signatures of a primary atmosphere but also – combined with global magma oceans – led to early degassing of mantle volatiles. Continued outgassing and the addition of some incoming, volatile-rich *chondritic* or cometary material replenished the terrestrial atmosphere [1-4].

In addition to volatiles accreted during the “late veneer”, the interior contains traces of primordially trapped volatiles [5-7]. These could have been incorporated directly from the nebula gas, e.g. by ingassing from a thick atmosphere into a global magma ocean [8], or were provided by the planetary building blocks. The latter may be best represented by originally *chondritic* material that was thermally or aqueously altered to different degrees and potentially even differentiated. Hence, the *primordially trapped* noble gas concentrations of the various chondrite classes but also achondrites are important parameters. To obtain these, members of all meteorite classes must be analysed. The buildup of radiogenic and cosmogenic noble gases, solar wind incorporation in recent asteroidal regoliths and terrestrial effects must be taken into account.

**New Results:** A large number of R, ungrouped C, CI and CR chondrites were recently analysed at ETH Zurich [9-13, this work]. At the symposium we will discuss correlations of these results with parent body metamorphism, aqueous alteration and terrestrial processing. We will present new data for primordially trapped noble gas concentrations for many meteorite classes and combine these with literature data to define concentration ranges for these meteorites. The ranges will be compared with terrestrial noble gas observations to better understand the origin of terrestrial volatiles.

**References:** [1] Alexander C.M.O'D. et al. (2012) *Science* 337, 721-723. [2] Marty B. et al. (2016) *EPSL* 441, 91-102. [3] Halliday A.N. (2013) *GCA* 105, 146-171. [4] Dauphas N. (2003) *Icarus* 165, 326-339. [5] Mukhopadhyay S. (2012) *Nature* 486, 101-106. [6] Caracausi A. et al. (2016) *Nature* 533, 82-85. [7] Hallis L.J. et al. (2015) *Science* 350, 795-797. [8] Mizuno H. et al. (1980) *EPSL* 50, 202-210. [9] Busemann H. et al. (2011) *LPSC XLII*, #2793. [10] Lee M.Y.P. et al. (2013) *LPSC XLIV*, #2681. [11] Vogel N. et al. (2011) *Chem. Erde* 71, 135-142. [12] Riebe M. et al. *subm. to GCA*. [13] Busemann H. et al. (2016) Workshop “DINGUE” #4 (Nancy, April 13-15, 2016).



## A cometary source for water on Mars from D/H of Allan Hills 84001

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The sources and abundance of water on the Red Planet has long intrigued Martian researchers. Hydrogen isotopes have the potential to place constraints on these two problems, and have been used to suggest that Mars lost most of its water to early hydrodynamic escape [1-4] or through later atmospheric escape [5]. The dominant paradigm, wherein heavy isotope enrichments of hydrogen, nitrogen, carbon, and the noble gases in the present Martian atmosphere are due to past loss of the Martian atmosphere [1-3], has recently been challenged using results from the Rosetta mission [6]. Marty et al. [6] suggest nitrogen isotopes and noble gases are sourced from comets. They further suggest that D/H is the only Martian isotopic signature that can be unambiguously ascribed to atmospheric loss [6]. Here we suggest otherwise.

Using the Cameca ims 1270 at Hokkaido University we have re-analyzed apatite in ALH 84001 for D/H. We find  $\delta D = +1960 \pm 138\%$  ( $2\sigma$ ) for apatite in ALH 84001. This is  $\sim 1000\%$  lower than [4] and is similar to the highest values of D/H found in this  $\sim 4.0$  Ga sample by previous researchers [7, 8]. A  $\delta D$  of  $\sim +2000\%$  is also measured by the Curiosity Rover in  $\sim 3.0$  Ga mudstones on Mars [9], suggesting that Mars was not losing atmospheric water to space between  $\sim 4.0$  and  $3.0$  Ga. Recent work on water in shock glasses of Martian basalt EETA 79001 has suggested a  $\delta D$  of  $\sim +1000$ – $+2000\%$  [10], and hypothesized that this is a global ice deposit. We also report new evidence for water with  $\delta D < +3000\%$  in QUE 94201, consistent with alteration fluids of  $\sim +2000\%$ . Here we suggest that this global ice reservoir has a  $\delta D \sim +2000\%$ , and has been present since at least  $4.0$  Ga. We suggest cometary delivery of this large surface water reservoir. This also implies that the majority of fractionation of D/H to present Mars atmospheric levels occurred since  $3.0$  Ga.

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## Cometary noble gases measured by the Rosetta orbiter spectrometer for Ion and Neutral Analysis (ROSINA): planetary implications

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Comets are among the most pristine solar system materials. Their abundant volatile species, mainly in the form of ices, are intimately mixed with refractory silicate-rich phases and organics, the origins of which - either in the protosolar disk or the molecular cloud/interstellar medium - are actively debated.

The origin of cometary matter and the potential contribution of comets to inner planet atmospheres are long-standing problems that were central in the definition of the ESA Rosetta mission exploring Comet 67P/Churyumov-Gerasimenko (67P/C-G). Noble gases are key tracers for the origin(s) and processing of volatile elements in the nascent solar system and in planetary atmospheres. The analysis of argon in Comet 67P/C-G has shown that comets are rich in noble gases [1], suggesting that a significant fraction of these elements in the terrestrial atmosphere could be cometary [2].

The Double Focusing Mass Spectrometer ROSINA DFMS has detected during a dedicated period in May 2016 not only argon, but also krypton and xenon. In this talk we will present the results with special emphasis on Xe, and discuss the implications for solar system formation scenarios, as well as for the origin of volatile species on inner planets.

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# Late veneer and late accretion to the terrestrial planets

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It is generally accepted that silicate-metal ('rocky') planet formation relies on coagulation from a mixture of sub-Mars sized planetary embryos and (smaller) planetesimals that dynamically emerge from the evolving circum-solar disc in the first few million years of our Solar System[1]. Once the planets have, for the most part, assembled after a giant impact phase[2], they continue to be bombarded by a multitude of planetesimals left over from accretion[3]. Here we place limits on the mass and evolution of these planetesimals based on constraints from the highly siderophile element (HSE) budget of the Moon. Outcomes from a combination of N-body and Monte Carlo simulations of planet formation lead us to four key conclusions about the nature of this early epoch. First, matching the terrestrial to lunar HSE ratio requires either that the late veneer on Earth consisted of a single lunar-size impactor striking the Earth before 4.45 Ga, or that it originated from the impact that created the Moon. An added complication is that analysis of lunar samples indicates the Moon does not preserve convincing evidence for a late veneer like Earth[4]. Second, the expected chondritic veneer component on Mars is 0.06 weight percent after 4.5 Ga; the majority of its chondritic late accretion must have arrived earlier. Third, the flux of terrestrial impactors must have been low ( $\lesssim 10^{-6} M_{\oplus} \text{ Myr}^{-1}$ ) to avoid wholesale melting of Earth's crust after 4.4 Ga[5], and to simultaneously match the number of observed lunar basins. This conclusion leads to an Hadean eon which is more clement than assumed previously. Last, after the terrestrial planets had fully formed, the mass in remnant planetesimals was  $\sim 10^{-3} M_{\oplus}$ , lower by at least an order of magnitude than most previous models[1] suggest. Our dynamically and geochemically self-consistent scenario requires that future N-body simulations of rocky planet formation either directly incorporate collisional grinding or rely on pebble accretion.

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