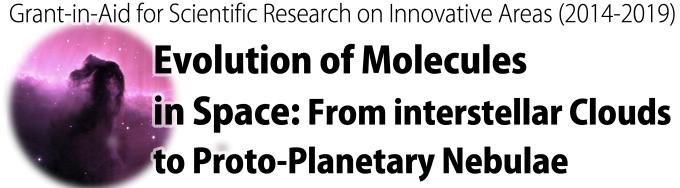


# Solar-System symposium in Sapporo 2016

Feb.17–19, 2016  
Rusutsu Resort, Hokkaido, Japan





Grant-in-Aid for Scientific Research on Innovative Areas (2014-2019)

**Evolution of Molecules  
in Space: From interstellar Clouds  
to Proto-Planetary Nebulae**

Sponsored by Research Project on Evolution of Molecules in  
Space, Grant-in-Aid for Scientific Research on Innovative Areas

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**DAY 1 — Feb. 17, 2016****8:30–8:50      Opening and Logistics****SESSION 1: Light Elements and Organic Matter from ISM to Small Bodies**

8:50–9:12 am L. Bonal

Interstellar Heritage by the Solar System Challenged by Cometary Nitrogen Isotopic Fractionation?

9:12–9:34 am P. Hily-Blant

Probing the Interstellar Heritage of the Solar System with the Nitrogen Isotopic Ratio

9:34–9:56 am H. Sugahara

Nitrogen Isotopic Fractionation of Ammonia by Adsorption on Mineral Surface

9:56–10:18 am F. Robert

Hydrogen Isotope Fractionation in Hydrocarbon Plasma: Cosmochemical Implications

10:18–10:40 am J. Duprat

On the Origin of Ultracarbonaceous Antarctic Micrometeorites

10:40–11:02 am L. Piani

Hydrogen Isotopic Evolution of Water and Organic Compounds on Carbon-Rich Asteroids

11:02–11:24 am G. D. Cody

Light Element Isotope Abundance of Chondritic Organic Solids: A Signature of Incomplete Isotope Exchange?

**Lunch and Free Discussion**

4:30–4:52 pm S. Itoh

Origin of Extremely Heavier Hydrogen Isotopic Compositions of Phosphate Minerals from LL4-6 Ordinary Chondrites

4:52–5:14 pm F. R. Orthous-Daunay

Interstellar Origin of Soluble Organic Matter from the Murchison Meteorite Revealed by Orbitrap-MS

5:14–5:36 pm H. Naraoka

Extensive Alkylated N-Containing Cyclic Compounds in the Murchison Meteorite

5:36–5:58 pm E. Quirico

Refractory and Semi-Volatiles Organics at the Surface of Comet 67P/Churyumov-Gerasimenko

5:58–6:20 pm M. Bizzarro

Isotopic Evidence for Primordial Molecular Cloud Matter in Metal-Rich Carbonaceous Chondrites

6:20–6:42 pm A. Kouchi

Evolution of Molecules in Space: From Interstellar Clouds to Protoplanetary Systems

6:42–7:10 pm **Summary of Day 1**7:10 pm– **Dinner and Discussion****DAY 2 — Feb. 18, 2016****SESSION 2: Presolar and Early Solar System History: Hot in the Beginning**

8:30–8:52 am A. Takigawa

Formation and Alteration History of a Unique Faceted Presolar Corundum

8:52–9:14 am T. Nakamoto

Homogenization of Isotopic Ratio in Solar Nebula

9:14–9:36 am N. Kawasaki

Chronological Study of Oxygen Isotope Composition for the Solar Protoplanetary Disk in a Fluffy Type A CAI from Vigarano

9:36–9:58 am M-C. Liu

Oxygen Isotopes and High  $^{26}\text{Mg}$  Excesses in a U-Depleted Fine-Grained Allende CAI

9:58–10:20 am A. N. Krot

High-Temperature Rims around CAIs from the CR, CB and CH Carbonaceous Chondrites

10:20–10:42 am F. Moynier

Coupling Vanadium and Boron Isotopes in CAIs

10:42–11:04 am N. Sakamoto

Opaque Minerals Bearing Forsterite in Carbonaceous Chondrites

**Group Photo, Lunch and Free Discussion****SESSION 3: Volatiles on Earth, Venus, and Mars — Lessons from ROSETTA**

4:30–5:30 pm B. Marty

Origins of Volatile Elements on Earth, Venus and Mars in Light of Recent Results from the ROSETTA Cometary Mission

**POSTER SESSION**

5:30–6:30 pm

L. Piani Photochemistry in Molecular Cloud: Evolution of Ice and Organic Residues through Warming and UV-Irradiation

K. Abe Occurrence and Chemical Variation of Cosmic Symplectite in Acfer 094 Carbonaceous Chondrite

- S. Yoneyama Petrography of a Large Perfect Shaped Type A/B CAI Formed by Multiple Heating
- Y. Yoshida Petrography of a Compact Type A CAI including Bubble-Like Voids from Ningqinag Carbonaceous Meteorite
- S. Arakawa A New Mechanism for Compound Chondrule Formation: Collisions of Supercooled Droplets
- N. Matsuda Petrography and Oxygen Isotope Distribution of Olivine from Coarse-Grained Igneous Rim around Chondrule in NWA3118 CV3 Chondrite
- M. Mori Cooling Speedometer for Chondrules: Eutectic Structure of Metallic Iron and Iron Sulfide
- M. Kuroda Mechanism of Water Diffusion in Silica Glass at 50 bar Water Vapor Pressure
- S. Tachibana Hayabusa2: Sample Return from C-Type Near-Earth Asteroid (162173) Ryugu

## Banquet

### DAY 3 — Feb. 19, 2016

#### SESSION 4: Volatiles in Protosolar Disk and Their Delivery to Terrestrial Planets

- 8:30–8:52 am C. Kato  
Gallium Isotopes in CAIs
- 8:52–9:14 am S. Tachibana  
Condensation and Evaporation Kinetics of Forsterite under Protoplanetary Disk Conditions
- 9:14–9:36 am E. A. Pringle  
Origin of Volatile Element Depletion in Early Solar System Material
- 9:36–9:58 am K. E. Miller  
Decoding the R Chondrite Record of a Volatile-Rich Environment
- 9:58–10:20 am D. Yamamoto  
Hydrous Mineral Formation in Protoplanetary Disks
- 10:20–10:42 am Q.-Z. Yin  
Dating the Earth-Like Reservoir Formation in the Solar Nebula with Enstatite Chondrite
- 10:42–11:04 am B. P. Weiss  
Lifetime of the Solar Nebula and Nebular Magnetic Field
- 11:04–11:26 am S. J. Mojzsis  
Onset of an “Early Heavy Bombardment” of the Inner Solar System

#### Lunch and Free Discussion

#### SESSION 5: Return Samples and Instrumentation to Open Up a New Era for Cosmochemistry

- 4:30–4:52 pm H. C. Connolly, Jr.  
OSIRIS-REx Sample Collection Requirement: Temperature and Volatiles
- 4:52–5:14 pm A. Tsuchiyama  
Observation of Water and Organics in Carbonaceous Chondrites in 3D using Scanning-Imaging X-Ray Microscopy: Development of a New Technique
- 5:14–5:36 pm R. Trappitsch  
Simultaneous Iron and Nickel Isotope Analyses with CHILI
- 5:36–5:58 pm H. Yurimoto  
LIMAS: Tunnel-Ionization Time-of-Flight Sputtered Neutral Mass Spectrometer
- 5:58–6:20 pm A. Tonotani  
Evaluation for Multi-Turn Time of Flight Mass Spectrum of Laser Ionization Mass Nanoscope
- 6:20–6:42 pm K. Bajo  
Depth Profiling Analysis of Solar Wind Helium Collected in Diamond-Like Carbon Film from GENESIS
- 6:42–7:15 pm **Summary of the Symposium**
- 7:15 pm– **Dinner and Discussion**
- Closing Remarks**

**INTERSTELLAR HERITAGE BY THE SOLAR SYSTEM CHALLENGED BY COMETARY NITROGEN ISOTOPIC FRACTIONATION?** L. Bonal\*, P. Hily-Blant, E. Quirico, A. Faure - IPAG (Grenoble-France); \*lydie.bonal@obs.ujf-grenoble.fr

As recently reviewed by Füri and Marty (2015), large nitrogen (N) isotope variations are observed in the Solar System. As they are unlikely to be explained by the remnants of nucleosynthetic heterogeneities, these variations are attributed to isotope fractionation. The environment (pre-natal molecular cloud, protoplanetary disk, Solar System) and the fractionating process (ion-molecule reactions, isotope selective photo-dissociation, self-shielding) are highly debated (ref. in [1]).

Based on a compilation of astronomical observations in prestellar cores, we showed that molecules carrying the nitrile functional group appear to be systematically  $^{15}\text{N}$ -enriched ( $^{14}\text{N}/^{15}\text{N}$  up to 140;  $\delta^{15}\text{N}$  up to  $\sim 1000 \text{ ‰}$ ) compared to those carrying the amine functional group ( $^{14}\text{N}/^{15}\text{N} > 400$ ;  $\delta^{15}\text{N} < -100 \text{ ‰}$ ) [2]. This differential fractionation allowed us to propose that the large N isotopic variations in the Solar System could be explained by the sampling of distinct interstellar N reservoirs [2]. Recent determinations of the N isotopic composition of cometary  $\text{NH}_3$  [e.g., 3, 4], similar to that of CN and HCN ( $^{14}\text{N}/^{15}\text{N} \sim 127$ ;  $\delta^{15}\text{N} > 1000 \text{ ‰}$ ), challenge our scenario. However, instead of directly discarding the idea of a potential interstellar heritage within the solar system, our objective here is to understand what these new cometary data could be teaching us.

First, based on its N isotopic composition,  $\text{NH}_3$  in cometary coma has not been directly inherited from the gas phase of the pre-natal dense molecular cloud. Nevertheless, a genetic link with interstellar matter could still be envisaged as  $\text{NH}_3$  ices could be  $^{15}\text{N}$ -enriched ( $\delta^{15}\text{N}$  up to 3000 ‰) depending on CO depletion and on the temperature [5]. Second, neither cometary HCN, CN, nor  $\text{NH}_3$  have an isotopic composition representative of the bulk solar nebula ( $^{14}\text{N}/^{15}\text{N}_{\text{comet}} \sim 140$  vs.  $^{14}\text{N}/^{15}\text{N}_{\text{PSN}} = 441$ ). Another N-carrying molecule (e.g.,  $\text{N}_2$ , N) might then represent the main cometary reservoir. However, recent results by the Rosetta mission show that in the coma of 67P/CG ( $\text{N}_2/\text{CO}_{67\text{P}} \ll (\text{N}_2/\text{CO})_{\text{PSN}}$ ) [6]. Whether the coma composition reflects that of the nucleus should be discussed. It should also be questioned whether comets accreted and/or trapped, without chemical fractionation, the matter initially present in the solar nebula [e.g., 7]. Last, as shown by Roueff et al. (2015) our current theoretical understanding of the N isotopic fractionation is far from complete. Spin-state dependence [9] and non-equilibrium effects [e.g., 10] might be more important than previously anticipated. For the coming workshop, we propose to confront observations from diverse astronomical setups (clouds, comets, cosmomaterials) to fractionation models, with a special emphasis on chemical carriers and relative abundances. Robust constraints may still be lacking to close the debate on the origin of N isotopic fractionation in the Solar System.

- [1] Füri and Marty (2015) *Nature Geoscience*, **8**, 515. [2] Hily-Blant et al. (2013) *Icarus* **223**, 582. [3] Rousselot et al. (2014) *ApJL* **780**, L17. [4] Shinnaka et al. (2014) *ApJL* **782**, L16. [5] Rodgers and Charnley (2008) *MNRAS* **385**, L48. [6] Rubin et al. (2015) *Science* **348**, 232. [7] Yokochi et al. (2012) *Icarus* **218** 760. [8] Roueff et al. (2015) *A&A* **576**, A99. [9] Wirstrom et al. (2012) *ApJL* **757**, L11. [10] Herbst et al. (2003) *SSR* **106**, 293.

## SESSION 1

### Light Elements and Organic Matter from ISM to Small Bodies

DAY 1 – Feb.17, 2016  
8:30 am – 11:25 am

**PROBING THE INTERSTELLAR HERITAGE OF THE SOLAR SYSTEM WITH THE NITROGEN ISOTOPIC RATIO.** P. Hily-Blant<sup>\*1</sup>, V. S. Magalhaes<sup>1</sup>, F. Daniel<sup>1</sup>, A. Faure<sup>1</sup>, <sup>1</sup>Institut de Planétologie et d'Astrophysique de Grenoble, Domaine Universitaire BP 53 F-38041 Grenoble Cedex 09 (France)  
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The extent to which the chemical reservoirs in interstellar molecular clouds are preserved during the formation of stars and planetary systems is a central question with implications from astrophysical, chemical, and biological perspectives. However, the degree to which the original cloud composition may be altered or even reset during the star and planet formation process is unknown. Isotopic ratios are powerful tools to trace the chemical heritage of the solar system, and planetary systems more generally<sup>1</sup>. In the case of nitrogen, the 14N/15N isotopic ratio indicates that comets have preserved, to some extent, the Sun's original interstellar chemical reservoir<sup>2</sup>. However, the mean cometary isotopic ratio of 150 is in sharp disagreement with the protosun value of 441<sup>3</sup>. The reasons are not clear. In this talk, we will address various scenarios that may explain this disagreement, based on observations and chemical models of prestellar precursors of protosolar nebula analogs.

In particular, one scenario may be that the N-carriers observed in comets (such as NH<sub>2</sub>, CN, HNC) derive from a single nitrogen reservoir which was not representative of the bulk nitrogen in the protosolar nebula. This would indicate a so-far unidentified reservoir of nitrogen in comets, perhaps in their deep interiors. Such a reservoir could be atomic nitrogen. Alternatively, using the IRAM/NOEMA and IRAM/30m instruments, we observationally explore the possibility that chemical fractionation taking place in interstellar ices could be at work since the prestellar phase or during the lifetime of the comets. Finally, we will open the discussion towards protoplanetary disks based on recent measurements of the double isotopic ratio in H<sub>13</sub>CN/HC<sub>15</sub>N in the MWC480 disk<sup>4</sup> which leads to a ratio consistent with Solar System comets. This work also puts the chemical history of the Solar system in perspective with the chemical evolution of interstellar matter as a result of the star formation history, and questions the birthplace of the Solar system in the Milky Way.

- [1] Cleeves et al, Nature 345, 6204 (2014)
- [2] Hily-Blant et al, Icarus 223, 582 (2013)
- [3] Füri and Marty, Nature Geoscience 8 (2015)
- [4] Guzman et al, The Astrophysical Journal 814 53 (2015)

## NITROGEN ISOTOPIC FRACTIONATION OF AMMONIA BY ADSORPTION ON MINERAL SURFACE.

H. Sugahara\*, Y. Takano, N. O. Ogawa, Y. Chikaraishi and N. Ohkouchi  
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Stable nitrogen isotopic composition ( $\delta^{15}\text{N}$ , relative to terrestrial air) in the solar system objects shows various degrees of  $^{15}\text{N}$ -enrichment compared to that in the Sun ( $-407\pm7\%$ ) [1] and Jupiter ( $-390\pm7\%$ ) [2]. Especially, pristine solar system materials, such as comets and carbonaceous chondrites are highly enriched in  $^{15}\text{N}$  by up to  $+1500\%$  as bulk samples [3,4]. Furthermore, they also have extremely  $^{15}\text{N}$ -enriched microscale domains, which are frequently called as hot spots, within a single material. The highest  $\delta^{15}\text{N}$  value reaches as high as  $+5000\%$  [5]. These  $^{15}\text{N}$ -enrichments may have inherited from the enrichments in cold interstellar environments or the outer protosolar nebula. Although several potential models have been proposed to explain the formation of extreme  $^{15}\text{N}$ -enrichments in molecular clouds (e.g., [6]), their nitrogen isotopic fractionation processes have not been fully understood.

In this study, we propose the isotopic fractionation between ammonia and their adsorption on mineral surface as another potential process to cause the  $^{15}\text{N}$ -enrichment in the interstellar or protosolar environments. Ammonia is a primitive nitrogen-containing molecule and distribute in abundance in molecular clouds and the protosolar nebula. Since Ammonia is highly reactive molecule, it is considered to be a precursor for other nitrogen-involving organic molecules. Adsorption of ammonia on mineral surface will be the first step in the grain surface chemistry to form more complex molecules.

To understand the isotopic fractionation of nitrogen associated with the adsorption of ammonia on mineral surface, we conducted simple adsorption experiments using ammonia gas and adsorbent materials. We chose typical clay minerals (montmorillonite, saponite, dickite, kaolinite, pyrophyllite, and halloysite) as the adsorbents. The each clay mineral was enclosed into a glass vial and vacuumed to remove air. Then 1 atm of ammonia gas (27%) was introduced and set at room temperature for a couple of days to adsorb. The nitrogen isotopic composition of the adsorbed ammonia was determined by nano-EA/IRMS [7]. The results showed that the adsorbed ammonia is generally enriched in  $^{15}\text{N}$  relative to initial ammonia gas. Moreover, there was a negative correlation between  $\delta^{15}\text{N}$  value and adsorption ratio. This correlation may be explained by Rayleigh fractionation or two end-member mixing model, which were related to different adsorption processes (adsorption as ammonium ion, ionized by water or adsorption as ammonia molecule in interlayer of clay minerals). Our findings suggest the adsorption of ammonia on mineral surface as a potential mechanism for the extreme  $^{15}\text{N}$ -enrichment in the interstellar or protosolar environments.

Reference: [1] Marty B. et al. (2011) *Science* **332**, 1533. [2] Abbas M.M. et al. (2004) *ApJ* **602**, 1063. [3] Bonal L. et al. (2010) *GCA* **74**, 6590. [4] Manfrroid J. et al. (2009) *A&A* **503**, 613. [5] Briani G. et al. (2009) *PNAS* **106**, 105222. [6] Chakraborty S. et al. (2014) *PNAS* **111**, 14704. [7] Ogawa N. O. et al. (2010) in *Earth, Life, and Isotopes*. pp.339.

## HYDROGEN ISOTOPE FRACTIONATION IN HYDROCARBON PLASMA: COSMOCHEMICAL IMPLICATIONS.

F. Robert<sup>(1)</sup>, S. Derenne<sup>(2)</sup>, G. Lombardi<sup>(3)</sup>, K. Hassouni<sup>(3)</sup>, A. Michau<sup>(3)</sup>, P. Reinhardt<sup>(4)</sup>, R. Duhamel<sup>(1)</sup>, A. Gonzalez<sup>(1)</sup>, K. Biron<sup>(1,2)</sup>.

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The deuterium-hydrogen isotope ratio (D/H) is commonly used to reconstruct the chemical processes at the origin of water and organic compounds in the early solar system<sup>(1)</sup>. On the one hand, the large enrichments in deuterium of the insoluble organic matter (IOM) isolated from the carbonaceous meteorites are interpreted as a heritage of the interstellar medium<sup>(2,3)</sup> or resulting from ion-molecule reactions taking place in the diffuse part of the solar disk<sup>(4)</sup>. On the other hand, the molecular structure of this IOM, suggests that organic radicals have played a central role in a gas phase organo-synthesis<sup>(5)</sup>.

During the course of experiments aiming at reproducing this type of chemistry between organic radicals, we observed large variations at a sub-micrometric spatial resolution in the IOM isolated from the black organic residues deposited from a microwave plasma of CH<sub>4</sub>. They likely reflect the differences in the D/H ratios of the CH<sub>x</sub> radicals whose polymerization is at the origin of the IOM. A possible interpretation of this isotope effect may hinge on the differences between the probabilities accounting for the interaction between distinguishable and indistinguishable isotopes (i.e. H-D compared to H-H).

These isotopic heterogeneities are commensurable with those observed in meteorite IOM. As a consequence, the appearance of organic radicals in the ionized regions of the T-Tauri solar disk may have triggered the formation of organic compounds.

### References

- (1) Ceccarelli, et al. *Protostars and Planets VI*. University of Arizona Press (Beuther, et al. eds.) 859-882 (2014). (2) Busemann, H., et al. *Science* **312**, 727-730 (2006). (3) Messenger, S. *Nature* **404**, 968-971 (2000). (4) Remusat, L., et al. *Earth Planet. Sci. Lett.* **243**, 15-25 (2006). (5) Derenne, S., Robert, F. *Meteoritics & Planetary Science* **45**, 1461-1475 (2010).

## ON THE ORIGIN OF ULTRACARBONACEOUS ANTARCTIC MICROMETEORITES.

J. Duprat<sup>1</sup>, C. Engrand<sup>1</sup>, N. Bardin<sup>1</sup>, E. Dartois<sup>2</sup>, D. Baklouti<sup>2</sup>, K. Benzerara<sup>3</sup>, L. Delauche<sup>1</sup>, E. Dobrica<sup>4</sup>, M. Godard<sup>1</sup>, J.-L. Guerquin-Kern<sup>5</sup>, Y. Kakazu<sup>1</sup>, H. Leroux<sup>6</sup>, E. Quirico<sup>7</sup>, L. Remusat<sup>3</sup>, G. Slodzian<sup>1</sup>, T.-D. Wu<sup>5</sup>.

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The central regions of Antarctica provide a unique opportunity to collect micrometeorites well preserved from terrestrial weathering [1, 2]. For more than a decade, we have developed a protocol to extract such grains from ultra-clean snow near the CONCORDIA station at Dome C. From such Antarctic collections, it is possible to recover Ultracarbonaceous Antarctic Micrometeorites (UCAMMs) characterized by a high concentration of organic matter (OM) (> 50 vol%) [3, 4]. The OM of UCAMMs exhibits extreme deuterium excesses and is nitrogen-rich, with N/C ratios significantly higher than those reported in IOM from carbonaceous chondrites [5-7].

We will present the latest results on isotopic analyses on UCAMM fragments obtained with the NanoSIMS-50 at Institut Curie. The isotopic compositions of light elements (H, C and N) were measured as C<sub>2</sub>D<sup>-</sup>/C<sub>2</sub>H<sup>-</sup>, <sup>13</sup>C<sup>-</sup>/<sup>12</sup>C<sup>-</sup>, <sup>12</sup>C<sup>13</sup>C<sup>-</sup>/<sup>12</sup>C<sub>2</sub><sup>-</sup> and C<sup>15</sup>N<sup>-</sup>/C<sup>14</sup>N<sup>-</sup> using a high mass resolution (HMR) protocol and a dedicated series of standards to infer the D/H instrumental mass fractionation [8, 9]. Together with NanoSIMS data, XANES and TEM data reveal that the OM of UCAMMs contains various components exhibiting different concentration in minerals and a wide range of hydrogen and nitrogen isotopic compositions [10, 11]. Both the elemental and isotopic compositions of UCAMMs indicate that these samples most probably originate from a cometary reservoir. The main part of the UCAMM OM is depleted in minerals and exhibits an intimate mixing of various D-rich components. One mineral-rich OM phase significantly differs from the rest of the OM. We will present a scenario that can account for their high nitrogen concentration and high heterogeneous isotopic composition assuming that the precursors of their OM result from the irradiation by galactic cosmic rays of N-rich ices at the sub-surface of a parent body orbiting at large heliocentric distances.

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**References :** [1] Nakamura, T., et al., Antarctic Meteorite Research, 1999. **12**: p. 183-198. [2] Duprat, J., et al., *Adv. Space Res.*, 2007. **39**: p. 605-611. [3] Nakamura, T., et al., *Meteoritics Planet. Sci. Suppl.*, 2005. **40** #5046. [4] Duprat, J., et al., *Science*, 2010. **328**: p. 742-745. [5] Yabuta, H., et al., *Meteoritics Planet. Sci. Suppl.*, 2012. **75**: p. 5196. [6] Yabuta, H., et al. LPSC. 2012, #2239. [7] Dartois, E., et al., *Icarus*, 2013. **224**: p. 243-252. [8] Slodzian, G., et al., *Microsc. & Microanal.*, 2014. **20**: p. 577-581. [9] Bardin, N., et al. *Int. J. Mass Spectrom.* 2015. 393: 17-24. [10] Engrand, C., et al. LPSC. 2015 #1902. [11] Bardin, N., et al. *Meteoritics Planet. Sci. Suppl.* 2015 # 5275.

**HYDROGEN ISOTOPIC EVOLUTION OF WATER AND ORGANIC COMPOUNDS ON CARBON-RICH ASTEROIDS.** L. Piani<sup>1</sup> and L. Remusat<sup>2</sup>, <sup>1</sup>Department of Natural History Sciences, Hokkaido University, Japan (laurette@ep.sci.hokudai.ac.jp). <sup>2</sup>IMPMC, UMR CNRS 7590 - Sorbonne Universités - UPMC - IRD - MNHN, France.

**Introduction.** Organic matter and hydrated minerals found in primitive meteorites (chondrites) are the remnants of organic and water components of the protoplanetary disk 4.6 billion years ago. These phases show systematic but variable enrichments in the heavy isotopes of hydrogen comparing to the Sun. Although at least a part of these enrichments argues for low temperature ion-molecule reactions in the protoplanetary disk or in the molecular cloud, it is unclear how these isotopic signatures might have been modified by chemical reactions (kinetic fractionation or isotope exchanges) occurring on the asteroidal parent body.

In situ variations of hydrogen isotope compositions at the micrometer-scale in chondrites can help to trace the chemical processes on water- and carbon-rich asteroids. By constraining the extent of these reactions, the composition of the initial water and organic components before incorporation in meteorite parent asteroids might also be constrained.

**Method.** We are measuring the D/H and C/H ratios of matrices in different carbonaceous chondrites (CCs) at the scale of some micrometers by using SIMS IMS-1280 at Hokkaido University. Depending on the position of the primary beam in the matrix, the D/H and C/H ratios vary as a function of the relative amount of organic matter to hydrated minerals. The presence of correlation between the two ratios allows the water isotopic composition to be estimated for each chondrite.

**Results and discussion.** Using multiple measurements in a first set of CCs included Orgueil (CI), Murchison (CM) and Renazzo (CR), we estimated the  $\delta D$  of water to be  $-15 \pm 90$ ,  $-75 \pm 84$ , and  $647 \pm 182\%$  ( $2\sigma$ ), respectively. As far as we know, this is the first direct measurement of water  $\delta D$  in individual carbonaceous chondrites. So far, water  $\delta D$  value was calculated by subtraction of the organic matter contribution to the bulk with an uncertainty difficult to estimate [1, 2]. Relative to the  $\delta D$  of initial water in CM and CR parent bodies (at the time of the accretion), i.e.  $-444$  and  $96\%$ , respectively [3], the higher  $\delta D$  values we measured for water after parent body processing show that interactions between water and organic matter probably occurred during aqueous alteration. However, the  $\delta D$  of water being still lower than the one of the organic compounds in a given chondrite, it seems that isotopic equilibrium was not reached between the two phases in agreement with previous observations [4].

Finally, other CCs are under investigation in order to cover a larger range of different degrees of parent body aqueous alteration and/or metamorphism.

**References.** [1] Robert and Epstein, 1982. GCA, 46, 81-95. [2] Alexander et al., 2010. GCA, 74, 4417–4437. [3] Alexander et al., 2012. Science, 337, 6095, 721-723. [4] Remusat et al., 2010. ApJ, 713:1048–1058.

**LIGHT ELEMENT ISOTOPE ABUNDANCE OF CHONDРИTIC ORGANIC SOLIDS: A SIGNATURE OF INCOMPLETE ISOTOPE EXCHANGE?** G. D. Cody<sup>1</sup>, Y. Kebukawa<sup>2</sup>, and C. M. O'D Alexander<sup>3</sup>. <sup>1</sup>Geophysical Laboratory (5251 Broad Branch Rd. NW, Washington DC, USA, 20015 gcod@ciw.edu), <sup>2</sup>Yokohama National University. <sup>3</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington.

The isotopic (hydrogen, carbon and nitrogen) abundances in chondritic organic matter and comets (observed as Interplanetary Dust Particles IDP's) has long fascinated cosmochemists. H and D abundances have enjoyed the greatest scrutiny. It is generally understood and agreed upon, that deuterium enrichment signals a connection to cold environments, such as in molecular clouds, what is less agreed upon is at what stage does deuterium enrichment imprint on the organic solids.

Over the past several years we have been studying the mechanism of organic solids synthesis. We find that formaldehyde (a very common molecule in the galaxy and ubiquitous in molecular clouds) polymerizes with itself yielding complex organic solids that, at a functional group level, are identical to organic solids observed in chondrites, IDP's and comets [1-3].

We now understand how organic solids form from formaldehyde and over what temperatures they can form [1-3]. In previous studies [4] no systematic relationship between organic molecular structure and  $\delta D$  was observed. This was surprising, as there exists a clear trend in molecular evolution of organic solids that reflect parent body processing [5,6]. This appeared to imply that there was no connection between processing within planetesimal interiors and bulk isotope compositions ( $\delta D$ ,  $\delta^{13}\text{C}$  or  $\delta^{15}\text{N}$ ); further suggesting that variation in light element isotope compositions were primordial, i.e., inherited from the beginning- i.e., before the organic solids formed.

The recent studies of the so-called Tagish Lake (TL) lithologies [7-9] provide a completely unique perspective on at least the  $\delta D$  content of organic solids. Surprisingly, within a single meteoroid, one finds the full range molecular structural variation observed across all primitive meteorite classes (CR, CI, and CM)[5] in a single object [7,8]. However, within the TL lithologies one now observes a very clear relationship between molecular structure and  $\delta D$  [8]. More significantly, a recent study comparing the deuterium abundance in mineral bound water and D abundance in isolated organic solids in the TL lithologies, appears to very clearly show evidence of incomplete isotope exchange [9]. These data suggest that isotope exchange is a fundamental process that affects isotope abundance in chondritic organic solids. This suggests that what happens in the parent body interior is key towards understanding light element stable isotopic abundance-this not a majority point of perspective.

We now think we understand how formation and subsequent alteration affects change in intrinsic isotope abundance ( $\delta D$ ,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). In this talk we will discuss these matters and their signifigance.

**References.** 1) Cody et al. (2011) PNAS, 108, 19171. 2) Kebukawa et al. (2013) ApJ, 771, 1. 3) Kebukawa and Cody (2015) Icarus, 248, 412. 4) Alexander et al (2010) GCA, 74, 4417. 5) Cody and Alexander (2005) GCA, 69,1085. 6) Cody et al. (2008) EPSL, 272, 446. 7) Herd et al. (2011) Science, 332, 1304. 8) Alexander et al. (2014) MAPS, 49, 503. 9) Alexander et al. (2012) Science, 337, 721.

**ORIGIN OF EXTREMELY HEAVIER HYDROGEN ISOTOPIC COMPOSITIONS OF PHOSPHATE MINERALS FROM LL4-6 ORDINARY CHONDRITES.** S. Itoh<sup>1</sup>, Y. Higashi<sup>1</sup>, K. Yanai<sup>2</sup>, S. Russell<sup>3</sup>, J. Greenwood<sup>4</sup> and H. Yurimoto<sup>2</sup>. <sup>1</sup>Dept. Earth Planet. Sci., Kyoto University, kitashirakawa oiwakecho sakyoku,Kyoto,606-8502,JAPAN.Email:sitoh@kueps.kyoto-u.ac.jp. <sup>2</sup>Natural History Sciences, Hokkaido University. <sup>3</sup>Dept. Earth Sci, Natural History Museum, London. <sup>4</sup>Dept. Earth Envi. Sci, Wesleyan University.

## SESSION 1 – *Cont.*

### Light Elements and Organic Matter from ISM to Small Bodies

DAY 1 – Feb.17, 2016  
4:30 pm – 7:10 pm

Recently many studies focused on the origin of water in the solar system and Earth with Chondrite, differentiated meteorite, Moon and Mars (e.g., [1][2][3]). One of significant possible precursor of H<sub>2</sub>O ice in Earth's orbit could be cometary ice but it is unclear. Deloule and Robert (1995) also reports that the hydrogen isotopic compositions of phyllosilicate from LL3.0 Semarkona OC are D-rich (~4000permil) and suggest the origin of this D-rich isotopic compositions come from the interstellar space or in the outer regions of the solar nebula, like cometary ice [2]. This results suggest that, as the Itokawa S-type asteroids close to Earth's orbit, the heavily hydrogen isotopic compositions of LL OCs resulted from cometary ice close to the earth. However, there is no systematic study of hydrogen isotopic compositions of LL4-6 OCs because it is difficult to estimate the planetesimal hydrogen isotopic compositions of water due to very low water contents and contamination from adsorbed water [3]. In this study, we applied the in-situ measurement technique [1] of water content and hydrogen isotopic compositions of phosphate minerals from LL4-6 OCs by SIMS. All D/H ratios in the phosphate minerals are D-rich ( $\delta D \sim +2000$  to  $+25000$ ). Water contents of these phosphate shows the range of 10-100ppm and that of LL6 is the highest water content and D-rich isotopic compositions ( $\delta D \sim +10000$  to  $+25000$ ). These results suggest that the origin of D-rich hydrogen isotopic compositions of LL6 phosphate mineral is resulting from extra-planetary with cometary ice. In this talk, the model of D-rich water exchange among apatite and water in the LL parent body using hydrogen diffusion coefficient of apatite. [6]. [1] Greenwood et al. (2008) *Geophys. Res. Lett.*, 35, L05203. [2] Greenwood et al. (2011) *Nature Geosci.*, 4, 79-82. [3] Robert, (2011) *Science*, 293, 1056–1058. [4] Deloule and Robert (1995) *GCA*, 59, 4695-4706. [5] Robert (2003) *Space science reviews*, 106, 87-101. [6] Itoh et al. (2015) Goldschmidt 2015 abstract: 5138.

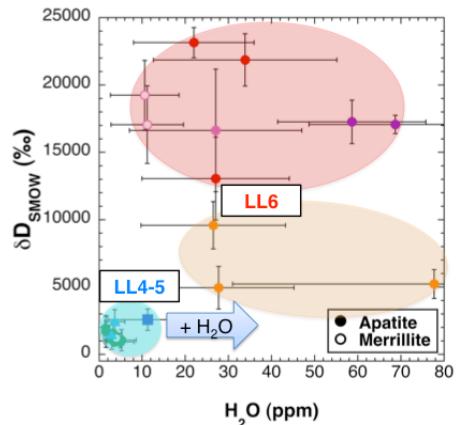


Fig. 1.  $\delta D$  vs H<sub>2</sub>O in phosphate from LL OCs.

**INTERSTELLAR ORIGIN OF SOLUBLE ORGANIC MATTER FROM THE MURCHISON METEORITE REVEALED BY ORBITRAP-MS.** 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>, E. Zinner<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, <sup>3</sup>Physics Department of Washington University, St-Louis, MO

**Introduction:** Organic matter in Murchison splits into large insoluble and small soluble molecules. The latter is made of thousands of compounds varying in mass up to 2000 Da [1] with an unmatched continuity in diversity. These compounds size is in-between the molecules detected in space environments [2] (tens of atoms) and heavier macromolecules found only in meteorites [3]. They may have recorded signatures of molecular complexification during the transition from the diffuse interstellar medium to dense molecular clouds. They also may have undergone hydrothermal transformation on the meteorite parent body [4], [5]. We seek for mass spectrum signature univocally related to one stage of the meteoritic material evolution.

**Method:** 65 g of Murchison were washed with water and freeze-thaw disaggregated to eliminate magnesium sulfates, which jeopardize the use of electrospray. The sample was macerated in Methanol and Toluene (1:2) for 1 week in a dark room. Glassware was washed in Ethanol with caustic soda and baked at 250°C for 12 hours before use. Extracts were recovered after centrifugation and stored in glass tubes. Mass spectra were acquired with a Thermo LTQ Orbitrap XL coupled with an Electrospray ionization (ESI) source, in the 150-1000 m/z range, both for cations and anions at resolving power  $m/\Delta m=100000$ .

**Results:** Detected ions are in the 150-750 Da range. For the cations, the average mass is ~350 Da and the average diversity is 5.1 ions per Da. In this mass range, the Orbitrap nominal 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. The maximal number of heteroatoms is 2 for N and 3 for O. The average H/C is 1.6 regardless of the mass. There is no convergence toward macromolecular-like low saturation. We interpret the periodicity in mass as a repetition of stoichiometric patterns. CH<sub>2</sub>, H<sub>2</sub> and C<sub>5</sub>H<sub>8</sub> are the most frequent patterns. The latter corroborates a very slow loss of saturation and is consistent with full sp<sup>3</sup> cyclization. Molecules varying only by a given number of CH<sub>2</sub> all exhibit a lognormal distribution. This requires randomly distributed sp<sup>3</sup> chains cut events to be interpreted. We will show that the H<sub>2</sub> distribution is correlated to the chains cut mechanism. The chain rearrangements, cuts and cycling signatures along with the very limited loss of hydrogen are all together consistent with chemical processes detected in space. Randomized additions of CH<sub>2</sub> and H<sub>2</sub> are reported to occur on grain surface in dense molecular clouds [6]. Their boundaries can be highly UV-irradiated, providing an efficient C bonds cut mechanism [7] as seen here in Murchison.

**References:** [1]Schmitt-Kopplin P. et al. (2010) *PNAS*, **107**, 7 pp. 2763–8. [2]Caselli P. and Ceccarelli C. (2012) *Astron. Astrophys. Rev.*, **20**, 1 p. 56. [3]Sephton M. a (2002) *Nat. Prod. Rep.*, **19**, 3 pp. 292–311. [4]Le Guillou C. et al. (2014) *GCA*, **131** pp. 368–392. [5]Cody G. D. et al. (2011) *PNAS*, **108**, 48 pp. 19171–19176. [6]Belloche A. et al. (2014) *Science* (80-. ), **345**, 6204 p. 15841587. [7]Alata I. et al. (2015) *A&A*, **123** pp. 1–9.

**EXTENSIVE ALKYLATED N-CONTAINING CYCLIC COMPOUNDS IN THE MURCHISON METEORITE.** H. Naraoka<sup>1</sup> Y. Yamashita<sup>1</sup> and M. Yamaguchi<sup>2</sup>, <sup>1</sup>Dept. Earth & Planet. Sci., Kyushu Univ. 744 Motoooka, Nishi-ku, Fukuoka, 819-0395 Japan; naraoka@geo.kyushu-u.ac.jp, <sup>2</sup>Thermo Fisher Scientific, C-2F, 3-9 Moriya-cho, Kanagawa-ku, Yokohama 221-0022 Japan.

Various organic compounds are reported in solvent extracts of carbonaceous meteorites. Recent ultrahigh-resolution mass spectral analysis has detected tens of thousands of different mass peaks in the Murchison meteorite [1]. Considering the structural and optical isomers, hundreds of thousands organic compounds may be present. However, the compound distribution is largely unknown, which is critical to understand the origins and formation processes of meteoritic organic compounds. In this study, we examined detailed compound distributions in the methanol extract of Murchison by HPLC/ultrahigh resolution mass spectrometry to reveal organic reaction mechanisms on the parent body in the early solar system.

Significantly large numbers of positive ions were observed between m/z 80 and 1400, where strong ion peaks were dominated between 90 and 400 with the maximum at m/z ~300. Most peaks have CHN compositions with minor CHO and CHNO compositions, even though the CHN compositions were not reported by [1]. More than 600 ions were assigned to C<sub>n</sub>H<sub>m</sub>N<sup>+</sup> and C<sub>n</sub>H<sub>m</sub>N<sub>2</sub><sup>+</sup> in elemental compositions, in which saturate and unsaturate-alkylated pyridines (C<sub>n</sub>H<sub>2n-3</sub>N and C<sub>n</sub>H<sub>2n-7</sub>N) and imidazoles (C<sub>n</sub>H<sub>2n-2</sub>N<sub>2</sub>) were predominant peaks followed by alkylpyrroles (C<sub>n</sub>H<sub>2n-3</sub>N) and alkylpiperidines (C<sub>n</sub>H<sub>2n</sub>N). Both alkylpyridines and alkylimidazoles could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline condition. Further redox reactions could have proceeded during water-rock interaction to give alkylpiperidines and pyridine carboxylic acids (e.g. nicotinic acid) on the parent body (Fig. 1). These redox reactions could be associated with aqueous alteration of meteoritic olivine (i.e. serpentinization; 3(Mg,Fe)<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> + 6H<sub>2</sub>O = 2Mg<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> + 2SiO<sub>2</sub> + 2Fe<sub>3</sub>O<sub>4</sub> + 2H<sub>2</sub>) under an alkaline environment.

Simulation experiments were performed to produce the N-containing cyclic compounds using aldehydes and ammonia in water in the presence of olivine. Several alkylpyridines were produced to show the similar isomer distributions as observed in Murchison [2]. Aldehyde polymerization with ammonia is an important process to produce the high-molecular alkylated N-containing cyclic compounds on the meteorite parent body.

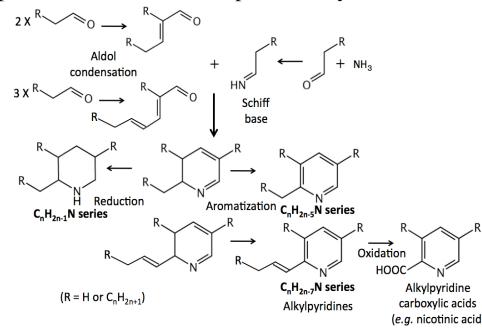


Fig. 1. Formation pathway of alkylpyridines in meteorites.

**References:** [1]Schmitt-Kopplin et al. (2010) *PNAS* **107**, 2763. [2]Yamashita & Naraoka (2014) *Geochem. J.* **48**, 519.

**REFRACTORY AND SEMI-VOLATILES ORGANICS AT THE SURFACE OF COMET 67P/CHURYUMOV-GERASIMENKO.** E. Quirico<sup>1</sup>, L. V. Moroz<sup>2,3</sup>, B. Schmitt<sup>1</sup>, G. Arnold<sup>3</sup>, M. Faure<sup>1</sup>, P. Beck<sup>1</sup>, L. Bonal<sup>1</sup>, M. Ciarniello<sup>4</sup>, F. Capaccioni<sup>4</sup>, G. Filacchione<sup>4</sup>, S. Erard<sup>5</sup>, C. Leyrat<sup>5</sup>, D. Bockelée-Morvan<sup>5</sup>, A. Zinzi<sup>4</sup>, E. Palomba<sup>4</sup>, P. Drossart<sup>5</sup>, F. Tosi<sup>4</sup>, M. T. Capria<sup>4</sup>, M. C. De Sanctis<sup>4</sup>, A. Raponi<sup>4</sup>, S. Fonti<sup>6</sup>, F. Mancarella<sup>6</sup>, V. Orofino<sup>6</sup>, A. Barucci<sup>5</sup>, M. I. Blecka<sup>7</sup>, R. Carlson<sup>8</sup>, D. Despan<sup>5</sup>, A. Faure<sup>1</sup>, Fornasier<sup>5</sup>, S., M. S. Gudipati<sup>8</sup>, A. Longobardo<sup>4</sup>, K. Markus<sup>3</sup>, V. Menella<sup>9</sup>, F. Merlin<sup>5</sup>, G. Piccioni<sup>4</sup>, B. Rousseau<sup>5</sup>, F. Taylor<sup>10</sup>, and the Rosetta VIRTIS team. (1) Université Grenoble Alpes, CNRS, IPAG, Grenoble France (2) University of Postdam, Germany (3) DLR, Berlin, Germany (4) IAPS-INAF, Rome, Italy (5) LESIA, Observatoire de Paris-Meudon, France (6) Università del Salento, Lecce, Italy (7) Space Research Centre, Polish Academy of Sciences, Warsaw, Poland (8) NASA JPL, Pasadena, USA (9) INAF Napoli, Italy. (10) Oxford University, Oxford, UK

The VIRTIS instrument onboard the Rosetta spacecraft has provided extensive spectral mapping of the surface of comet 67P/Churyumov-Gerasimenko, in the range 0.3-5  $\mu\text{m}$ . The reflectance spectra collected across the surface display a low reflectance factor through the whole spectral range, two spectral slopes in the visible and the near-infrared ranges, and a broad band centered at 3.2  $\mu\text{m}$ . The first two of these characteristics are typical of dark small bodies of the Solar System, and in this respect their interpretation in terms of composition is difficult. Solar wind irradiation may modify the structure and composition of surface materials, and there is no univocal assignment for those spectra devoid of vibrational bands. In order to circumvent these problems, we developed an analysis by constraining the nature of cometary materials from the study of cometary grains analyzed in the laboratory and by considering results on surface rejuvenation and solar wind processing provided by the OSIRIS and ROSINA instruments, respectively. Our results show that (1) The low albedo of comet 67P/CG is accounted for by a dark refractory polyaromatic carbonaceous component mixed up with opaque minerals. VIRTIS data do not provide direct insights into the nature of these opaque minerals. (2) A semi-volatile component, consisting of a complex mix of low weight molecular species not volatilized at T~220 K, is likely a major carrier of the 3.2  $\mu\text{m}$  band. Water ice has a significant contribution to this feature in the neck region, but not in other regions of the comet. COOH in carboxylic acids is the only chemical group that encompasses the broad width of this feature. It appears as a highly plausible candidate, along with the NH<sub>4</sub><sup>+</sup> ion. (3) Photolytic/thermal residues, produced in the laboratory from interstellar ice analogs, appear as potential interesting spectral analogs. (4) No hydrated minerals were identified and our data support the lack of generic links with the CI, CR and CM primitive chondrites. This concerns in particular the Orgueil chondrite, which had been suspected to have a cometary origin. (5) The comparison between fresh and aged terrains revealed no effect of solar wind irradiation on the 3.2  $\mu\text{m}$  band. This is consistent with the presence of efficient resurfacing processes, such as dust transport from the interior to the surface as revealed by the OSIRIS camera.

**ISOTOPIC EVIDENCE FOR PRIMORDIAL MOLECULAR CLOUD MATTER IN METAL-RICH CARBONACEOUS CHONDrites.** E. Van Kooten<sup>1</sup>, D. Wielandt<sup>1</sup>, M. Schiller<sup>1</sup>, K. Nagashima, A. Thomen, K. Larsen<sup>1</sup>, M. Olsen<sup>1</sup>, Å. Nordlund<sup>1</sup>, A. Krot<sup>1,2</sup> and M. Bizzarro<sup>1</sup>, <sup>1</sup>Centre for Star and Planet Formation, University of Copenhagen, Copenhagen, Denmark, <sup>2</sup>HIGP, University of Hawai'i at Manoa, Honolulu, USA.

The short-lived <sup>26</sup>Al radionuclide is thought to have been admixed into the initially <sup>26</sup>Al-poor protosolar molecular cloud prior to or contemporaneously with its collapse. Bulk inner solar system reservoirs record positively correlated variability in mass-independent <sup>54</sup>Cr and <sup>26</sup>Mg\*, the decay product of the short-lived <sup>26</sup>Al radionuclide. This correlation is interpreted as reflecting progressive thermal processing of in-falling <sup>26</sup>Al-rich molecular cloud material [1, 2]. Planetesimals formed in the outer solar system could have accreted a significant fraction of primordial and, hence, thermally unprocessed molecular cloud matter. This material reflects the nucleosynthetic make-up of the molecular cloud prior to the last addition of stellar-derived <sup>26</sup>Al. Therefore, unlike inner solar system objects, the isotopic signature of the thermally unprocessed and <sup>26</sup>Al-poor primordial molecular cloud matter is expected to show a decoupling between their <sup>26</sup>Mg\* and <sup>54</sup>Cr compositions.

To search for the signature of primordial molecular cloud material, we analyzed the magnesium and chromium isotope composition of metal-rich carbonaceous chondrites (CH, CB and CR) and their components, including 3 bulk samples, 13 chondrules and 5 hydrated lithic clasts. Several observations suggest that metal-rich chondrites may have incorporated primordial molecular cloud material of possible outer solar system origin, including enrichment in <sup>15</sup>N, high abundance of presolar grains and the presence of <sup>26</sup>Al-poor CAIs. Our results show that CH, CB and CR chondrites and their components have a unique <sup>26</sup>Mg\* and <sup>54</sup>Cr isotope signature, falling off the solar system correlation line. Our samples defined an array extending from the composition of CM chondrites to that expected for thermally-unprocessed and <sup>26</sup>Al-free molecular cloud material ( $\mu^{54}\text{Cr} = 160$  ppm and  $\mu^{26}\text{Mg}^* = -16$  ppm). This requires the presence of significant amount (25-50%) of primordial molecular cloud material in bulk metal-rich chondrites. Given that such high fractions of primordial molecular cloud material are expected to survive only in the outer Solar System, we infer that, similarly to cometary bodies, metal-rich carbonaceous chondrites are samples of planetesimals that accreted beyond the orbits of the gas giants. The presence of chondrules in CR, CH and CB chondrites with an isotopic signature requiring the incorporation <sup>26</sup>Al-poor primordial molecular cloud component suggests that chondrule formation was not limited to the inner Solar System, indicating that chondrules present in cometary bodies such as Wild2 may be locally derived. The lack of isotopic evidence for primordial molecular cloud material in other chondrite groups requires isolation from the outer Solar System, possibly by the opening of disk gaps from the early formation of gas giants.

[1] K.K. Larsen *et al.* (2011) *Astrophys. J.* **735**, L37. [2] M. Schiller *et al.* (2015) *Geochim Cosmo Acta* **148**, 88.

**EVOLUTION OF MOLECULES IN SPACE: FROM INTERSTELLAR CLOUDS TO PROTOPLANETARY SYSTEMS.** A. Kouchi<sup>1</sup> and S. Tachibana<sup>2</sup>. <sup>1</sup>Inst. Low Temp. Sci., Hokkaido Univ., <sup>2</sup>Dept. Natural History Sci., Hokkaido Univ. E-mail: kouchi@lowtem.hokudai.ac.jp.

Star and planet formation have been extensively studied from a physics point of view, but the chemical aspects of their formation and evolution, including the Solar System, have not yet been thoroughly understood in spite of many meteoritical and observational evidence.

In order to understand the chemical evolution of stellar and planetary system, meteoritical and observational approaches should be systematically combined with laboratory and theoretical approaches, and a research project on “Evolution of molecules in space” has begun with a support by Grant-in-Aid for Scientific Research on Innovative Areas from Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (FY2013–2017) [PI: A. Kouchi].

The project focuses on the formation and evolution of ice and organic matter in molecular clouds and during stellar and planetary formation because 1) hydrogen, oxygen, carbon, and nitrogen are the most abundant elements in space, 2) organic molecules are observable in various systems as a tracer of chemical evolution, and 3) ice and organic matter record the formation and evolution history of proto-stellar cores and outer protoplanetary disks in their isotopic and structural properties.

The project consists of five research-oriented sub-teams with different research approaches; **A01:** Laboratory experiments on molecular cloud processes [PI: A. Kouchi], **A02:** Laboratory experiments on protoplanetary disk processes [PI: H. Nagahara], **A03:** Modeling of surface chemical reactions and chemical evolution of molecular clouds and protoplanetary disks [PI: T. Fukazawa], **A04:** Astronomical observation of young stellar objects [PI: S. Yamamoto], and **A05:** Analysis of extraterrestrial and laboratory-simulated organic matter [PI: H. Yurimoto]. There are also two administration-oriented sub-teams (**X00:** Integration and management [PI: A. Kouchi] and **Y00:** International coordination [PI: A. Kouchi]) and 15 publicity-offered research projects (FY2014-2015).

With intense research activity within a sub-team and collaboration between sub-teams, A01, A02, and A05 have found that photon-irradiated  $\text{H}_2\text{O}-\text{CH}_3\text{OH}-\text{NH}_3$  ice bubbles at 60–150 K, possibly implying the presence of super-cooled liquid [1]. A01, A04, and A05 with a publicity-offered project found the formation of chiral glycine ( $\text{NH}_2\text{CHD}\text{COOH}$ ) by quantum tunneling hydrogen-deuterium substitution reactions [2]. This chiral molecule formed in molecular cloud conditions could be a potential source of homochirality in molecules in space. A03 and A04 found a drastic change of chemistry of infalling gas forming a disk around a protostar IRAS 04368+2557 with ALMA [3]. Unsaturated cyclic- $\text{C}_3\text{H}_2$  resides in the infalling rotating envelope, whereas SO is enhanced in the transition zone at the radius of the centrifugal barrier. This chemical change may be caused by local heating processes due to the discontinuous infalling motion at the centrifugal barrier [3, 4].

We will present the whole project and details of research activities at the meeting.

**References:** [1] Piani L. et al. *this symposium*. [2] Oba Y. et al. (2015) *Chem. Phys. Lett.* **634**, 53. [3] Sakai N. et al. (2014) *Nature* **507**, 78. [4] Aota T. et al. (2015) *Astrophys. J.* **799**, 141.

**FORMATION AND ALTERATION HISTORY OF A UNIQUE FACETED PRESOLAR CORUNDUM.** A. Takigawa<sup>1,2</sup>, R. M. Stroud<sup>3</sup>, L. R. Nittler<sup>4</sup>, C. M. O'D. Alexander<sup>5</sup>, and A. Miyake<sup>2</sup>, <sup>1</sup>The Hakubi Center for Advanced Research, Kyoto University, Kyoto, Japan (takigawa@kueps.kyoto-u.ac.jp), <sup>2</sup>Department of Geology and Mineralogy, Kyoto University, Kyoto, Japan, <sup>3</sup>Naval Research Laboratory, Washington DC, USA, <sup>3</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington DC, USA.

## SESSION 2

### Presolar and Early Solar System History: Hot in the Beginning

DAY 2 – Feb.18, 2016  
8:30 am – 11:05 am

Presolar grains are survivors of circumstellar dust grains formed around evolved stars such as Asymptotic Giant Branch (AGB) stars, Red Giants, and supernovae (SNe) prior to the birth of the solar system. They condensed from gas phases at ~a few stellar radii from the central stars and injected into the interstellar medium (ISM) along with the outflows (Woitke et al. 2004). They have then experienced processing in the ISM and protosolar disk. The grain morphology and crystal structure of presolar grains may reflect condensation conditions in circumstellar envelopes and alteration in the ISM and protosolar disk as well.

Corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) is the most abundant refractory dust condensed in envelopes around oxygen-rich asymptotic giant branch (AGB) stars. In this study, we performed detailed analysis of presolar corundum grains and discuss the formation and alteration of circumstellar dust grains.

Aluminum oxide grains were identified from acid residues of QUE97008 (LL3.05) by energy dispersive X-ray spectroscopy (EDS) and observed by field-emission scanning electron microscope (FE-SEM) at the Carnegie Institution of Washington (CIW) according to Takigawa et al. (2013). Oxygen and Mg-Al isotopic measurements were performed with the Cameca NanoSIMS 50L ion-microprobe at CIW. Ultra-thin sections of presolar grains were prepared with the NRL FIB-SEM and were observed with transmission electron microscopes (TEMs) at NRL (JEOL JEM-2200FS) and Kyoto University (JEOL JEM-2100F).

Eight presolar grains were identified from acid residues of QUE97008 by oxygen isotopic measurements. We found a unique presolar  $\text{Al}_2\text{O}_3$  grain with clearly faceted faces, QUE060. Grains with edges and relatively flat faces were reported by Takigawa et al. (2014) but such clearly flat and/or smooth faces have not been observed on any other presolar  $\text{Al}_2\text{O}_3$  grains in this study and previous studies (Choi et al. 1998; Makide et al. 2004; Takigawa et al. 2014). The oxygen and Al-Mg isotopic compositions of Grain QUE060 indicate that its origin is a  $1 \text{ M}_{\odot}$  AGB star undergoing the cool-bottom-processing (Nittler et al. 1997).

A cavity was observed in the bright-field (BF) TEM image of the FIB lift-out section of QUE060. Magnesium is detected at any points on the grain with EDS but distributed heterogeneously within the grain. There are several domains containing a high amount of Mg. The detected Mg is essentially pure radiogenic  $^{26}\text{Mg}$  ( $^{26}\text{Mg}/^{24}\text{Mg} \sim 0.01$ ). The selected-area electron diffraction patterns of Mg-concentrated domains show satellite spots, which reflects the modulated structure in the crystal.

The subhedral shape and smooth surface of QUE060 suggest that this grain was single crystalline corundum when it condensed in a circumstellar envelope of a low-mass AGB star and the distorted crystal structure inside the grain, voids, and the modulated structure accompanying the high Mg concentration are secondary features.

## HOMOGENIZATION OF ISOTOPIC RATIO IN SOLAR NEBULA.

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**Introduction:** It is known that the isotopic compositions, except for some highly volatile elements, of solar system materials show very little variations; deviations from normal are of the order of a few parts in  $10^4$  or less. It is supposed that the material formed the solar system came from various nucleosynthesis sites, such as supernovae, AGB stars, and so forth, so dust particles involved in the parental molecular cloud that formed the solar system had various isotopic ratio. This implies that the isotopic ratio of solar system material was homogenized at a certain stage in a course of the solar system formation processes.

**Aim and Model:** Here, we explore some possibilities that all the solid material in the solar system was once evaporated and mixed well to become isotopically homogeneous in the solar nebula. To examine that, we model the gravitational collapse of a molecular cloud core with a certain rotation, which is characterized by the rotation angular velocity, and model the disk accretion formed by the cloud collapse, which is characterized by the strength of turbulence in the disk. The temperature of the disk is calculated, and if the temperature is high enough, say 2000 K in our current model, it is supposed that dust particles there are evaporated completely. When such a high temperature gas cools and the temperature becomes below 2000 K, solid dust particles, which have a common isotopic ratio, are assumed to condense. And we think that these solid particles will form planets and other objects in the solar system seen today.

**Results:** According to our numerical simulations with a wide range of model parameters, we have found that (1) almost all the materials in the disk may be once evaporated and isotopically homogenized if the rotation angular velocity of the initial molecular cloud core is low enough, e.g.,  $1 \times 10^{-15} \text{ s}^{-1}$ ; (2) the disk formed from such a low rotation cloud core has a small radius, smaller than 100 AU, and the total mass of the disk is of the order of one hundredth of the solar mass. These results seem to be consistent with observed features of our solar system.

**Discussions:** In the present work, we explored a possibility that a high temperature disk homogenized the isotopic ratio of materials. The disk was globally hot. But some other mechanisms may produce isotopically homogenized materials. For example, a huge number of local heating events, which may relate to chondrule formation, evaporate and homogenize almost all the materials in the solar nebula, if isotopically heterogeneous dust particles are mechanically well mixed in advance. This possibility would be explored in future.

## CHRONOLOGICAL STUDY OF OXYGEN ISOTOPE COMPOSITION FOR THE SOLAR

PROTOPLANETARY DISK IN A FLUFFY TYPE A CAI FROM VIGARANO.

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**Introduction:** Fluffy Type A Ca-Al-rich inclusions containing reversely zoned melilite crystals are suggested to be direct condensates from solar nebular gas [1]. We conducted an investigation of  $^{26}\text{Al}$ - $^{26}\text{Mg}$  systematics of a fluffy Type A CAI from Vigarano, named V2-01, with known O isotopic distributions of reversely zoned melilite crystals [2]; we also conducted O isotope measurements of coexisting minerals. The O and Al-Mg isotope measurements were conducted using SIMS of Hokkaido University (Cameca ims-1280HR).

**Results and discussion:** Two of six reversely zoned melilite crystals showed continuous variations in Mg isotopic composition, with  $\delta^{25}\text{Mg}$  becoming small along the direction of crystal growth, which supports the idea that they originated through condensation. Petrography suggests that the constituent minerals of V2-01 formed in the following order: first spinel and fassaite enclosed by melilite, then reversely zoned melilite crystals, and spinel and diopside in the Wark-Lovering rim. The spinel enclosed by melilite has  $^{16}\text{O}$ -rich compositions ( $\Delta^{17}\text{O} \sim -24\text{\textperthousand}$ ) and an initial value of  $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$ . The fassaite enclosed by melilite crystals shows variable O isotopic compositions ( $\Delta^{17}\text{O} \sim -12\text{\textperthousand}$  and  $-17\text{\textperthousand}$ ) and plots on the isochron with  $(^{26}\text{Al}/^{27}\text{Al})_0 = (5.6 \pm 0.2) \times 10^{-5}$ . The O isotopic compositions of reversely zoned melilite showed continuous variations in  $\Delta^{17}\text{O}$  along the direction of crystal growth, suggesting that surrounding nebular gas, during the formation of the reversely zoned melilite, changed from  $^{16}\text{O}$ -poor ( $\Delta^{17}\text{O}$  values larger than  $-10\text{\textperthousand}$ ) to  $^{16}\text{O}$ -rich ( $\Delta^{17}\text{O} \sim -25\text{\textperthousand}$ ) [2]. The six reversely zoned melilite crystals show indistinguishable initial  $(^{26}\text{Al}/^{27}\text{Al})_0$  values with an average  $(^{26}\text{Al}/^{27}\text{Al})_0$  of  $(4.7 \pm 0.3) \times 10^{-5}$ , which is clearly distinguishable from the value of enclosed spinel and fassaite, indicating a younger formation age than the enclosed spinel and fassaite. The spinel and diopside from the Wark-Lovering rim show  $^{16}\text{O}$ -rich compositions ( $\Delta^{17}\text{O} \sim -23\text{\textperthousand}$ ) with  $(^{26}\text{Al}/^{27}\text{Al})_0 = (4.5 \pm 0.4) \times 10^{-5}$ . The values of  $(^{26}\text{Al}/^{27}\text{Al})_0$  are consistent with the formation sequence inferred from petrography. The formation period for the V2-01 CAI is estimated to be  $0.18 \pm 0.07$  Myr from the difference in initial  $(^{26}\text{Al}/^{27}\text{Al})_0$  values. These data suggest that the O isotopic composition of solar nebular gas surrounding the CAI changed from  $^{16}\text{O}$ -rich to  $^{16}\text{O}$ -poor and back to  $^{16}\text{O}$ -rich at least recorded as one cycle during the first  $\sim 0.2$  Myr of Solar System formation.

**References:** [1] MacPherson G. J. and Grossman L. 1984. *Geochimica et Cosmochimica Acta* 48: 29–46. [2] Katayama J. et al. 2012. *Meteoritics and Planetary Science* 47: 2094–2106.

## OXYGEN ISOTOPES AND HIGH $^{26}\text{Mg}$ EXCESSES IN A U-DEPLETED FINE-GRAINED ALLENDE CAI.

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**Introduction:** CAIs are among the first solids formed in the early Solar System (ESS). As such, they are prime samples to study when (1) investigating ESS high-temperature processes, and (2) searching for evidence of short-lived radionuclides at the time of formation of the SS. A recent systematic study of fine-grained CAIs characterized by Group II REE patterns from Allende [1], found an extremely large  $^{235}\text{U}$  excess ( $\delta^{235}\text{U} > 50\text{‰ rel. to CRM-112a}$ ) in one sample: ME-3364 3.2. The discovery of this large  $^{235}\text{U}$  excess provides convincing evidence of the existence of live  $^{247}\text{Cm}$  in the ESS, as previously suggested by [2]. In this study, we analyzed the oxygen isotope compositions and Al-Mg systematics of CAI ME-3364 3.2 to constrain the conditions of its formation.

**Method:** Petrologic and mineralogical studies were carried out by an SEM equipped with an EDS at UCLA. Secondary minerals such as nepheline, sodalite, Fe-rich pyroxene, and Fe-rich spinel were observed in ME-3364 3.2. Analyses for oxygen isotopes and Al-Mg systematics were performed on the IMS 1270 and IMS 1290 ion probes at UCLA. The instrumental mass fractionation for both oxygen and Mg isotopes was corrected for by comparison to San Carlos olivine, pyroxene, Burma spinel and an NBS610 glass. Excesses in  $^{26}\text{Mg}$  ( $\Delta^{26}\text{Mg}^*$ ) were calculated by adopting an exponential law with a mass fractionation exponent of 0.516 obtained from the analysis of standards.

**Results and Discussion:** Despite being U-anomalous and full of secondary phases, the oxygen isotopic compositions of this fine-grained CAI are not too different from those of other non- FUN CAIs. The  $\Delta^{17}\text{O}$  values of sodalite and nepheline range from  $-15\text{‰}$  to  $-5\text{‰}$ , similar to values previously obtained on Efremovka fine-grained CAIs [e.g., 3]. Large excesses in  $^{26}\text{Mg}$  have been identified in ME-3364 3.2 over a large range of  $^{27}\text{Al}/^{24}\text{Mg}$  values (from 42 to 667), yet the data do not define an isochron. Instead, the  $^{26}\text{Mg}$  excess is approximately uniform across all spots analyzed. All the spots are characterized by large but variable negative  $\delta^{25}\text{Mg}$  (from  $\sim -9\text{‰}$  to  $-19\text{‰}$ ).

The elevated, yet homogenous,  $\Delta^{26}\text{Mg}^*$  and negative  $\delta^{25}\text{Mg}$  in ME-3364 3.2 indicates Mg isotope exchange must have taken place in a closed system to avoid dilution with chondritic Mg, although our data cannot constrain a reliable timescale of the formation of secondary phases. Further investigation is required to explain  $^{26}\text{Mg}$  excesses and negative  $\delta^{25}\text{Mg}$  associated with U depletion in this fine-grained inclusion.

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## HIGH-TEMPERATURE RIMS AROUND CAIS FROM THE CR, CB AND CH CARBONACEOUS CHONDRITES.

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We describe the mineralogy, petrology and oxygen isotopic compositions of high-temperature rims (not all of them are Wark-Lovering rims) around Ca,Al-rich inclusions (CAIs) from the CR, CH, and CB carbonaceous chondrites.

**Wark-Lovering (WL) rims:** In CR chondrites, most CAIs are surrounded by WL rims; the only exception are rare igneous CAIs extensively melted during chondrule formation, which lack the rims. A complete multilayered WL rim sequence (spinel + hibonite + perovskite  $\rightarrow$  melilite replaced to a various degree by anorthite  $\rightarrow$  Al-diopside  $\rightarrow$  forsterite) is rarely observed around CR CAIs; Al-diopside  $\pm$  forsterite rims are more common. In CH chondrites, most CAIs are surrounded by WL rims mineralogically similar to those in CR chondrites; however, anorthite replacing rim melilite is rare. The CR and CH CAIs and their WL rims are uniformly  $^{16}\text{O}$ -rich ( $\Delta^{17}\text{O} \sim -24\text{‰}$ ), indicating formation in an  $^{16}\text{O}$ -rich (solar-like) gaseous reservoir. Based on the mineralogy, petrology and O-isotope compositions, we infer that WL rims formed by evaporation, condensation, melting, and thermal annealing in the CAI-forming region. There is no correlation between O-isotope compositions and the presence or absence of  $^{26}\text{Al}$  in the CAIs surrounded by WL rims, suggesting that the  $^{16}\text{O}$ -rich gaseous reservoir in the CAI-forming region existed during addition and homogenization of  $^{26}\text{Al}$  in the protoplanetary disk.

**Wark-Lovering rims melted during chondrule formation:** Some  $^{16}\text{O}$ -rich CR and CH CAIs are surrounded by Al-diopside rims depleted in  $^{16}\text{O}$  to varying degrees ( $\Delta^{17}\text{O}$  range from  $\sim -10$  to  $\sim +2\text{‰}$ ). These rims are typically thick and compact. They are often intergrown with ferromagnesian (chondrule-like) olivine and low-Ca pyroxene grains and contain inclusions of Fe,Ni-metal nodules, suggesting incomplete melting and O-isotope exchange during brief heating events, most likely during formation of porphyritic chondrules.

**Igneous rims formed in an impact-generated plume:** All CB CAIs and about 10% of CH CAIs are surrounded by single- or double-layered igneous rims composed of Ca-rich forsterite or Al-diopside + Ca-rich forsterite. Host CAIs have diverse mineralogy (grossite-rich, hibonite-rich, melilite-rich, spinel-rich, and Al-diopside-rich) and appear to be igneous. The CB CAIs, CB-like CAIs in CH chondrites and their igneous rims are uniformly  $^{16}\text{O}$ -poor ( $\Delta^{17}\text{O} \sim -5\text{‰}$ ), indicating formation in an isotopically distinct gaseous reservoir. We suggest that (i) this reservoir is related to an impact-generated plume of gas and melt invoked for the origin of magnesian non-porphyritic chondrules in CB and CH chondrites, and (ii) the  $^{16}\text{O}$ -poor igneous rims formed during melting of the originally  $^{16}\text{O}$ -rich host CAIs in the plume followed by gas-melt O-isotope exchange, condensation of SiO and Mg into the CAI melts, and crystallization.

We conclude that rims around CAIs from CR, CH, and CB chondrites recorded high-temperature processing in gaseous reservoirs with different oxygen isotopic compositions, prior to and during chondrule formation. In contrast to CAIs surrounded by isotopically heterogeneous WL rims from hydrothermally altered CV chondrites, our data provide no evidence that CAIs surrounded by WL rims were transported between  $^{16}\text{O}$ -rich and  $^{16}\text{O}$ -poor gaseous reservoirs multiple times.

**COUPLING VANADIUM AND BORON ISOTOPES IN CAIs.** F. Moynier, P. Sossi, Chizu Kato, M. Chaussidon  
Institut de Physique du Globe de Paris

After a few decades of dormancy, irradiation models for phenomena in the early Solar System have recently been considered more closely by astrophysicists and cosmochemists on two important grounds. First, the detection of high (relative to solar) and variable X-ray activity in protostars suggests that particle acceleration, and hence irradiation, is a common phenomenon in low-mass protostars [1]. X-ray flares accompanied by intense fluxes of accelerated particles have been detected in almost all young stars. X-ray absorption and Fe fluorescent emission line measurements show that X-rays efficiently irradiate protoplanetary disks [2-4]. Second, the discovery that the short-lived isotope  $^{10}\text{Be}$  ( $T_{1/2} = 1.5 \text{ Ma}$ ) was alive in the early solar system [5, 6] has revived the idea that some short-lived radionuclides were produced by irradiation in the early solar system [7], since  $^{10}\text{Be}$  cannot be produced in stars. However, this interpretation has been challenged by Desch et al. [8] who calculated that a fraction of  $^{10}\text{Be}$  can also be formed by Galactic Cosmic Rays (GCR) trapped in the presolar nebular cloud. V has one stable isotope (mass 51) and a very long-lived isotope (mass 50,  $T_{1/2} = 1.4 \times 10^{17} \text{ y}$ ). The main isotope of V,  $^{51}\text{V}$  (99.75 %) is produced through explosive nucleosynthesis [9], with a significant contribution from type Ia supernovae [10]. The origin of the nuclei  $^{50}\text{V}$  is poorly understood. A variety of mechanisms have been considered: p-process [11], cosmic-ray spallation origin [12] photonuclear nucleosynthesis [13, 14], and n-process [15]. Because of the low cosmic abundance (0.25 %) of  $^{50}\text{V}$  [16], the ratio  $^{50}\text{V}/^{51}\text{V}$  has long been proposed to be a good tracer of irradiation in an early solar system environment [17, 18]. The X-wind model predicts an excess  $d^{50}\text{V}/d^{51}\text{V} \sim 3\%$  relative to cosmic composition [19]. Therefore, knowledge of the V isotope composition of Solar System material would be a critical test of the irradiation models. Here we will present the V isotopic composition of 7 CAIs measured by MC-ICP-MS at IPG Paris coupled with in-situ determination of the  $^{10}\text{Be}/^{9}\text{Be}$  initial ratio determined by SIMS (ims1280 at CRPG Nancy). Our preliminary results on 5 CAIs show an enrichment in  $^{50}\text{V}$  in the order of magnitude predicted by [19]. By the time of the workshop we will have both V and B data for 10 CAIs.

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**OPAQUE MINERALS BEARING FORSTERITE IN CARBONACEOUS CHONDRITES.** N. Sakamoto<sup>1</sup>,  
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**Introduction:** Amoeboid olivine aggregates (AOAs) are obvious nebular objects having the longest record of nebular condensation and no clear evidence of being molten [1, 2]. The AOAs contain forsterite enriched in  $^{16}\text{O}$  and Fe-Ni metal that is a highly sensitive indicator of metamorphism based on the decomposition of martensite [3-5]. Thus, AOAs has a possibility to provide not only the information of whole thermal history in the nebular and parent body but also nebular pressure because the order of condensation of metal and forsterite has a crossover in the vicinity of 10<sup>-4</sup> bar in a system of solar composition. In this study, opaque minerals enclosed in forsterite were used as a tracer that is one of conceivable basic components of AOAs from several carbonaceous chondrites (Figure 1).

**Results and Discussion:** Opaque minerals bearing forsterite were found in polished thin sections of Acfer 094 (ung.), Adelaide (ung.), ALHA77307 (CO), Yamato-81020 (CO), Murchison (CM) and Efremovka (CV) carbonaceous chondrites. All forsterite of the objects were enriched in  $^{16}\text{O}$  measured by point and imaging isotope analysis using Hokudai isotope microscopes. The forsterite layer has almost constant thickness of about 10  $\mu\text{m}$  and show almost the same crystallographic orientation except for broken part would be chipped on the parent body.

The assemblage of opaque minerals enclosed in forsterite were different depend on the chondrites. In the case of Acfer 094, Fe-Ni metal with 5wt% of Ni is nearly homogeneous suggesting martensite as previously reported [4]. Murchison has mixture of tochilinite and philosilicate inside of the forsterite layer. Yamato-81020 shows the assemblage of kamacite, teanite, magnetite and FeS with dusty texture. These characteristics of opaque minerals enclosed forsterite are consistent with the distribution of Fe among chondrites groups [6] indicating that the martensite bearing forsterite formed in the nebular would be metamorphosed to each assemblage on their parent body.

**References:** [1] Petaev & Wood. 2005. *Chondrites and the Protoplanetary Disk* 341: 373. [2] Scott & Krot. 2014. *Treatise on Geochemistry 2<sup>nd</sup> Edition*: 65. [3] Wood. 1967. *Icarus* 6:1. [4] Kimura et al. 2008. *MAPS* 43:1161. [5] Yang et al. 1997. *GCA* 61:2943. [6] Campbell et al. 2005. *Chondrites and the Protoplanetary Disk* 341: 407.

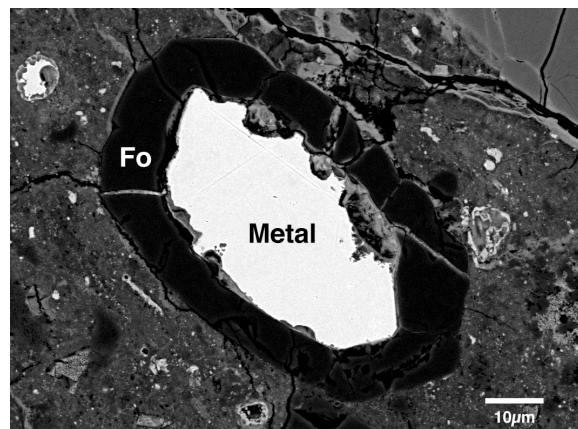


Fig.1 BSE image of metal bearing forsterite in Acfer 094 carbonaceous chondrite.

**ORIGINS OF VOLATILE ELEMENTS ON EARTH, VENUS AND MARS IN LIGHT OF RECENT RESULTS FROM THE ROSETTA COMETARY MISSION.** B. Marty<sup>1\*</sup>, G. Avice<sup>1</sup>, Y. Sano<sup>2</sup>, K. Altwegg<sup>3</sup>, H. Balsiger<sup>3</sup>, M. Hässig<sup>3</sup>, A. Morbidelli<sup>4</sup>, O. Mousis<sup>5</sup>, M. Rubin<sup>3</sup>, and the ROSINA Team. <sup>1</sup>CRPG-CNRS, Université de Lorraine, 54501 Vandoeuvre lès Nancy, France. <sup>2</sup>Ocean and Atmosphere Research Institute, The University of Tokyo, Kashiwa-shi, Chiba 277-8564 Japan <sup>3</sup>Physikalisches Institut, University of Bern, CH-3012 Bern, Switzerland. <sup>4</sup>Université Côte d'Azur, CNRS, Observatoire de la Côte d'Azur, BP 4229, 06304 Nice Cedex 4, France <sup>5</sup>Aix Marseille Université, CNRS, LAM 13388, Marseille, France.

## SESSION 3

### **Volatiles on Earth, Venus, and Mars – Lessons from ROSETTA**

#### ***Invited Lecture***

DAY 2 – Feb.18, 2016  
4:30 pm – 5:30 pm

Recent measurements of the volatile composition of the coma of Comet 67P/Churyumov-Gerasimenko (hereafter 67P) allow constraints to be set on the origin of volatile elements (water, carbon, nitrogen, noble gases) in inner planets' atmospheres. Analyses by the ROSINA mass spectrometry system onboard the Rosetta spacecraft indicate that 67P ice has a D/H ratio three times that of the ocean value and contains significant amounts of N<sub>2</sub>, CO, CO<sub>2</sub>, and importantly, argon. Here we establish a model composition of cometary composition based on literature data and the ROSINA measurements. From mass balance calculations, and provided that 67P is representative of the cometary ice reservoir, we conclude that the contribution of cometary volatiles to the Earth's inventory was minor for water ( $\leq 1\%$ ), carbon ( $\leq 1\%$ ), and nitrogen species (a few % at most). However, cometary contributions to the terrestrial atmosphere may have been significant for the noble gases. They could have taken place towards the end of the main building stages of the Earth, after the Moon-forming impact and during either a late veneer episode or, more probably, the Terrestrial Late Heavy Bombardment around 4.0–3.8 Ga ago. Contributions from the outer solar system via cometary bodies could account for the dichotomy of the noble gas isotope compositions, in particular xenon, between the mantle and the atmosphere. A mass balance based on 36Ar and organics suggests that the amount of prebiotic material delivered by comets could have been quite considerable – equivalent to the present-day mass of the biosphere. On Mars, several of the isotopic signatures of surface volatiles (notably the high D/H ratios) are clearly indicative of atmospheric escape processes. Nevertheless, we suggest that cometary contributions after the major atmospheric escape events, e.g., during a Martian Late Heavy Bombardment towards the end of the Noachian era, could account for the Martian elemental C/N/<sup>36</sup>Ar ratios, solar-like krypton isotope composition and high <sup>15</sup>N/<sup>14</sup>N ratios. Taken together, these observations are consistent with the volatiles of Earth and Mars being trapped initially from the nebular gas and local accreting material, then progressively added to by contributions from wet bodies from increasing heliocentric distances. Overall, no unified scenario can account for all of the characteristics of the inner planet atmospheres. Advances in this domain will require precise analysis of the elemental and isotopic compositions of comets and therefore await a cometary sample return mission.

**PHOTOCHEMISTRY IN MOLECULAR CLOUD: EVOLUTION OF ICE AND ORGANIC RESIDUES THROUGH WARMING AND UV-IRRADIATION.** L. Piani<sup>1</sup>, S. Tachibana<sup>1</sup>, T. Hama<sup>2</sup>, I. Sugawara<sup>1</sup>, Y. Oba<sup>2</sup>, H. Tanaka<sup>2</sup>, Y. Kimura<sup>2</sup>, A. Miyake<sup>3</sup>, J. Matsuno<sup>3</sup>, A. Tsuchiyama<sup>3</sup>, H. Yurimoto<sup>1</sup> and A. Kouchi<sup>2</sup>, <sup>1</sup>Department of Natural History Sciences, <sup>2</sup>Institute of Low Temperature Science, Hokkaido University, Japan. <sup>3</sup>Division of Earth and Planetary Science, Kyoto University, Japan.

## POSTER SESSION

DAY 2 – Feb.18, 2016  
5:30 pm – 6:30 pm

**Introduction.** In the interstellar medium (ISM), photochemical reactions in ice lead to the formation of relatively complex organic molecules [1]. These molecules are among the potential building blocks of our solar system and could be the precursor of a part of the organic matter found in comets and meteorites. However, it is not clear how the organic ice formed in the ISM may have evolved through temperature increase and irradiations by UV-photons and cosmic rays until their incorporation into the Solar System.

**Method.** To simulate the formation and evolution of organic ice through UV irradiation and heating under ISM conditions, we developed an experimental apparatus called PICACHU, an acronym for Photochemistry in Interstellar Cloud for Astro-Chronicle in Hokkaido University. Typical ISM gases ( $H_2O$ , CO,  $NH_3$ , and  $CH_3OH$ ) are deposited onto the faces of a refrigerated substrate (~12K) and simultaneously irradiated by UV under high vacuum. Gases, desorbed from the ice during heating and post-irradiation, are monitored by a quadrupole mass spectrometer (QMS) in the vacuum chamber. The morphological evolution of the ice deposits during warm-up and/or irradiation is observed *in situ* using a microscope and correlated with desorbed gases measured by the QMS. Some organic residues formed after the ice sublimation were re-irradiated with UV photons at a room temperature for 65–235 hours. The residual organic materials were examined with a laser microscope, an atomic force microscope (AFM), FE-SEM, and TEM. Viscoelastic measurements were done with a Nano-indentation technique.

**Results and discussion. Ice and released gases.** We have previously reported [2] the occurrence of bubbles in the ice appearing from ~65 K during the warming-up to room temperature and associated with gas outburst (mostly  $H_2$ ). Nucleation and growth of bubbles of volatile species thus occur in the ice, which behaved like a supercooled liquid at 65 K. We are now investigating this phenomenon by changing the heating rate and initial gas compositions. We also have replicated the experimental conditions with another experimental apparatus equipped with an *in situ* FTIR spectrometer to monitor the evolution of the ice.

**Photo-processing of organic residues.** Significant morphological changes were observed in the organic residues due to short-duration UV-irradiation: increase of porosity and roughness and, appearance of nanoparticles similar to the ones found in the organic matter within chondrites and cometary samples. The viscoelastic properties of the organic residues indicate that organic-coating on inorganic dust could play as efficient glue on dust aggregation but, at the same time, could also enhance the aggregate brittleness.

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**OCCURRENCE AND CHEMICAL VARIATION OF COSMIC SYMPLECTITE IN ACFER 094 CARBONACEOUS CHONDRITE.** K. Abe<sup>1</sup>, N. Sakamoto<sup>2</sup> A. N. Krot<sup>3</sup> and H. Yurimoto<sup>1,2</sup>, <sup>1</sup>Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, JAPAN. E-mail: abeken@ep.sci.hokudai.ac.jp, <sup>2</sup>Isotope Imaging Laboratory, Creative Research Institution Sousei, Hokkaido University, Sapporo, 001-0021, JAPAN, <sup>3</sup>Hawai'i Institute of Geophysics and Planetology, School of Ocean and Earth Science and Technology, University of Hawai'i at Manoa, Honolulu, HI 96822, USA.

**Introduction:** Cosmic symplectite (COS) has been discovered from matrices of a primitive carbonaceous chondrite Acfer 094. The COS consists of nanocrystalline aggregates of iron sulfide and magnetite with a symplectitic texture and the oxygen isotope composition is extremely enriched in  $^{17}, ^{18}\text{O}$  ( $\delta^{17}, ^{18}\text{O} = +180\text{ ‰}$ ) [1, 2]. The occurrence and chemical information of COS has limited and further study would helpful to characterize COSs. Therefore we performed systematic COS survey in Acfer 094 carbonaceous chondrite using X-ray elemental mapping technique in order to reveal the abundance, occurrence and chemical variation to confirm the formation process of COS previously proposed [1, 2].

**Results and Discussion:** We have studied 314 COS grains from two thin sections of Acfer 094 using X-ray elemental mapping technique described in [7]. COS grains were scattered ubiquitously in the Acfer 094 matrix with a 611 ppm volume abundance. COSs can be classified into five categories: (1) symplectitic structure composed of column-shaped magnetite (10–30 nm in diameter and 100–200 nm in length) and worm-shaped iron sulfide (100–300 nm in size) [2], (2) wormy grain (about 200 nm in diameter) having the symplectite inner structure, (3) irregular rope-like grain (few microns in width) consisting of the wormy grains, (4) bundle of the entangled rope-like grain (few tens of micron in size) and (5) aggregate of the (4) spread within the matrix area of  $100 \times 100\text{ } \mu\text{m}$  [8].

Whereas COS grains were often accompanied or surrounded by iron sulfide with a fractured structure, we have not been observed Fe,Ni-metal attached to COS grains. On the phase diagram calculated by [1], Fe-metals disappeared from the system when precursor metals or sulfides were oxidized to magnetites by water vapor below  $\sim 360\text{ K}$ . Our observations are consistent with the process.

All COS grains analyzed in this study have almost same atomic ratio of  $\text{Fe,Ni} : \text{O} : \text{S} = 4 : 4 : 1$ , which means  $(\text{Fe,Ni})\text{S} : \text{Fe}_3\text{O}_4 = 1 : 1$ . Ni contents in COS grains show wide variation ranging from 0 to 0.4 as atomic ratio of  $\text{Ni}/(\text{Fe}+\text{Ni})$ . If COS grains were formed by the formation process proposed by [2] that iron sulfides except for pentlandite were completely oxidized to magnetites, the  $(\text{Fe,Ni})\text{S}/\text{Fe}_3\text{O}_4$  ratio of the COS grains should increase with increasing the Ni content. Therefore new mechanism of COS formation is needed.

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**PETROGRAPHY OF A LARGE PERFECT SHAPED TYPE A/B CAI FORMED BY MULTIPLE HEATING.** S. Yoneyama<sup>1</sup> and S. Itoh<sup>1</sup>, <sup>1</sup>Dept. Earth Planet. Sci., Kyoto University, kitashirakawa oiwakecho sakyoku, Kyoto, 606-8502, JAPAN. Email:yoneyama.shun.23n@st.kyoto-u.ac.jp.

Calcium-aluminum-rich inclusions (CAIs) are the oldest solid materials in the early solar system [1]. Coarse-grained CAIs are divided into three groups, type A, type B and type C by the petrography and the bulk chemical composition [2]. All type of CAIs has partially melted more than once [e.g., 3, 4, 5]. However, the petrography and isotopography about multiple heating process are limited.

A large (about 8mm in diameter) perfect rounded shaped CAI, named KU-N-01, has a bulk chemical composition between type A and type B was used in this study. The petrography of a CAI is studied with FE-SEM-EDS at Kyoto University (KU). This CAI has some spinel-rich areas enclosed by fassaite in the mantle, likely Type B CAIs. The core mostly consists of melilite ( $\text{Åk}_{30-50}$ ), likely Type A CAIs. In particular, this CAI has a unique structure with some domains divided by spinel layers (Fig. 1). Three domains are existed. The rim is surrounded by Wark-Lovering rim. In addition, this CAI has a double-layered structure divided by spinel layer in the rim. These layered consists of gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_4$ )-rich layer, spinel layer (~5 wt% FeO),  $\text{Åkermanite}$  ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ )-rich layer and spinel layer (~0.4 wt% FeO) from outside to inside. This suggests that at least the CAI has melted more than three times and KU-N CAI has gradually evolved by multiple heating process. In this talk, the detail petrography with a trace element mapping by LA-ICP-MS and the formation process of CAI will be discussed.

**Acknowledgment:** We thank Akira Tsuchiyama for the use of FE-SEM-EDS. [1] Connelly et al. (2012) *Science*, **338**, 651–655. [2] Grossman (1975) *GCA*, **39**, 433–454. [3] Yurimoto et al. (1998) *Science*, **282**, 1874–1877. [4] MacPherson and Davis (1993) *GCA*, **57**, 231–243. [5] Kawasaki et al. (2015) *GCA*, **169**, 99–114.

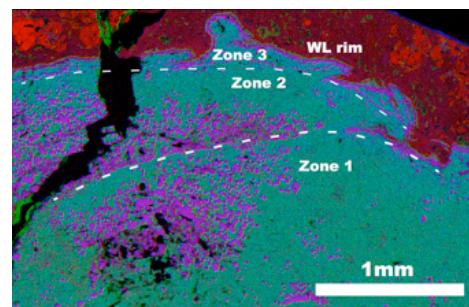


Fig. 1. X-ray map of zoned area by multiple heating. Mg=red, Ca=green, Al=blue. WL rim: Wark and Lovering rim.

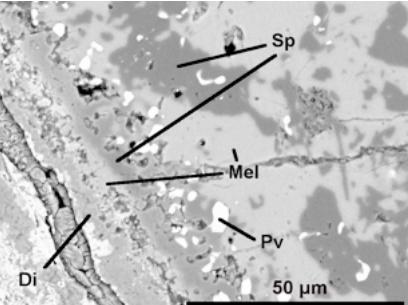


Fig. 2. WL-rim of BSE image. Sp: spinel, Mel.: Melilite, Pv: perovskite, Di:diopside.

**PETROGRAPHY OF A COMPACT TYPE A CAI INCLUDING BUBBLE-LIKE Voids FROM NINGQINAG CARBONACEOUS METEORITE.** Y. Yoshida<sup>1\*</sup>, R. Hamada<sup>1</sup>, N. Sakamoto<sup>2</sup>, and H. Yurimoto<sup>1,2</sup>, Department of Natural History Sciences, Hokkaido University, Sapporo 060-0810, JAPAN, <sup>2</sup>Isotope Imaging Laboratory, Creative Research Institution Sousei, Hokkaido University, Sapporo 001-0021, JAPAN. \*E-mail: insomnia@ep.sci.hokudai.ac.jp.

**Introduction:** Calcium-, aluminum-rich inclusions (CAIs) are considered to have formed in the early solar system, and hence the physical and chemical processes may be preserved in CAIs. Bubble-like voids have been reported in melilite crystals of CAIs [1-4]. However, processes of the formation have not been clarified. In order to reveal the bubble formation, we studied petrology and chemical distribution of a Type A CAI containing bubble-like voids from Ningqiang carbonaceous chondrite.

**Experimental:** Petrographic and chemical analyses were performed with using a FE-SEM (JEOL JSM-7000F) equipped with an EDS (Oxford XMAX-150) and an EBSD detector (HKL channel 5).

**Results:** A hibonite-bearing coarse-grained compact Type A CAI, named as HKN01, in a thin section of Ningqiang (C3-ung) meteorite was studied. The CAI appears nearly round shape surrounded by Wark-Lovering rim ( $\sim 2.5$  mm in diameter). The most abundant mineral is melilite in the CAI. From petrographic textures of melilite, the CAI consists of two different mosaic regions: (1) large melilite crystals and (2) small melilite crystals.

(1) The large melilite crystals ( $> 150 \mu\text{m}$  in size) are anhedral with reverse chemical zonation. The crystals include spinel (from  $\sim 2$  up to  $\sim 35 \mu\text{m}$ ), perovskite and clinopyroxene ( $< 5 \mu\text{m}$  in size), and rarely hibonite ( $< 20 \mu\text{m}$  in size) and refractory metal alloy ( $\sim 1 \mu\text{m}$  in size). The clinopyroxene often coexists with the perovskite and spinel as surrounding rind ( $< 2 \mu\text{m}$  in thickness). Bubble-like voids ( $< 30 \mu\text{m}$ ) appear within melilite and at grain boundaries of melilite. The voids are sometimes partially fringed by clinopyroxene. Alteration minerals such as plagioclase, feldspathoids, and Fe-bearing pyroxene have often replaced melilite along cracks.

(2) The small melilite crystals are from  $\sim 3$  to  $\sim 50 \mu\text{m}$  with concentric reverse zonation in composition for each crystal. Perovskite ( $< 3 \mu\text{m}$ ), spinel and hibonite (from  $\sim 2$  to  $15 \mu\text{m}$ ) exist at grain boundary of melilite crystals and in melilite crystals. Clinopyroxene locates at grain boundary of melilite and surrounding voids. Small round-shaped voids ( $< 5 \mu\text{m}$ ) are observed at grain boundaries of melilite.

The Wark-Lovering rim totally encloses the object with varying thickness from  $\sim 50$  to  $\sim 300 \mu\text{m}$ . The rim consists of fine grains ( $< 10 \mu\text{m}$ ) of melilite, spinel, perovskite, hibonite and clinopyroxene, with a layer sequence of melilite, spinel, melilite, and clinopyroxene toward outside of the CAI.

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**A NEW MECHANISM FOR COMPOUND CHONDRULE FORMATION: COLLISIONS OF SUPERCOOLED DROPLETS.** S. Arakawa<sup>1</sup> and T. Nakamoto<sup>1</sup>, <sup>1</sup>Dept. of Earth and Planetary Sciences, Tokyo Institute of Technology, Meguro, Tokyo, 152-8551, Japan. E-mail: arakawa.s.ac@m.titech.ac.jp

Some chondrules consist of two or more chondrules fused together. They are called compound chondrules. We focus on three features of compound chondrules [1]. First, most (80% of primaries and 90% of secondaries) of compound chondrules have non-porphyritic texture while non-porphyritic chondrules are minor components of chondrites. Second, in most of compound chondrules, larger ones keep round shapes, and smaller ones are deformed. It means that larger ones crystallized earlier than smaller ones, and smaller ones stuck later. Finally, about 20% of non-porphyritic chondrules are compounds, and in contrast, only 0.5% of porphyritic ones are compounds. In previous studies, these three features are remained to explain.

We propose a new scenario for compound chondrule formation reproducing these features; collisions of supercooled droplets form compound chondrules. This scenario is based on experimental facts that completely molten dust droplets are not crystallized at their liquidus or solidus, and supercooled droplets turn into non-porphyritic chondrules after crystallization [2]. The scenario can explain why most of compound chondrules are non-porphyritic. Experimental studies reveal that supercooled droplets do not crystallize spontaneously at a temperature slightly below liquidus, and supercooled droplets crystallize owing to collision [2]. Then we can obtain the second feature that larger ones of compound chondrules keep round shapes while smaller ones are deformed, because larger ones are likely to be collided more than smaller ones. We also calculate the duration of compound chondrule formation for reproducing the fraction, 20% of non-porphyritic ones, and we find that the fraction of compound chondrules can be explained if the duration of supercooling is of the order of  $10^4$  seconds. This result is consistent with planetesimal bow shock model for chondrule formation [3].

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## PETROGRAPHY AND OXYGEN ISOTOPE DISTRIBUTION OF OLIVINE FROM COARSE-GRAINED IGNEOUS RIM AROUND CHONDRULE IN NWA3118 CV3 CHONDRITE.

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**Introduction:** Coarse-grained igneous rims record thermal histories after chondrule formation [1-3]. Olivine with  $^{16}\text{O}$ -rich composition was reported in coarse-grained igneous rims from CR chondrites, suggesting that these  $^{16}\text{O}$ -rich parts are relict and correspond a low degree of melting of fayalitic rim [4, 10, 11]. Existence of  $^{16}\text{O}$ -rich olivine in the rims indicates that the chondrule rims preserve isotopic information about chondrule precursor and chondrule formation environment [5]. In addition, chemical zoning in olivine allows the determination of time and temperature of thermal metamorphism on the parent body [6]. Here we report on petrology and oxygen-isotope distribution of olivine from coarse-grained igneous rim around chondrule in NWA3118 CV3 chondrite.

**Experimental:** The sample used in this study is a polished thin section from NWA 3118 CV3 chondrite. The petrographic observation and chemical analysis were performed by FE-SEM-EDS (JEOL JSM-7000F + Oxford X-Max 150). Crystal orientation analysis was studied by EBSD (Oxford HKL). Isotope imaging for oxygen was obtained using an isotope microscope (Cameca ims-1270 + SCAPS).

**Results and discussion:** The chondrule studied here has 1.4 millimeters in diameter and Mg-rich (type I) porphyritic texture mainly composed of forsterite, low-Ca pyroxene and feldspathic mesostasis. The chondrule is surrounded by rim with the thickness of up to 400 micrometers that shows evidences of igneous process.

The rim is mostly dominated by ferromagnesian olivine and also contains low-Ca pyroxene, high-Ca pyroxene, nepheline, Fe-Ni metal and sulfide. The olivins in the rim have two types of compositions: (1) Mg-rich grains that show higher FeO content (about  $\text{Fa}_{12-37}$ ) than olivine in host chondrule and, (2) Fe-rich grains ( $\text{Fa}_{40-50}$ ). The Mg-rich olivine displays Fe-Mg zoning and contains Fe-rich veins [7]. The Fe-rich olivine is located as rim around Mg-rich olivine and along interstitial area between Mg-rich olivine grains. Fe-rich olivine and vein often show crystallographic continuity with the Mg-rich olivine in contact [8].

Seven  $^{16}\text{O}$ -rich olivine grains with 10-30 micrometers in diameter were found in the igneous rim.  $^{16}\text{O}$ -enrichments are observed in core of Mg-rich olivine crystals and the olivine also has Fe-Mg zoning. The existences of  $^{16}\text{O}$ -enrichments does not find in Fe-rich olivine. The oxygen isotope heterogeneity, therefore, survived metamorphism on the parent body [9].

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## COOLING SPEEDOMETER FOR CHONDRULES: EUTECTIC STRUCTURE OF METALLIC IRON AND IRON SULFIDE. M. Mori<sup>1</sup>, S. Tachibana<sup>1</sup>, and L. Piani<sup>1</sup>, <sup>1</sup>Department of Natural History Sciences, Hokkaido University (N10W8, Kita-ku, Sapporo, Hokkaido, Japan, 060-0810, mori@eps.sci.hokudai.ac.jp).

Chondrules are sub-millimeter sized silicate spherules formed by instantaneous heating of solid precursors at the early stage of the solar system evolution [e.g., 1]. Many heating models have been proposed such as nebular shock wave, lightning, X-wind, and asteroidal impacts, but there is not yet a consensus about the formation mechanism of chondrules. In order to constrain the chondrule formation mechanism, it is important to understand the thermal history of chondrules. Dynamic crystallization experiments have shown that chondrules were heated up to 1800–2200 K and cooled at the rate of 10–1000 K/h [e.g., 2]. The absence of fractionation of sulfur isotopes in chondrule sulfides indicates that chondrule precursors were heated at the rate of  $>10^4$  K/h [3]. However, there is no tight constraint on the cooling rate of chondrules at lower temperatures (below the solidus of silicates) although it would provide information on formation environments of chondrules.

Chondrules contain opaque phases consisting of metallic Fe-Ni and troilite. The eutectic melt of these phases solidify below their eutectic temperature (988°C for Fe-FeS) with supercooling. The eutectic solidification texture depends on the degree of supercooling, i.e., the cooling rate at or below the eutectic temperature. Therefore the solidification texture of metal-troilite mixture may be used as a cooling speedometer of chondrules below the solidus of silicates.

In this study, we conducted cooling experiments of the Fe-FeS eutectic melt to evaluate the relation of the eutectic texture with the cooling rate. Powders of metallic Fe and FeS with a molar ratio of S/(Fe+S) of 0.46 (slightly S-richer than the eutectic composition) were heated at 1400°C in a sealed evacuated silica glass tube, in which graphite was put as a reducing agent. The mixture was then quenched in water and was ground into particles of 50–300 μm to be used as a starting material. The ground particles were loaded onto silica wool and placed in a silica glass tube with graphite and a mm-sized FeS grain. Large FeS grains were added in the tube to make sulfur-rich vapor conditions that suppressed evaporation of sulfur from the starting material. The silica glass tube was evacuated and sealed under vacuum, and were heated at 1330°C for 3 hours and cooled at different cooling rates (25, 100, 500 K/hr, and quench in air). Run products were observed with a laser microscope and FE-SEM (JEOL JSM7000F) with EDS and electron backscattered diffraction (EBSD).

Metallic iron in the eutectic textures of samples shows differences in morphology and size depending on the cooling rate. The metal grains observed on cross sections of run products are spherical for the samples with controlled cooling rates of 25, 100, and 500 K/h while dendritic or fan-shaped grains are observed for quenched samples. The size distribution of metal grains shows that metal grains cooled at 25 and 100 K/h are typically larger than 1 μm and those cooled at 500 K/h are smaller than 1 μm.

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**MECHANISM OF WATER DIFFUSION IN SILICA GLASS AT 50 BAR WATER VAPOR PRESSURE.** M. Kuroda<sup>\*1</sup>, S Tachibana<sup>1</sup>, N. Sakamoto<sup>2</sup> and H. Yurimoto<sup>1</sup>.  
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Water diffusion in silicate melt is one of the main controlling factors of magmatism in subduction zones (e.g. degassing and crystallization). Water diffusivity in silicate melts has been known to depend on its own concentration. However, the diffusion mechanism responsible for the observed water concentration dependence has not yet been clarified.

In this study, in order to understand the mechanism of water diffusion in silicate melts, we carried out diffusion experiments of water in silica glass at 650–850°C and water vapor pressure of 50 bar. Silica glass was used to evaluate the water concentration dependence of water diffusion without any other compositional effects (e.g. NBO/T). Diffusion profiles of <sup>1</sup>H and <sup>30</sup>Si were measured on the cross section of run product using Cameca ims-6f at Hokkaido University. Ion images of <sup>1</sup>H and <sup>30</sup>Si along the diffusion profile were also taken with a SCAPS detector attached to Cameca ims-1270 at Hokkaido University. Glasses with known water contents were used for conversion of secondary ion count ratio (<sup>1</sup>H/<sup>30</sup>Si) to the water content in the samples.

The diffusion profiles of water in silica glass cannot be simply explained by previous diffusion models for silicate glasses, and show much stronger water concentration dependence (Fig. 1). We explain this stronger water concentration dependence of water diffusion in silica glass as follows: (1) The main diffusion species is molerular H<sub>2</sub>O, and its relative abundance to OH groups decreases with lowering the water content in the glass; (2) The number of pathways available for diffusion is controlled by the number of NBO determined by the concentration of OH groups. Because the water diffusivity is proportional to the above two factors and both depend on the total water content in the glass, the water concentration dependence of water diffusion is larger than the previous models. The smaller water concentration dependence observed for water diffusion in other silicate glasses can be attributed to the little dependence of NBO concentration on water contents because it is controlled extrinsically by other network modifier cations.

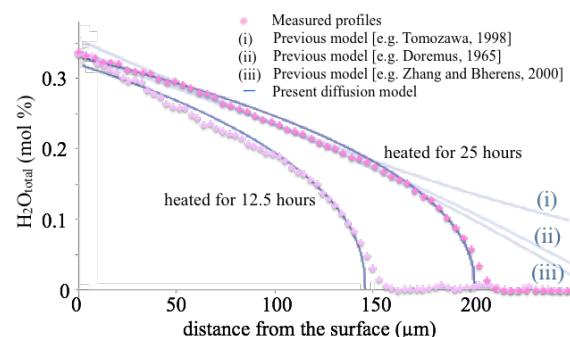


Fig.1 Diffusion profile of water in the sample heated at 850°C with fitting curves with previous models (i)-(iii) and with the present model.

**HAYABUSA2: SAMPLE RETURN FROM C-TYPE NEAR-EARTH ASTEROID (162173) RYUGU.** S. Tachibana<sup>1</sup>, H. Sawada<sup>2</sup>, R. Okazaki<sup>3</sup>, Y. Takano<sup>4</sup>, K. Sakamoto<sup>2</sup>, Y. Miura<sup>5</sup>, and Hayabusa2 Project Team. <sup>1</sup>Dept. Natural History Sci. Hokkaido Univ. <sup>2</sup>Hayabusa2 Project, JAXA. <sup>3</sup>Dept. Earth Planet. Sci., Kyushu Univ., <sup>4</sup>Dept. Biogeochemistry, JAMSTEC. <sup>5</sup>Earthquake Research Inst., Univ. Tokyo. E-mail: tachi@ep.sci.hokudai.ac.jp.

Hayabusa2 is an asteroid exploration mission to return surface samples from a near-Earth C-type asteroid (162173) Ryugu [1]. Carbonaceous-type asteroids are expected to preserve the most pristine materials in the solar system that are an interacted mixture of minerals, ice, and organic matter, which would have later evolved to the Earth, ocean, and life, respectively. Space missions are the only way to obtain such pristine minerals, organics and volatiles with geological context. Moreover, because asteroids are the evolved remnants of planetesimals, on-site observation by a spacecraft and analyses of returned samples will provide direct evidence of planet formation and dynamical evolution of the Solar System.

Hayabusa2 launched off on December 3, 2014 and performed a swing-by of the Earth on December 3, 2015, which successfully pushed the spacecraft into the orbit to Ryugu. The spacecraft will get to Ryugu mid 2018, and will fully investigate the asteroid for 18 months, and sample the asteroid at three different locations. The samples from Ryugu will be delivered to the Earth in December 2020. The returned samples will be classified into three categories due to structural design of the Hayabusa2 sampler [1-3]. (1) Millimeter-sized coarse grains stored separately in three chambers, (2) <100 μm-sized fine particles that could be mixed in the sample container, and (3) volatiles released from the samples in the sealed container. Millimeter-sized coarse grains collected at different locations would represent local characteristics of the asteroid surface, and petrologic and mineralogical studies of them would allow us to constrain the history of the asteroid and material evolution in the early solar system. Fine particles would possess the information on the global average surface feature and surface geologic processes such as space weathering and regolith evolution. Volatile components released from the samples would be the first returned volatiles from space and would thus be an important target to investigate the origin and evolution of organic matter and water in the solar system.

Curation work of the returned samples will be first done at the JAXA Curation Facility, which will be the initial sample preparatory work for subsequent studies (phase 1 curation). The curation work for a fraction of the samples will be done in collaboration with institutes outside JAXA for detailed and thorough analysis (phase 2 curation). A different fraction of samples will be investigated by the Initial Analysis team in the Hayabusa2 project to accomplish the scientific goal of the mission [1]. The samples will be analyzed by multiple analysis teams focusing on non-destructive analyses of grains, elemental and isotopic analyses of grains, petrology and mineralogy of coarse and fine particles, chemistry and isotopes of volatiles, and chemistry of organic materials.

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**GALLIUM ISOTOPES IN CAIS** C. Kato<sup>1</sup>, and F. Moynier<sup>1</sup> <sup>1</sup>Institut de Physique du Globe de Paris (kato@ipgp.fr)

Calcium-Aluminium rich Inclusions (CAIs) are assumed to be the first condensates of the early solar system [1]. Previous studies on the moderately volatile element Zinc in CAIs show a large isotopic fractionation and enrichment in light Zn isotopes suggest that the CAI interacted with isotopically light nebular gas after formation [2]. This is thought due to a volatile depleted CAI interacting with a Zn rich nebula gas [3]. Gallium is also a moderately volatile element, but the difference in condensation temperature may allow further understanding in the environment of CAI formation and the early solar system.

Samples were analyzed using an Aligent Technologies 7900 ICP-MS for REE concentration measurement and a Thermo-Fisher Neptune Plus MC-ICP-MS for isotope measurements. We developed an ion-exchange chromatography protocol to extract and purify 100% of the Ga. This leads to reliable  $\delta^{71}\text{Ga}$  ( $^{71}\text{Ga}/^{69}\text{Ga}$  permil deviation from a standard) analysis with a precision around 0.06‰ (2SE). We will present data for 3 CAIs from Allende, various terrestrial samples (OIBs, basalt, granite, MORBs), 5 carbonaceous chondrites, 4 ordinary chondrites, and 2 enstatite chondrites.

Terrestrial samples have a narrow range of isotopic composition with statistically similar values (average  $\delta^{71}\text{Ga} = 0.01\text{\textperthousand}$ , 2SE = 0.05, n = 14). The chondrite average (carbonaceous, ordinary, enstatite)  $\delta^{71}\text{Ga} = -0.27\text{\textperthousand}$  (2SE = 0.14, n = 3) is isotopically lighter than the Earth. All 3 CAIs show a Type 2 REE pattern and all have an isotopically light value of  $\delta^{71}\text{Ga} = -0.92 \sim -3.56\text{\textperthousand}$  with a Ga concentration of 13~16ppm.

There is a clear difference between the Ga isotope composition of CAIs, chondrites and the terrestrial samples. Previous elemental studies report an enrichment of Ga on the rim of the CAIs [4, 5]. The high Ga concentration in the CAIs compared to its host meteorite (6 ppm) coupled with its large enrichments in the light isotope suggest that after that the CAIs were formed, they interacted with an isotopically light Ga-rich nebular gas prior to incorporation in to the chondrite.

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## SESSION 4

### Volatiles in Protosolar Disk and Their Delivery to Terrestrial Planets

DAY 3 – Feb.19, 2016  
8:30 am – 11:30 am

**CONDENSATION AND EVAPORATION KINETICS OF FORSTERITE UNDER PROTOPLANETARY DISK CONDITIONS.** S. Tachibana<sup>1</sup> and A. Takigawa<sup>2</sup>  
<sup>1</sup>Dept. Natural History Sci., Hokkaido Univ., <sup>2</sup>Hakubi Center for Advanced Research/Division Earth Planet. Sci., Kyoto Univ. E-mail: tachi@ep.sci.hokudai.ac.jp.

Evaporation from solid and condensation from vapor are responsible for phase transition and elemental fractionation in protoplanetary disks. Evaporation and condensation do not necessarily occur in equilibrium because pressure, temperature, and gas chemistry vary with time in protoplanetary disks. The presence of refractory components in chondrites such as CAIs and AOAs (amoeboid olivine aggregates) cannot be predicted solely by thermodynamic calculation for equilibrium condensation, and should be explained by kinetics of dust formation processes possibly with physical separation of dust particles from the reaction system. In this study, we report quantitative estimates of evaporation and condensation kinetics of forsterite ( $Mg_2SiO_4$ ), one of the major mineral species in the Solar System materials, from condensation and evaporation experiments of forsterite under protoplanetary disk conditions.

Evaporation experiments of single crystal forsterite were done at 1383 and 1317 K and hydrogen pressure of  $2 \times 10^{-5}$  bar. The evaporation conditions were close to typical temperatures and pressures of protoplanetary disks and lower than those in previous experimental studies [e.g., 1]. We obtained the evaporation coefficient, a non-dimensionless parameter representing kinetic hindrance for evaporation, of ~0.02–0.04 at 1383 and 1317 K, which is consistent with that obtained at higher temperatures [1].

Condensation experiments of forsterite were done in the system of forsterite–H<sub>2</sub>–H<sub>2</sub>O system using an infrared vacuum furnace. A mixed gas of hydrogen and water vapor (H<sub>2</sub>O/H<sub>2</sub>~0.025) was flowed into the system at a controlled rate to keep a pressure constant (~ $5.5 \times 10^{-5}$  bar). Synthetic forsterite powder in an iridium crucible was heated as a gas source. A part of evaporated gases were condensed on a substrate of platinum mesh located at a cooler region in the chamber (~1350 K). The pressure and temperature conditions during the experiment were close to those of protoplanetary disks.

The platinum mesh was fully covered with sub-micron to micron-sized condensates. Chemical compositions of condensates were consistent with stoichiometric forsterite. A variety of electron back-scattered diffraction (EBSD) patterns corresponding to crystalline forsterite were obtained from the condensates, and the condensates are thus a thin film of polycrystalline forsterite.

The supersaturation ratio for the present experiments ranged from ~15 to ~30. Based on the incoming flux of SiO onto the substrate and the ideal evaporation flux, the condensation coefficient of forsterite was evaluated to be ~0.005 at ~1350 K. The obtained condensation coefficient is much smaller than that of metallic iron [2] and similar to that for corundum [3].

We will present details of experimental results and their implication for dust formations in protoplanetary disks at the meeting.

**References:** [1] Takigawa A. et al. (2009) *Astrophys. J. Lett.* **707**, L97. [2] Tachibana S. et al. (2011) *Astrophys. J.* **736**, 16. [3] Takigawa A. et al. (2015) *Astrophys. J. Suppl.* **218**, doi:10.1088/0067-0049/218/1/2.

**ORIGIN OF VOLATILE ELEMENT DEPLETION IN EARLY SOLAR SYSTEM MATERIAL.** E. A. Pringle<sup>1</sup>, F. Moynier<sup>1</sup>, P. Beck<sup>2</sup>, R. Paniello<sup>3</sup>, and D. Hezel<sup>4</sup>, <sup>1</sup>Institut de Physique du Globe de Paris (1 rue Jussieu, 75005 Paris France; pringle@ipgp.fr), <sup>2</sup>Institut d'astrophysique et de planétologie de Grenoble, <sup>3</sup>Washington University in St. Louis, <sup>4</sup>Universität zu Köln.

Planetary materials are characterized by specific abundances of moderately volatile lithophile elements, with volatile element depletions observed in differentiated bodies and most chondrite groups when compared to CI chondrites [1]. Hypotheses for this volatile element depletion in bulk chondrites include incomplete condensation from the solar nebula, volatile loss during accretion, or mixing of distinct reservoirs consisting of a volatile-rich CI component and a volatile-poor refractory component. The stable isotope systematics of moderately volatile elements can be used to trace the origin of volatile element abundance variations among planetary materials.

Zinc is a moderately volatile element with a 50% condensation temperature of ~730 K [2]. Samples with significant volatile element depletions, including the Moon and terrestrial impact rocks, display heavy Zn isotope compositions possibly indicating Zn isotope fractionation during evaporation [3, 4]. However, Luck et al. [5] found a negative correlation between  $\delta^{66}\text{Zn}$  and  $1/\text{Zn}$  among CV, CM, CO, and CI chondrites, opposite to what is expected if evaporation was the cause of Zn abundance variations between chondrite groups, suggesting that nebular processes caused the volatile element variability in chondrites.

We have analyzed the Zn isotopic composition of an extended range of carbonaceous chondrites: CI (4), CM (4), CO (4), CV (3), CB (2), CH (2), CK (4), and CR (1). Bulk samples define a negative correlation in a  $\delta^{66}\text{Zn}$  vs Mg/Zn or Ca/Zn plot, which further confirms that Zn abundance variations between carbonaceous chondrites are not due to evaporation but rather due to nebular processes. The exceptions are CB and CH, which display Zn systematics consistent with a collisional formation mechanism that created a re-enrichment in heavy Zn isotopes relative to the trend defined by CI-CR. Therefore, Zn isotopes support the origin of CH and CB parent body by collisional accretion.

In addition, we present the first Zn isotope analyses of individual chondrules, including chondrules from Allende (CV3) and Mokoia (CV3) and an aliquot of Allende matrix. The Zn isotope data for Allende components show a chondrule-matrix complementarity, indicating that the accretion of chondrite components was a localized process. Furthermore, all chondrules exhibit light Zn isotope enrichments relative to the bulk, suggesting that the Zn depletion observed in chondrules is not due to evaporation. We suggest sulfide removal was the mechanism responsible for the Zn systematics of chondrite components.

**References:** [1] O'Neill, H. S. C. & Palme, H. 2008. Collisional erosion and the non-chondritic composition of the terrestrial planets. PTRS A 366. [2] Lodders, K. 2003. Solar System abundances and condensation temperatures of the elements. *Astrophys. J.* 591. [3] Moynier, F. et al. 2009. Isotopic fractionation of zinc in tektites. *Earth Planet. Sci. Lett.* 277. [4] Day, J. & Moynier, F. 2014. Evaporative fractionation of volatile stable isotopes and their bearing on the origin of the Moon. PTRS A 372. [5] Luck, J. M., et al. 2005. Zn and Cu isotopic variations in chondrites and iron meteorites: Early solar nebula reservoirs and parent-body processes. *GCA* 69.

**DECODING THE R CHONDRITE RECORD OF A VOLATILE-RICH ENVIRONMENT.** K. E. Miller<sup>1\*</sup>, D. S. Lauretta<sup>1</sup>, H. C. Connolly Jr.<sup>1,2</sup>, K. Nagashima<sup>3</sup>, and K. Domanik<sup>1</sup>, <sup>1</sup>University of Arizona, Tucson, AZ 85721, USA. <sup>2</sup>Kingsborough Community College, Brooklyn, NY 11235, USA and The Graduate Center of CUNY. <sup>3</sup>University of Hawai'i at Manoa, Honolulu, HI 96822, USA.

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The Rumuruti (R) chondrites are distinguished by their high oxidation state [1], high sulfidation state [2, 3], and high bulk  $\Delta^{17}\text{O}$  values [4, 5]. Together, these traits suggest interaction with a distinctive volatile-rich environment. Most R chondrites are thermally or hydrothermally altered, with petrologic types commonly above 3.6. Previous work on primitively textured R chondrite clasts indicate a highly heterogeneous parent body [6], with chondrule oxygen isotopes that are most closely related to the ordinary chondrites [7-10]. Our recent work on unequilibrated (type  $\leq 3.2$ ) material in two thin sections clarifies the setting of the volatile enhancement recorded by the R chondrites.

The material is from thin sections 19 and 21 of Antarctic meteorite Mount Prestrud (PRE) 95404. The primitive texture, unequilibrated chemistry, dark, fine-grained matrix, and preservation of glassy mesostasis suggest minimal parent body alteration. Chondrules include both FeO-rich ( $> 10$  wt.%) and FeO-poor ( $< 10$  wt.%) members. Non-porphyritic chondrules include cryptocrystalline and barred olivine. The average chondrule size is  $308 \mu\text{m}$  in thin section 19, and  $413 \mu\text{m}$  in thin section 21. The clasts are consistent with accretion of oxidized and reduced components.

Both thin sections contain abundant sulfide assemblages. These assemblages average  $\sim 200 \mu\text{m}$  in diameter, and are nearly as numerous as the silicate chondrules. They are composed of pentlandite, pyrrhotite, and accessory iron oxide. Cu-rich and Ca-P-rich inclusions are common. Assemblage morphology is rounded. In both thin sections, multiple sulfide assemblages have concave shapes that are filled by silicate grains or chondrules, similar in appearance to compound chondrules. We hypothesize that the sulfide assemblages originated as pre-accretionary, molten droplets, and that the compound objects formed during collisions above the solidus temperature. There is one instance of deformation of a silicate chondrule in a sulfide-silicate compound.

We will present isotopic, petrologic and thermodynamic data constraining the formation environment for silicate chondrules and sulfides in the R chondrites.

- [1]K. Righter, K. E. Neff. *Polar Science* 1, 25-44 (2007).
- [2]M. C. McCanta *et al.* *GCA* 72, 5757-5780 (2008).
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- [5]A. Bischoff, N. Vogel, J. Roszjar. *Chemie der Erde-Geochemistry* 71, 101-133 (2011).
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- [9]N. T. Kita, T. J. Tenner, D. Nakashima, T. Ushikubo, A. Bischoff, 76th Annual MetSoc, 2013 2013.
- [10]N. T. Kita *et al.*, *LPSC XLVI*, 2015 2015.

**A KINETIC STUDY ON HYDROUS MINERAL FORMATION REACTION BETWEEN AMOPHROUS SILICATE FORSTERITE AND WATER VAPOR IN PROTOPLANETARY DISKS.** D. Yamamoto<sup>1</sup>. S. Tachibana<sup>1</sup>, <sup>1</sup>Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan (daiki@ep.sci.hokudai.ac.jp).

Hydrous silicates formed by a reaction between anhydrous silicate and water vapor are one of the possible water carriers to the rocky planet forming region because hydrous silicates are thermodynamically stable at  $\sim 250$ - $225$  K in protoplanetary disks. Prinn and Fegley (1989) explored this possibility through the Simple Collision Theory (SCT) with the activation energy of MgO hydration, which yielded  $\sim 70$  kJ/mol. It was concluded that the reaction between anhydrous crystalline Mg-silicate and water vapor is too sluggish to occur within the lifetime of protoplanetary disks. Infrared observations and investigations of extraterrestrial materials have shown that both crystalline and amorphous silicate dust exist as primary solids in protoplanetary disks. Amorphous silicates are thermodynamically unstable and may thus react with water vapor more effectively and/or rapidly than crystalline silicates. In this study, in order to explore the possibility of hydrous mineral formation by the reaction between amorphous silicates and water vapor in protoplanetary disks, we performed reaction experiments between amorphous forsterite and water vapor at relatively low temperatures and water vapor pressures.

Gas-solid reaction experiments were carried out using an autoclave with an inner capsule at 323-373 K and water vapor pressure ( $P_{\text{H}_2\text{O}}$ ) of  $\sim 0.1$ -1 bar for 0.5-60 hours. The starting material was 10-100 nm-sized amorphous forsterite powder synthesized by a thermal plasma method. Run products were analyzed with FT-IR and XRD.

Infrared spectra of run products showed that  $10 \mu\text{m}$  broad feature attributed to Si-O stretching vibration in amorphous have gradually changed to sharp features as the reaction proceeded. We also found the gradual development of  $\sim 2.7 \mu\text{m}$  sharp feature, which is assigned to free -OH stretching vibration of hydrous mineral(s). The XRD pattern of run products changed the original halo peak of amorphous forsterite to those of serpentine polymorphs and brucite. Quantitative analysis of the serpentinization degree was made based on the spectral fitting at  $\sim 10 \mu\text{m}$  and the development of the free -OH stretching vibration. The time evolution of the serpentinization degree was fitted with the Johnson-Mehl-Avrami (JMA) equation and the equation of interface-controlled reaction.

The reasonable fit of experimental data by the JMA equation with Avrami exponent  $n \sim 1$  and the equation of interface-controlled reaction suggests the reaction is controlled by the hydrous mineral formation reaction at the interface between amorphous forsterite and hydrous phases. The activation energy of the rate constant for serpentinization are  $\sim 21$  kJ/mol and  $\sim 16$  kJ/mol for the spectral evolution at  $\sim 10$  and  $\sim 2.7 \mu\text{m}$ , respectively.

When the obtained activation energies are applied to the SCT by Prinn and Fegley (1989), amorphous forsterite may hydrate to form serpentine and brucite within the lifetime of protoplanetary disks ( $< 10$  Myr) at the total pressure of solar nebula of  $10^{-3}$  bar, which will be discussed in more detail in the presentation.

*Reference:* Prinn R. G. and Fegley B. J. (1989) In *Origin and Evolution of Planetary and Satellite Atmospheres* (Eds. S. Atreya et al.). Univ. Arizona Press. Tucson.

**DATING THE EARTH-LIKE RESERVOIR FORMATION IN THE SOLAR NEBULA WITH ENSTATITE CHONDRITE.** Q.-Z. Yin<sup>1</sup>, E. Gaidos<sup>2</sup>, M. E. Sanborn<sup>1</sup>, and Shijie Li<sup>3</sup>. <sup>1</sup>Dept. Earth & Planet. Sci., Univ. of California, Davis, CA 95616, (qyin@ucdavis.edu), <sup>2</sup>Dept. Geol. & Geophys., Univ. of Hawai'i at Manoa, Honolulu, HI 96822. <sup>3</sup>Institute of Geochemistry, CAS, Guiyang, China

Here we report the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age of chondrules extracted from the most primitive EH3-type enstatite chondrite, *Qingzhen*, one of the most reduced meteorites, well known for its Si-bearing metal, and sulfide phases that contain typically lithophile elements. The  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  isochron obtained for *Qingzhen* gives an initial  $^{53}\text{Mn}/^{55}\text{Mn}$  of  $(3.69 \pm 1.08) \times 10^{-6}$  and  $\epsilon^{53}\text{Cr}_i = -0.11 \pm 0.08$  (MSWD = 0.44). Relative to the D'Orbigny age anchor with its U isotope-corrected Pb-Pb age (Amelin, 2008; Brennecke and Wadhwa, 2012) and its precise  $^{53}\text{Mn}/^{55}\text{Mn}$  (Glavin et al., 2004; Yin et al., 2009), we obtain a  $4,564.8 \pm 1.6$  Ma formation age of *Qingzhen*'s chondrules.

Unlike Allende (CV3) chondrules (Yin et al., 2009), the  $\epsilon^{54}\text{Cr}$  anomaly of each individual chondrule in *Qingzhen* is uniform and Earth-like (with an average  $\epsilon^{54}\text{Cr} = 0.12 \pm 0.14$ ). Enstatite chondrites (ECs) and enstatite achondrites (aubrites) are remarkable in their isotopic similarity, as well as their chemical dissimilarity to Earth (*c.f.* Gaidos and Yin 2015). We argue that our *Qingzhen* chondrule  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age dates the Earth-like pre-planetary reservoir formation/isolation in the solar nebula, which is distinct isotopically from most materials in the inner Solar System. Isotopic homogeneity of this reservoir is clearly established at both micro- and macroscopic levels by  $4,564.8 \pm 1.6$  Ma. Because our  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age and a few other established sulfide ages of ECs and aubrites (Wadhwa et al., 1997; Guan et al., 2007; Telus et al., 2007) all precede the Moon-forming giant impact (Yin et al., 2002; Kleine et al., 2009) and the fact that post-impact Earth and the Moon are isotopically very similar to ECs and aubrites, the impactor *Theia* must also have been isotopically very similar to ECs and Earth. Otherwise, the post-giant impact Earth and the Moon would deviate isotopically from that of ECs. Likewise, the isotopic similarity of Earth and ECs and the Earth's unique end-member position in multi isotopic space constrains the amount of any non-enstatite-like material accreted either before or after core closure (Dauphas et al., 2004; Fischer Goeddele et al., 2015).

We infer that the closure of the Earth/EC-like isotopic reservoir by  $4,564.8 \pm 1.6$  Ma represents the formation of Jupiter and the clearing of the disk immediately outside the terrestrial planet formation zone, as well as excitation of planetesimals. This is consistent with the latest observations and models. We suggest that the EC reservoir deviated at  $4,564.8 \pm 1.6$  Ma, or shortly thereafter, from that of the Earth's chemically, by SiO/SiS gas interactions with solids (Lehner et al., 2015), creating its unique chemistry, explaining its low  $\delta^{30}\text{Si}$  and low Mg/Si ratio (Dauphas et al., 2015). The processes responsible for changes in EC chemistry must be a local phenomena, as it did not affect the bigger reservoir represented by the bulk Earth composition. Existing  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  dates on sulphide phases in ECs (e.g. Telus et al., 2012) tend to be much later than  $4,564.8 \pm 1.6$  Ma. However, the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  systematics in sulphides could be affected by parent body processes, whereas SiO/SiS gas interaction with solids which changed the EC chemistry could not have occurred on a parent body.

**LIFETIME OF THE SOLAR NEBULA AND NEBULAR MAGNETIC FIELD.** B. P. Weiss<sup>1</sup>, H. Wang<sup>1</sup>, R. Fu<sup>2</sup>, B. Downey<sup>1</sup>, X. Bai<sup>3</sup>, <sup>1</sup>Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA, <sup>2</sup>Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA, <sup>3</sup>Institute for Theory and Computation, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, USA.

A key stage in planet formation is the evolution of a gaseous and magnetized solar nebula and protoplanetary disk. The solar nebula magnetic field is thought to play an important role in stellar accretion and the formation of the first solids, but its lifetime is poorly constrained. Here we present paleomagnetic analyses of volcanic angrites demonstrating that they formed in a near zero-field ( $<0.1$   $\mu\text{T}$ ) environment  $\sim 4$  million years (My) after the formation of calcium-aluminum-rich inclusions (CAIs). Combined with our paleomagnetic analyses of LL and CR chondrules, this indicates that the solar nebula field, and likely the nebular gas itself, dispersed sometimes between 2.5 and 4 My after CAI formation. This implies that accretion of the Sun and gas giants was largely complete by this time and favors formation of younger chondrules by planetesimal collisions over nebular shocks and electric currents. Our data also indicate that the onset of the core dynamo on the angrite parent body was delayed until between  $\sim 4$ -11 My after solar system formation, consistent with thermal blanketing of planetesimal cores by  $^{26}\text{Al}$ -enriched mantles.

**ONSET OF AN “EARLY HEAVY BOMBARDMENT”  
OF THE INNER SOLAR SYSTEM.** S.J. Mojzsis<sup>1,2</sup>, R.

Brasser<sup>3</sup> and S. Werner<sup>4</sup>, <sup>1</sup>Collaborative for Research in Origins (CRIo), Department of Geological Sciences, University of Colorado, 2200 Colorado Avenue, Boulder, Colorado 80309-0399 USA (mojzsis@colorado.edu),

<sup>2</sup>Institute for Geological and Geochemical Research, Research Center for Astronomy and Earth Sciences, Hungarian Academy of Sciences, Budapest, Hungary,

<sup>3</sup>Earth-Life Science Institute, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan, <sup>4</sup>Centre for Earth Evolution and Dynamics, University of Oslo, Norway.

Nectarian, Tolstojan and Noachian (pre-3900 Ma) terranes are the oldest and most heavily cratered on the Moon, Mercury and Mars, respectively. The latter two have crater densities vs. time comparable to the ancient highlands of the Moon as established from direct sampling in the Apollo and Luna missions; all three bodies were heavily bombarded during the first 600 Myr of the Solar System. Post-formation accretion impact bombardment has been suggested to follow a “Sawtooth” intensity profile, but its precise timing remains elusive. From high-precision U-Pb zircon and apatite-merrillite-whitlockite geochronology of lunar rocks, martian and Vestoid and other asteroidal meteorites, NASA MSL Curiosity radiometric age estimates and an updated martian crater chronology, we show that the inner Solar System experienced not one but two intense episodes of bombardment well after the primary formation stage of the terrestrial planets. From the thermal and mechanical records of impact re-setting of U-Pb systems on the Moon, Mars and Vesta, we determine the onset of the Early Heavy Bombardment (EHB) to be at ca. 4240 Ma. This “Early Heavy Bombardment” lasted about 200 Myr, and culminated in the “Late Heavy Bombardment” (LHB) at 3950–3850 Ma. We argue that this double profile was caused by an episode of late giant planet migration followed by depletion of impactor sources (left-over planetesimals, E-belt and Main Belt asteroids, in that order). The LHB principally tapped the innermost (E-Belt) region of the asteroid belt. The age of the EHB pushes the surface age estimates of Mars and Mercury back by another 200 Myr from current estimates.

**OSIRIS-REx SAMPLE COLLECTION REQUIREMENT: TEMPERATURE AND VOLATILES.** H. C. CONNOLLY Jr<sup>1,2,3</sup>, D. S. LAURETTA<sup>3</sup> and OSIRIS-REx Sample Analysis Team  
<sup>1</sup>Dept. of Physical Sciences, Kingsborough Community College of CUNY Brooklyn NY, NY 11235 USA and Earth and Environmental Sciences, The Graduate Center of CUNY, 365 5<sup>th</sup> Ave, NY, NY 10016 USA (hconnolly@gc.cuny.edu), Dept. Earth and Planetary Sciences, American Museum of Natural History, Central Park West, NY, NY USA. <sup>3</sup>Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, USA.

## SESSION 5

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

DAY 3 – Feb.19, 2016  
4:30 pm – 7:20 pm

NASA's New Frontiers 3 asteroid sample return mission, OSIRIS-REx (O-REx), will return a minimum of 60 g and up to 2 kg of pristine asteroid regolith. The target asteroid, Bennu, is a spectral type B and hypothesized to be carbonaceous chondrite-like (1). The O-REx mission has a level 2 requirement to maintain the temperature of the collected sample to  $\leq 75$  C from collection through to Earth return. This requirement levees an important constraint on the mission: If sample collection occurs close to or at asteroid perihelion, the TAGSAM collector head may reach temperatures  $> 75$  C after collection due to direct exposure to solar radiation, thus violating the mission temperature requirement.

The O-REx temperature requirement is generated from the science team and based on the analyses of analog (to Bennu) chondrites that have shown the behavior of labile elements during heating experiments (2,3). However, the database on the behavior labile elements during heating events within carbonaceous chondrites is fairly limited. One major confining factor within the community at large for investigating these elements may have been the lack in applicability of the data to practical problems in the field. With the return of samples from Itokawa by Hayabusa and the future return of asteroid samples by Hayabusa2 and O-REx, understanding in detail behavior of labile elements is now a science issue propelled to the forefront.

It has been shown (2,3) that heating Murchison to  $\sim 100$  C begins to affect the bulk composition, with a release of S from a yet unknown phase, with maximums at 300 and 600 C. At  $> 200$  C Se begins to release from a yet unknown phase. According to (1), based on VIR data, CM or CI chondrites may be the most analogous chondrite types to Bennu. Thus, the level 2 requirement for O-REx is directly based on the results of (3). A major science question that needs to be addressed in the future is to determine what phases are the source(s) of S and Se, along with other labile element.

Finally, the O-REx Design Reference Asteroid (4) defines the average surface temperature at the equator of Bennu at be  $\sim 77$  C with a maximum at perihelion slightly above 100 C. Therefore, why does the O-REx mission impose the level 2 temperature requirement on the collection and storage of the sample? It is entirely possible that the collector will penetrate the subsurface regolith and thus collect cooler regolith that could be richer in organic and other volatiles compared with the current surface that is directly exposed to solar radiation.

References: (1) Clark B. E. et al., (2011) *Icarus* **216**, 462-475. (2) Goreva J. S. and Lauretta D. S. (2005) *LPCS* #1462. (3) Lauretta et al. (2001) *LPSC* #1356. (4) Hergenrother C. W. et al., (2014) *Earth and Planetary Astrophysics*, arXiv:1409.4704.

**OBSERVATION OF WATER AND ORGANICS IN CORBONACEOS CHONDTRITES IN 3D USING SCANNING-IMAGING X-RAY MICROSCOPY: DEVELOPMENT OF A NEW TECHNIQUE.** A. Tsuchiyama<sup>1</sup>, A. Takeuchi<sup>2</sup>, K. Uesugi<sup>2</sup>, Y. Suzuki<sup>2</sup>, T, Nakano<sup>3</sup>, A. Miyake<sup>1</sup>, J. Matsuno<sup>1</sup> and M. E. Zolensky<sup>4</sup>, <sup>1</sup>Graduate School of Science, Kyoto University, <sup>2</sup>JASRI/SPring-8, <sup>3</sup>AIST/GSJ, <sup>4</sup>NASA/JSC.

In order to search for fluid inclusions in carbonaceous chondrites, we have developed a nondestructive technique using X-ray absorption micro-tomography combined with FIB micro-sampling [1]. We found fluid inclusion candidates in micron-size in calcite grains, which were formed by aqueous alteration. However, we could not determine from the absorption contrast images whether they are really aqueous fluids or merely voids.

Phase and absorption contrast images can be simultaneously obtained in 3D by using a new technique named scanning-imaging x-ray microscopy (SIXM) [2]. The phase contrast may enable us to discriminate water from void. Organic materials may also be discriminated by this technique as well as some mineral identification. This technique has potential availability for Hayabusa-2 sample analysis.

In this study, we observed standard materials by SIXM to check quantitative phase and absorption contrasts and the spatial resolution. We also applied this technique to carbonaceous chondrite samples.

Complex refractive index can be expressed by  $n=1-\delta+i\beta$ , where the real part,  $1-\delta$ , is the refractive index with refractive index decrement,  $\delta$ , which is nearly proportional to the density, and the imaginary part,  $\beta$ , is the extinction coefficient, which is related to the liner attenuation coefficient,  $\mu$ . The phase and absorption contrast images in SIXM can be regarded as spatial distributions of  $\delta$  and  $\mu$ , respectively. As  $\mu = 0.0, 10.4$  and  $204.3 \text{ cm}^{-1}$  at  $8 \text{ keV}$  for air, water and calcite, respectively, for example, it is hard to discriminate between air and water. In contrast,  $\delta \times 10^6 = 0.00, 3.62$  and  $8.88$ , respectively, which makes easy to discriminate between them. If we compare  $\mu$  and  $\delta$  in SIXM images, many phases can be identified.

We used POM ( $[\text{CH}_2\text{O}]_n$ ), silicon, forsterite, corundum, magnetite and nickel as standard materials for  $\mu$  and  $\delta$  quantitative performance test. A fluid inclusion in terrestrial quartz and bivalve shells (*Atrina vexillum*), which are composed of calcite and organic layers with different thickness, were also used for the spatial resolution test. The Ivuna (CI), Sutter's Mill (CM) and Tagish Lake meteorites were also used as carbonaceous chondrite samples.

A rod- or cube-shaped sample ( $20\text{-}30 \mu\text{m}$  in size) was extracted mostly from a polished thin section, which was previously observed with SEM, by using FIB. Then, the sample was attached to a thin W-needle and imaged by an SIXM system at beamline BL47XU, SPring-8, Japan. The slice thickness was  $109 \text{ nm}$  and the pixel size was mostly  $100 \text{ nm}$ .

In preliminary results, we found almost linear relation between the  $\mu$  and  $\delta$  values obtained by SIXM and their theoretical values, respectively, with a proportional coefficient of  $\sim 0.9$ . We can identify an organic layer about  $3 \mu\text{m}$  thick in the shell by its  $\delta$  value but not about  $300 \text{ nm}$  thick. The results including carbonaceous chondrites will be given.

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**SIMULTANEOUS IRON AND NICKEL ISOTOPE ANALYSES WITH CHILI.** R. Trappitsch<sup>1,2,\*</sup>, T. Stephan<sup>1,2</sup>, M. J. Pellin<sup>1,2,3,4</sup>, M. R. Savina<sup>1,5</sup>, and A. M. Davis<sup>1,2,4</sup>, <sup>1</sup>Chicago Center for Cosmochemistry, <sup>2</sup>Department of the Geophysical Sciences, The University of Chicago, <sup>3</sup>Materials Science Division, Argonne National Laboratory, <sup>4</sup>Enrico Fermi Institute, The University of Chicago, <sup>5</sup>Physical and Life Sciences Division, Lawrence Livermore National Laboratory. \*trappitsch@uchicago.edu

**Introduction:** The CHICAGO Instrument for Laser Ionization (CHILI) is a resonance ionization mass spectrometer designed to analyze trace element isotopic composition and elemental abundances with a lateral resolution of  $\sim 10 \text{ nm}$  and a useful yield of  $\sim 40\%$  [1]. CHILI uses six tunable Ti:sapphire lasers to resonantly ionize up to three elements simultaneously and avoid isobaric interferences. The goal of this study is to measure Fe and Ni isotopes in presolar grains that condensed in the vicinity of dying stars. These isotopes can be used as proxies for galactic chemical evolution for grains that formed around asymptotic giant branch stars. In grains originating from supernovae, Fe and Ni isotopes can be used to constrain the stellar nucleosynthesis.

**Methods:** We developed ionization schemes for Fe and Ni isotopes that use three photons each [2]. CHILI measures the sample at a repetition rate of  $1 \text{ kHz}$ . One shot consists of first desorbing material from the sample surface using a  $351 \text{ nm}$  desorption laser and electrostatically ejecting the prompt secondary ions. The ion optics are then brought to extraction potential, and, subsequently, the ionization lasers fire and resonantly ionize neutral Fe and Ni atoms above the sample surface. The photoions then travel through a time-of-flight (TOF) mass spectrometer and are detected with a microchannel plate. The start signal for the TOF measurement is given by the ionization laser pulse. Delaying the Ni ionization lasers by  $200 \text{ ns}$  relative to the Fe ionization lasers allows separation of  $^{58}\text{Fe}$  from  $^{58}\text{Ni}$  so that all nuclides of interest can be measured without isobaric interferences. The CHILI control software allows each shot to be recorded individually, which will help to correct for dead time effects resulting from variabilities in the laser desorption process. As done for atom probe tomography [3], we are exploring using correlated events from different isotopes in individual shots as a dead time correction method.

**Results:** We previously reported presolar grain data for Zr, Sr, and Ba measured with CHILI [4]. For Fe and Ni, we found that we fully saturate all laser transitions and that the isotopic ratios are stable. For standards,  $\delta$ -values for all even-numbered isotopes are zero within uncertainty when comparing standards with isotopic ratios from the literature. Odd-numbered isotopes show the well-known odd-even effect from laser ionization. Uncertainties are a few  $\text{\AA}$  ( $2\sigma$ ).

**Conclusion and Outlook:** Presolar SiC grains will be measured for their Fe and Ni isotopic composition in the next few weeks. Within the next few months, we will also study Fe and Ni isotopic anomalies in hibonite grains that show  $^{50}\text{Ti}$  anomalies and will constrain the initial  $^{60}\text{Fe}$  abundance in chondrules. The capability to measure isotopic compositions of trace elements at high spatial resolution is furthermore critical for samples brought back from space by the Genesis, Hayabusa, and Stardust missions, as well as future samples from Hayabusa 2 and OSIRIS-REx.

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## LIMAS: TUNNEL-IONIZATION TIME-OF-FLIGHT SPUTTERED NEUTRAL MASS SPECTROMETER.

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**Introduction:** Secondary ion mass spectrometry (SIMS) is considered to be an extremely sensitive, micro-area analytical technique of solid surfaces. Quantification of He is often difficult, however, because of the extremely low secondary-ionization yields for He due to its high ionization energy [1-3]. Recently, sputtered neutral mass spectrometry (SMNS) successfully measured the depth-profile distribution of solar wind helium from a NASA Genesis target [3]. They used a unique SMNS instrument called LIMAS (laser ionization mass nanoscope) applied strong-field tunnel ionization to detect He neutrals sputtered from a  $\sim 1 \mu\text{m}^2$  area of the surface.

**Instrumental setup and performances:** LIMAS consists of a liquid metal ion source and an aberration corrector for sputtering of nanometer scale area on samples, a femtosecond laser for tunneling-ionization of the sputtered neutrals, and a multi-turn time-of-flight (TOF) mass spectrometer for isotope analysis [5].

A fine Ga primary ion beam down to 8 nm is carried out by an aberration corrector installed in the primary ion optics column. The aberration corrector corrects chromatic and spherical aberrations. The femtosecond laser beam was focused to a diameter of  $\sim 50 \mu\text{m}$  above the sample surface achieving a power density of  $\sim 10^{20} \text{ W m}^{-2}$ . Ionization efficiency for sputtered neutrals by the laser are achieved to about 10% for He and about 100% for other all elements due to tunneling effect by the strong field.

A multi-turn time-of-flight mass spectrometer, MULTUM II [6], is equipped with LIMAS. MULTUM II is designed to achieve perfect space and time focusing ion optics for a multi-turn TOF mass spectrometer. Flight path lengths of ion species are expanded by using multi-turning on the same trajectory in MULTUM II under the constant temporal width of the ion packet. Mass-resolving power of 620,000 is achieved at TOF of 5 ms corresponding to flight path length of 1.3 km. The measured useful yields for Si are  $2 \times 10^{-3}$  at the high mass-resolving power.

Ion detection system consists of microchannel plates, preamplifier and 3 GHz 8 bit digitizer. The pulse width of single ion signal is 1.3 ns for the TOF mass spectrum. The system can quantifies up to 10 ions in an ion packet with time resolution of 0.2 ns. The performances are enough to acquire mass spectrum and can process data in real-time.

We conclude that LIMAS is an instrument with satisfactory high mass-resolving power and a high useful yield for microanalysis.

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## EVALUATION FOR MULTI-TURN TIME OF FLIGHT MASS SPECTRUM OF LASER IONIZATION MASS NANOSCOPE.

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**Introduction:** A sputtered neutral mass spectrometer (SNMS) called LIMAS [1] was developed for measuring solar wind particles from extraterrestrial materials collected by planetary exploration missions, such as JAXA Hayabusa and NASA Genesis [2]. LIMAS consists of a Ga liquid metal ion source and an aberration corrector for sputtering of nanometer scale area on samples, a femtosecond laser for tunneling-ionization of the sputtered particles, and a multi-turn time-of-flight mass spectrometer (MULTUM II) for isotope analysis. We have evaluated the performance of MULTUM II equipped with the ion injection optics of LIMAS.

**Experimental procedure:** We carried out numerical simulations of ion trajectories in the ion injection optics from a sample surface for calculating load voltages for the lenses. The ion trajectories were simulated by using SIMION 8.1 (Scientific Instrument Service, Inc.). We investigated the relationship between the loading voltages of L1 and L2 of extraction lenses for obtaining optimal parameter in LIMAS. Finally, we evaluated mass resolving power and transmittance of LIMAS using the optimal parameters.

**Results and Discussion:** Ion intensities as a function of L1 and L2 voltages are similar to the simulation results, indicating that the characteristics of the ion injection optics are basically designed by the simulation. From both results, we determined voltages -700 V for L1 and -3300 V for L2 as optimal parameter for extraction lenses of LIMAS.

Mass-resolving power increased up to the TOF of 1000  $\mu\text{s}$  (200 multi-turn cycles). After 1000  $\mu\text{s}$ , mass-resolving power became saturated. Saturation of the mass-resolving power ( $R = \sim 10^5$ ) indicates that the averaged peak width increases linearly with increasing the number of cycles. Averaged peak-width consists of single spectra with different TOF in each cycle, which depends on modulations of the acceleration voltage, the injection timing for the ion injection optics, and the electric field for the electric sectors in MULTUM II. Therefore, we developed mass calibration methods for correcting those modulations. The mass calibration introduce that the mass-resolving power of LIMAS increased linearly with increasing the flight path length, and reached 620,000 (FWHM) at 1,000 multi-turn cycles of MULTUM II (flight path length: 1,312 m).

The transmittance of LIMAS decreased to 60–70% after 20 multi-turn cycles of MULTUM II, compared with the linear mode transmittance. The transmittance per multi-turn cycle became constant (99.96%) after 20 multi-turn cycles. A useful yield of  $3 \times 10^{-3}$  for Si ions was obtained for LIMAS at 30 multi-turn cycles of MULTUM II. The calculated useful yields for LIMAS are comparable to those for Cameca ims 6f of  $7 \times 10^{-3}$  [3].

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**DEPTH PROFILING ANALYSIS OF SOLAR WIND HELIUM COLLECTED IN DIAMOND-LIKE CARBON FILM FROM GENESIS.** K. Bajo<sup>1</sup>, C. T. Olinger<sup>2</sup>, A. J. G. Jurewicz<sup>3</sup>, D. S. Burnett<sup>4</sup>, I. Sakaguchi<sup>5</sup>, T. T. Suzuki<sup>5</sup>, S. Itose<sup>6</sup>, M. Ishihara<sup>7</sup>, K. Uchino<sup>8</sup>, R. Wieler<sup>9</sup>, and H. Yurimoto<sup>1</sup>. <sup>1</sup>Department of Natural History Sciences, Hokkaido University, IIL, Sapporo 001-0021, Japan. <sup>2</sup>Applied Modern Physics Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA. <sup>3</sup>CMS/SESE, Arizona State University, Tempe, AZ 85287-1404, USA. <sup>4</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA. <sup>5</sup>National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan. <sup>6</sup>JEOL Ltd., Musashino, Akishima, Tokyo 196-8558, Japan. <sup>7</sup>Department of Physics, Osaka University, Toyonaka, Osaka 560-0043, Japan. <sup>8</sup>Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan. <sup>9</sup>Institute for Isotope Geology and Mineral Resources, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland.

NASA's *Genesis* mission collected samples of solar wind that can be analyzed with high precision in laboratories with the ultimate goal of determining the composition of the sun and the solar nebula from which it was formed [1].

In this study, we used a sputtered neutral mass spectrometry using strong-field ionization to measure He profiles in *Genesis* collectors. We can depth-profile because our instrument can quantify <sup>4</sup>He present at tens of ppma by analyzing an area of a solid surface only a few-microns in size. Here we report depth distribution profile of solar wind <sup>4</sup>He from a *Genesis* collector, a diamond-like carbon film on a silicon (DOS) wafer [2].

A volume of  $2.5 \times 4 \mu\text{m}^2$  and 140 nm in depth was measured for the depth profiling. The peak concentration of implanted solar wind <sup>4</sup>He was about  $2.2 \times 10^{20} \text{ cm}^{-3}$  at ~20 nm in depth. The implantation profile was traced to 100 nm in depth until the blank level was reached. The blank of He was  $\sim 3 \times 10^{18} \text{ cm}^{-3}$ . The solar wind He fluence calculated using depth profiling is  $\sim 8.5 \times 10^{14} \text{ cm}^{-2}$ . The shape of the solar wind <sup>4</sup>He depth profile is consistent with TRIM [3] simulations using the observed <sup>4</sup>He velocity distribution during the *Genesis* mission. It is therefore likely that all solar-wind elements heavier than H are completely intact in this *Genesis* collector and, consequently, the solar particle energy distributions for each element can be calculated from their depth profiles. Ancient solar activities and space weathering of solar system objects could be quantitatively reproduced by solar particle implantation profiles when we measure natural sample surface irradiated by solar wind, such as Moon regolith grains and Itokawa particles.

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