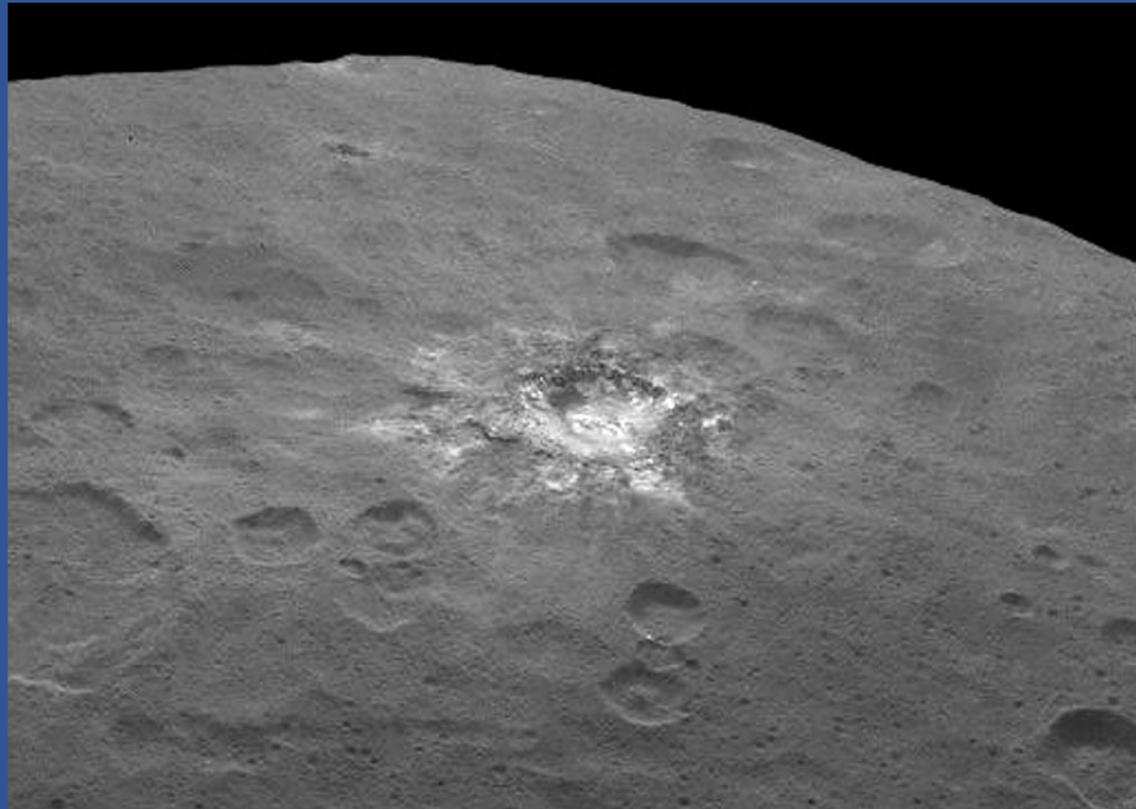


# CARBONACEOUS LITHOLOGIES FROM OUTER SOLAR SYSTEM BODIES IN METEORITE REGOLITH BRECCIAS

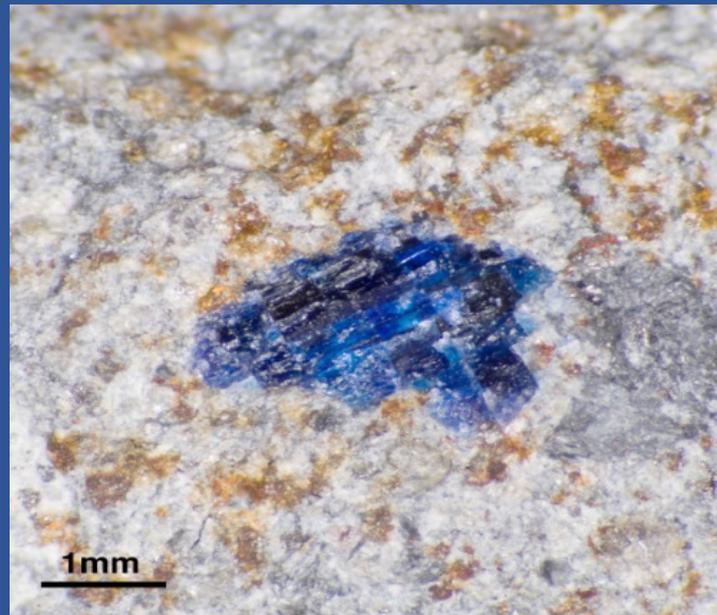
Mike Zolensky  
Queenie H.-S. Chan  
Yoko Kebukawa  
Andrew Steele  
Bob Bodnar  
Cyrena Goodrich  
Qing-Zhu Yin  
Matt Sanborn  
Yoshi Yurimoto  
Motoo Ito  
Daisuke Nakashima  
Shoichi Itoh  
Karen Ziegler  
Bill Bottke  
Jess Johnson  
Richard Greenwood  
Peter Jenniskens  
Marc Fries  
Anna Fiorelli  
Brent Turrin  
Bob Clayton



# Halite in Monahans (H5) and Zag

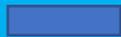


Dated by K-Ar, Rb-Sr and I-Xe systematics to be ~4.5 billion years old (Zolensky et al. 1999; Whitby et al. 2000; Bogard et al., 2001)

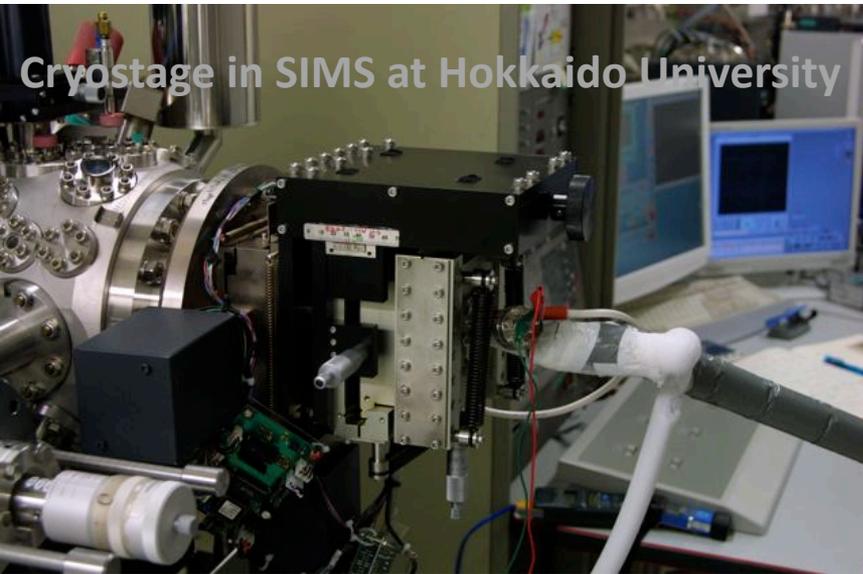




10  $\mu\text{m}$



# SIMS Measurements by Shoichi Itoh and Yoshi Yurimoto



We waited 10 years to find a collaborator to put a freezing stage inside of their SIMS

# SIMS Measurements by Shoichi Itoh and Yoshi Yurimoto

**Lines are expected mixing lines between cometary (or interstellar) water and ordinary chondrite**

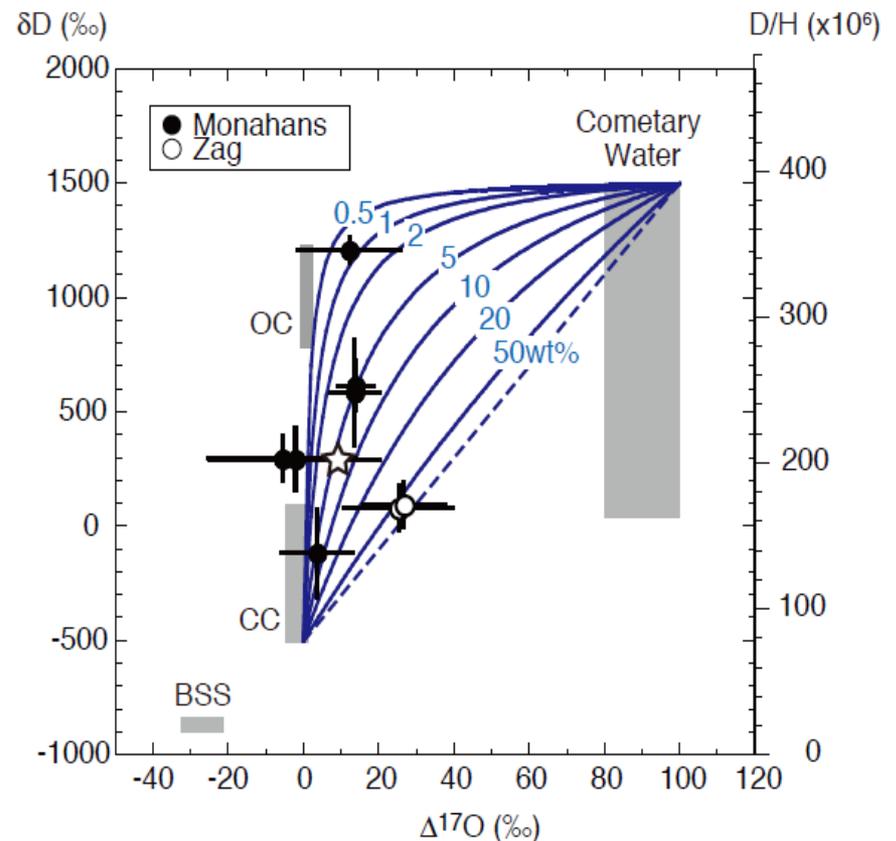
**CC: phyllosilicates of carbonaceous chondrites**

**OC: phyllosilicates of ordinary chondrites**

**Comet: comet coma water**

**Interstellar: Interstellar water components in ordinary chondrites**

**BSS: bulk solar system**



Yurimoto et al., 2014

# Solid Inclusions – first spotted by SIMS and Raman



Marc Fries



Steelie

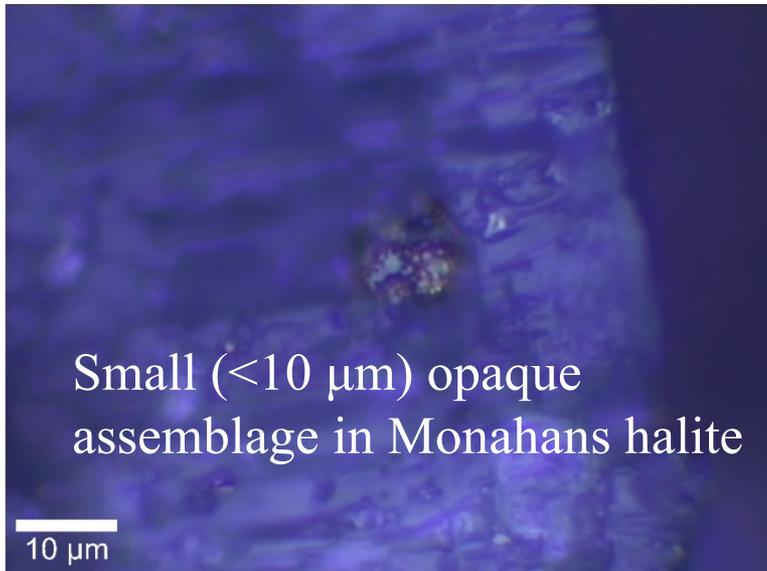


Queenie Chan

Solid inclusions are abundant in the Monahans and Zag halite.

These were entrained within the brines during eruption, and should include unaltered protolith rocks from the rocky mantle and surface of the halite parent object

The solid inclusions include **abundant and widely variable organics** *which cannot have been significantly heated after formation of the halite* (which would have resulted in the loss of fluids from the halite)



Small (<10 μm) opaque assemblage in Monahans halite

10 μm

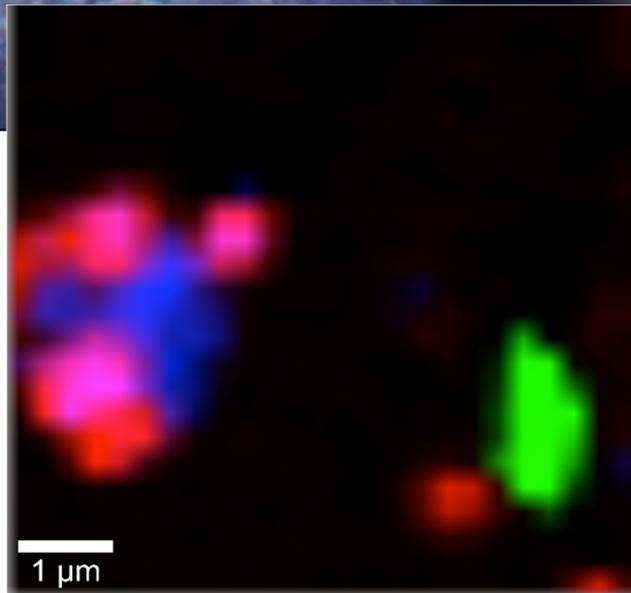
# Inclusion Mineralogy by Confocal Raman Microspectroscopy



Typical inclusion on the left from  
Monahans halite

Overall mineralogy **Not consistent with  
H chondrite mineralogy**

**Halites came from elsewhere!**

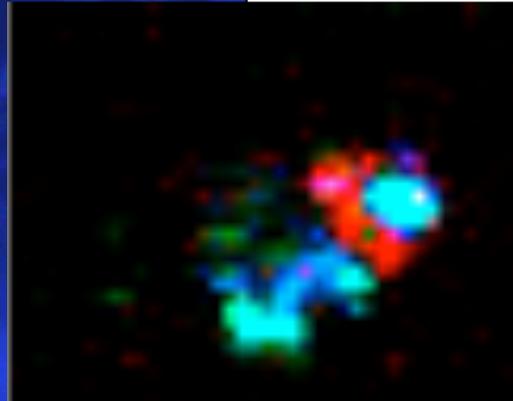
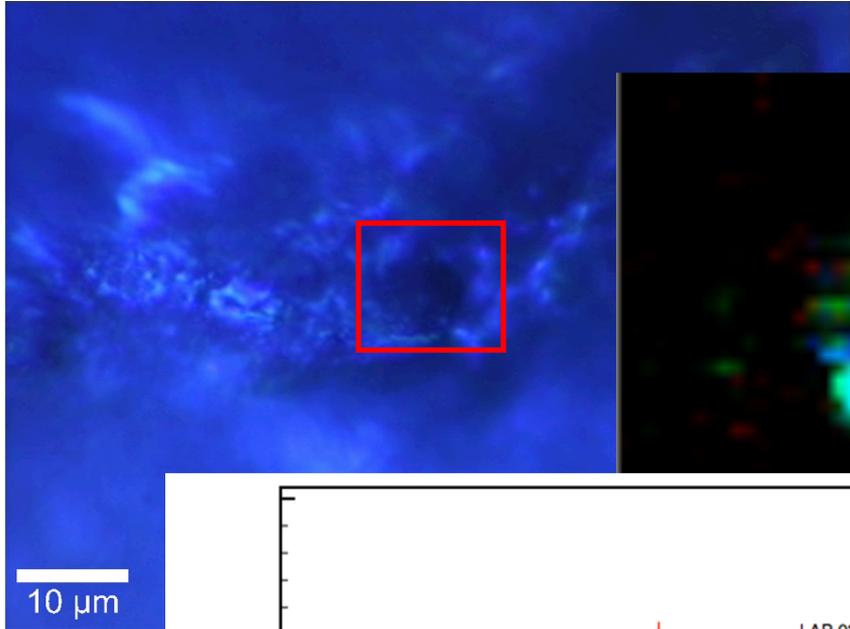


Red: MMC

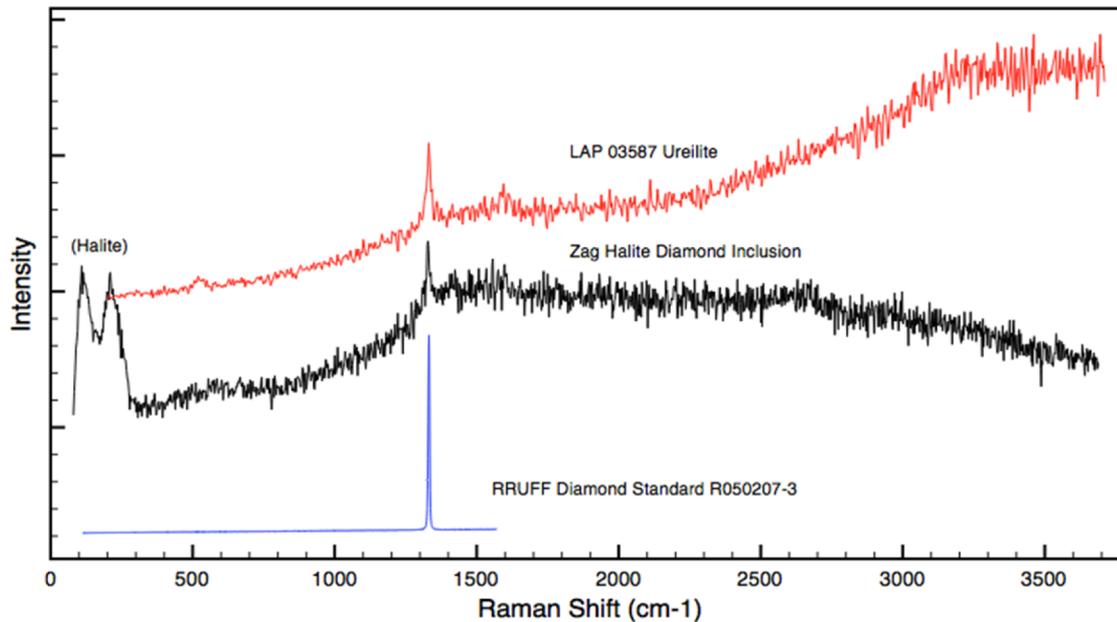
Green: Pyx

Blue: Olivine

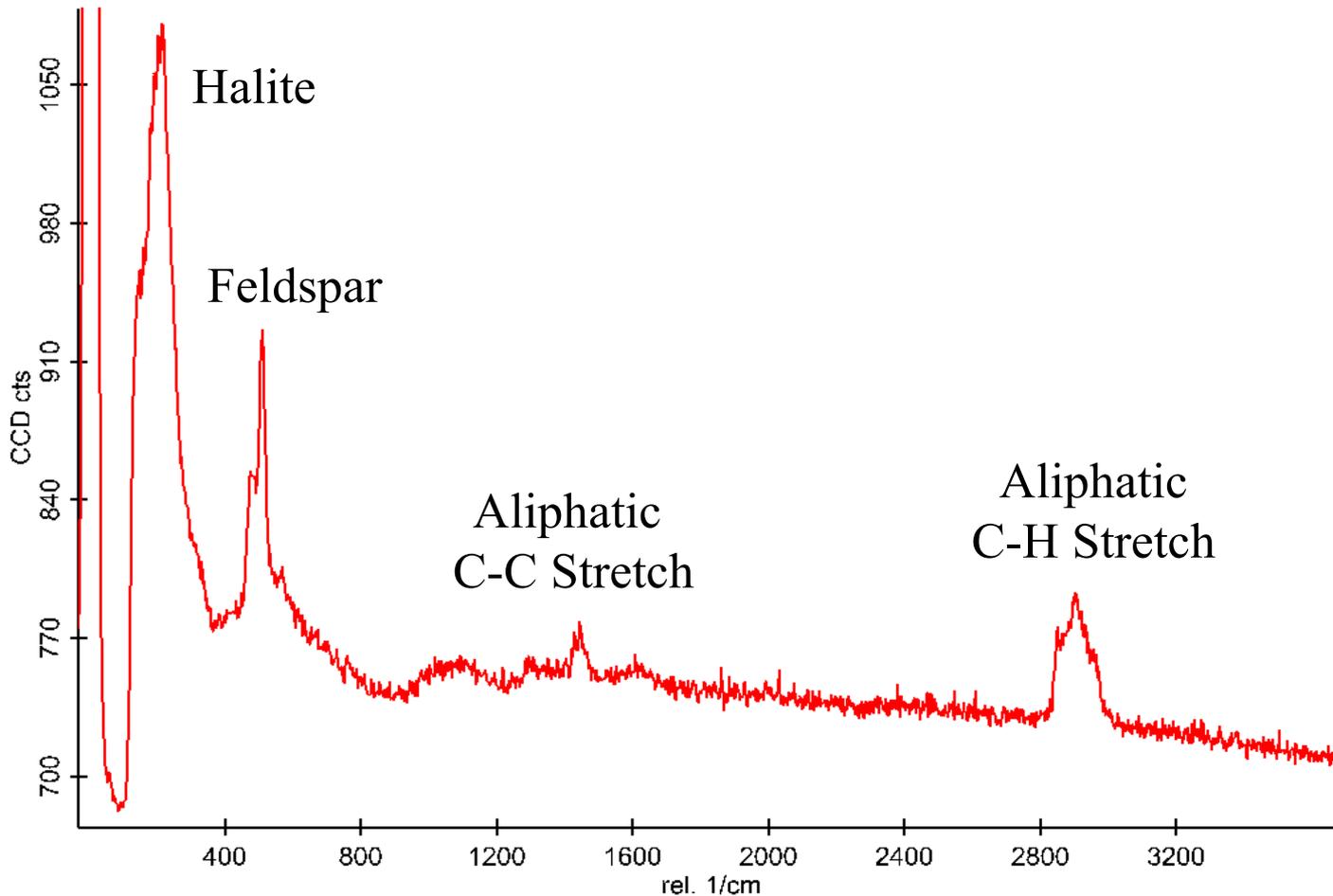
# Diamonds in Zag Halite



- Red: Carbonates
- Green: Graphitic MMC
- Blue: Diamond



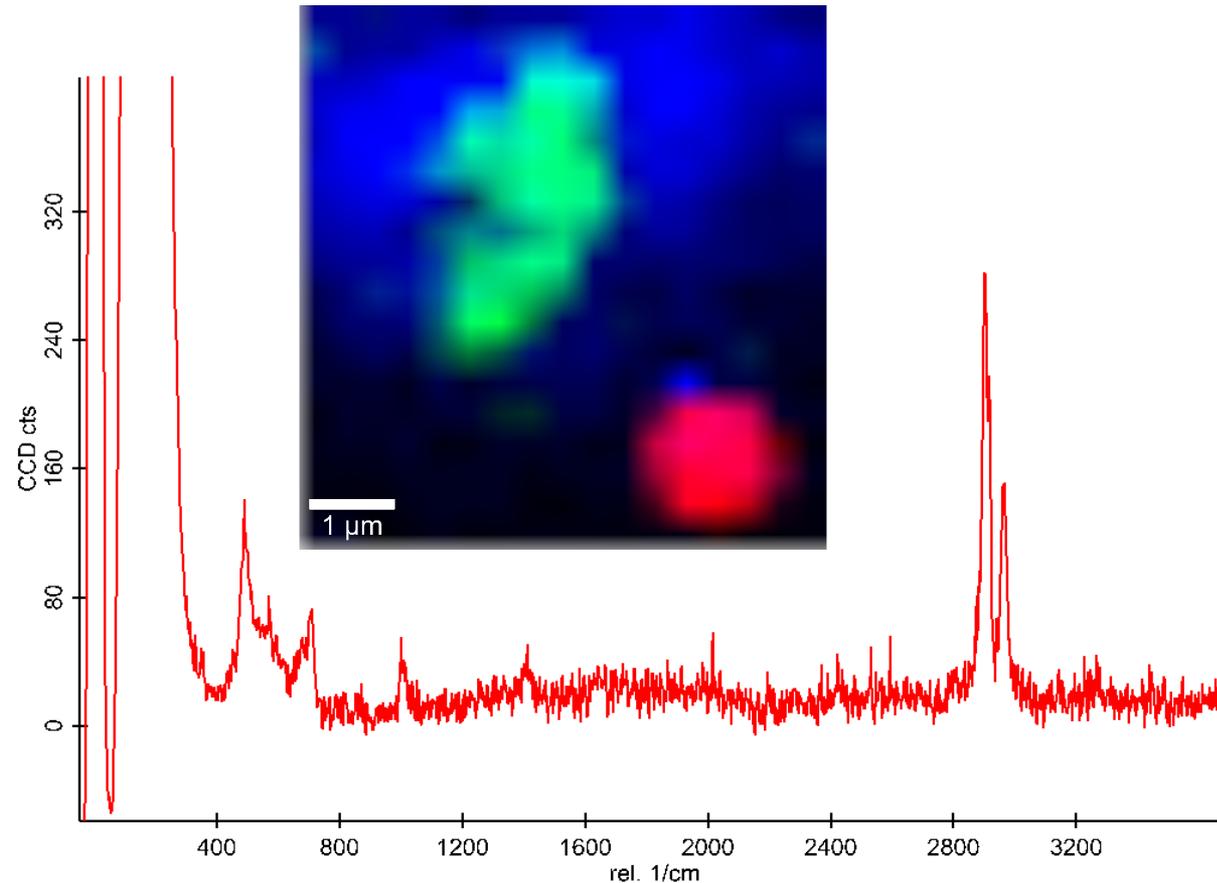
# Aliphatic Compounds



One inclusion  
features  
aliphatic  
compounds

Raman  
spectra are  
consistent  
with a mixture  
of short-chain  
aliphatic  
compounds

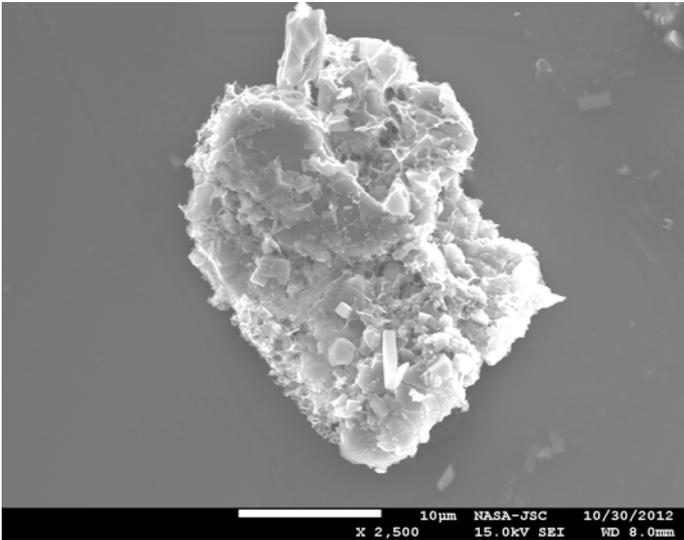
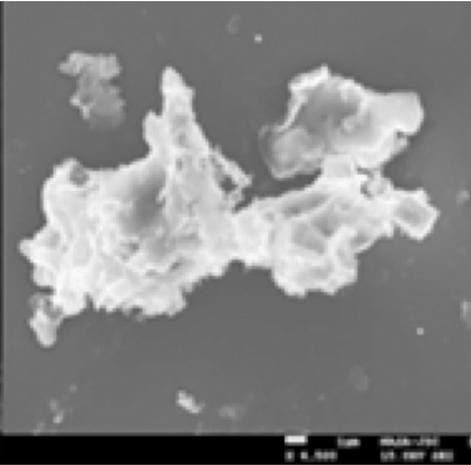
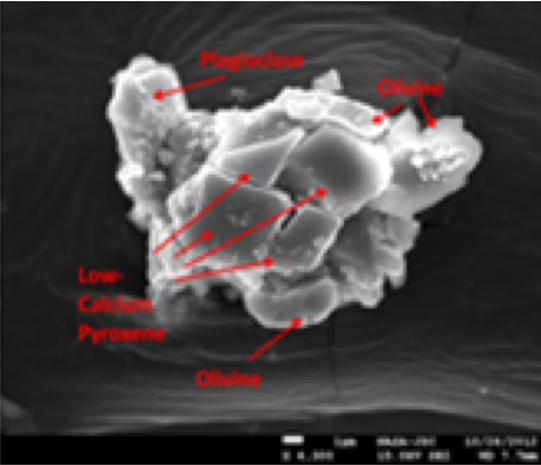
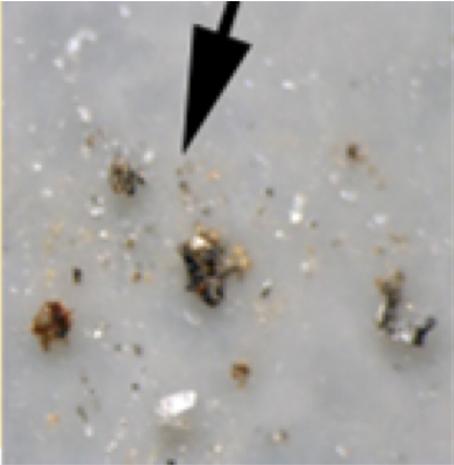
# Methyl Chloride



- Red: MMC
- Green: Apatite
- Blue: Methyl Chloride
- Raman peaks are consistent with Cl-substituted methane

**Geysers on Enceladus are observed to include salt (Postberg *et al*, Nature 2009), organics, and *methane* (Waite *et al*, Science 2006)**

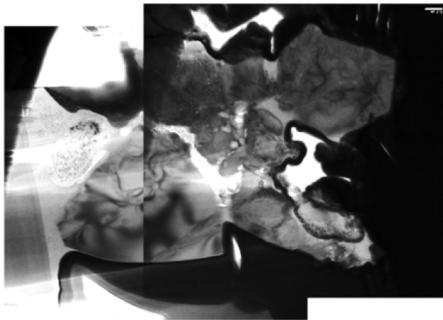
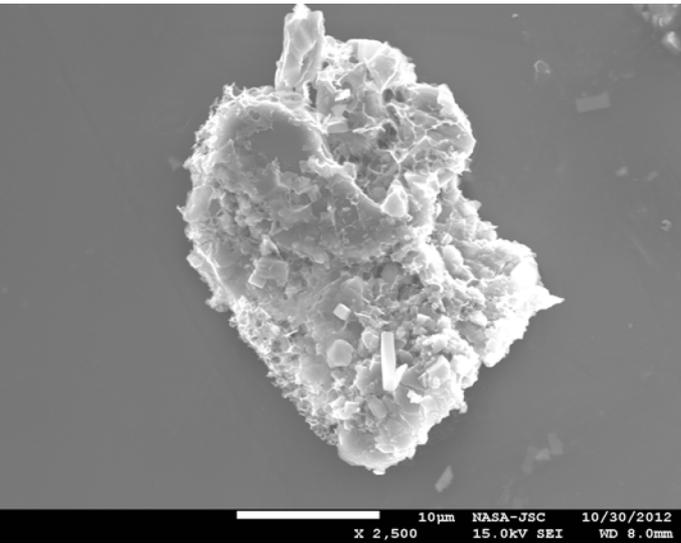
# Solid Residue Grains



# Monahans Residue Grain 4

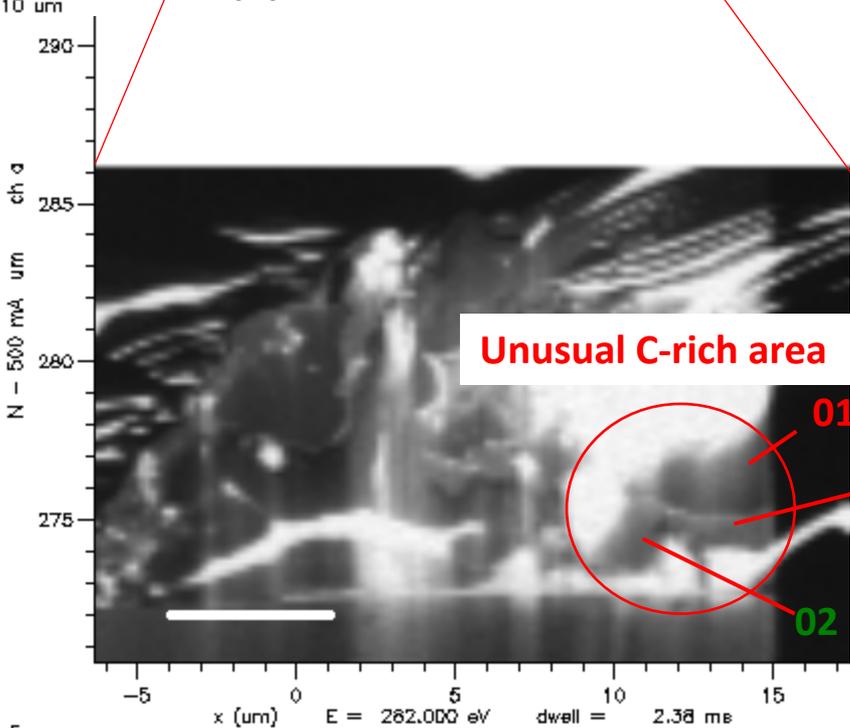
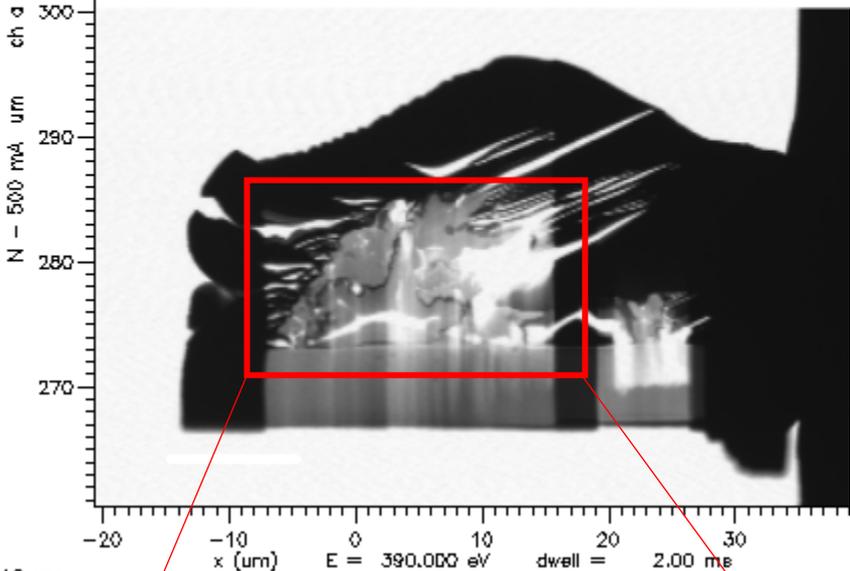
Olivine, High- and low-Ca Pyroxene,  
Troilite/Pyrrhotite, Glass, and  
*Carbon-bearing phases*  
Being analyzed by FTIR and C –XANES\*

Yoko Kebukawa

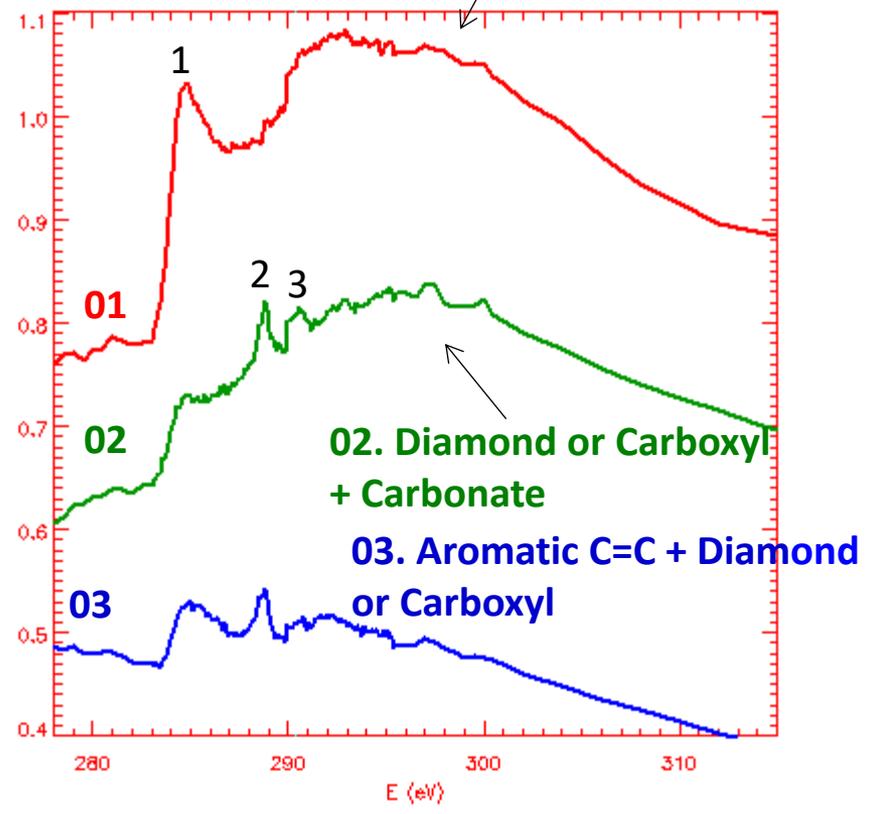


\*X-ray Absorption  
Near Edge Structure

# Monahans Residue 4 analyzed by C-XANES



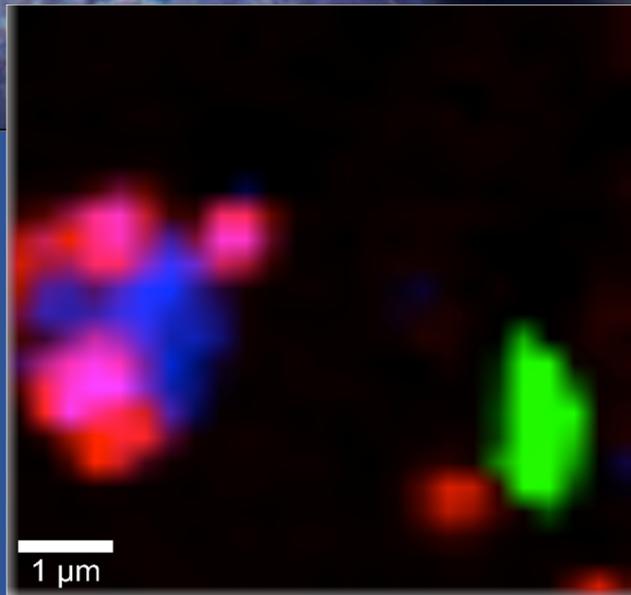
**01. Highly condensed aromatic carbon**



- 1: 284.7eV C=C
- 2: 288.8eV Diamond or Carboxyl
- 3: 290.6eV Carbonate

# Inclusion Mineralogy by Confocal Raman Microspectroscopy

- Typical inclusion on the left from Monahans halite
- Overall mineralogy consists of:
  - Olivine (wide range)
  - Low- and High-Ca Pyroxene
  - Feldspars
  - Phosphate minerals
  - Saponite
  - Macromolecular carbon
  - Light, condensed organics
  - Methyl chloride
  - Diamond
  - Carbonates
  - Metal
  - Lepidocrocite (on metal?)
  - Magnetite
  - Sulfides
- **Not consistent with H chondrite mineralogy**
- **Halites came from elsewhere!**



R: MMC  
G: Pyx  
B: Olivine

# Measurements of Amino Acids in Zag Bulk and Zag Halite

## Samples



Figure 2 Bulk meteorite Zag (NHM)

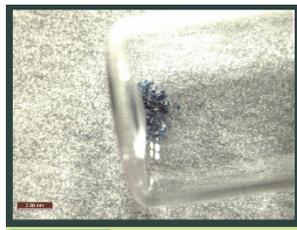
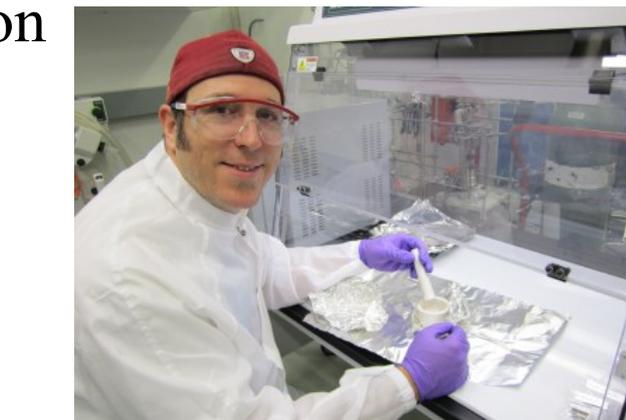


Figure 3 Zag halite (JSC) in a glass ampoule

- Meteorite bulk:  
Zag (JSC): 87 mg & Zag (NHM): 67 mg
- Halite crystals:  
Zag halite (JSC): 3 mg Zag halite (NHM): 2 mg



Queenie Chan



Aaron Burton

## Analytical technique



Figure 4 The UPLC is capable of performing both fluorescence and mass spectrometry measurements from a single sample injection

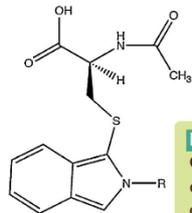
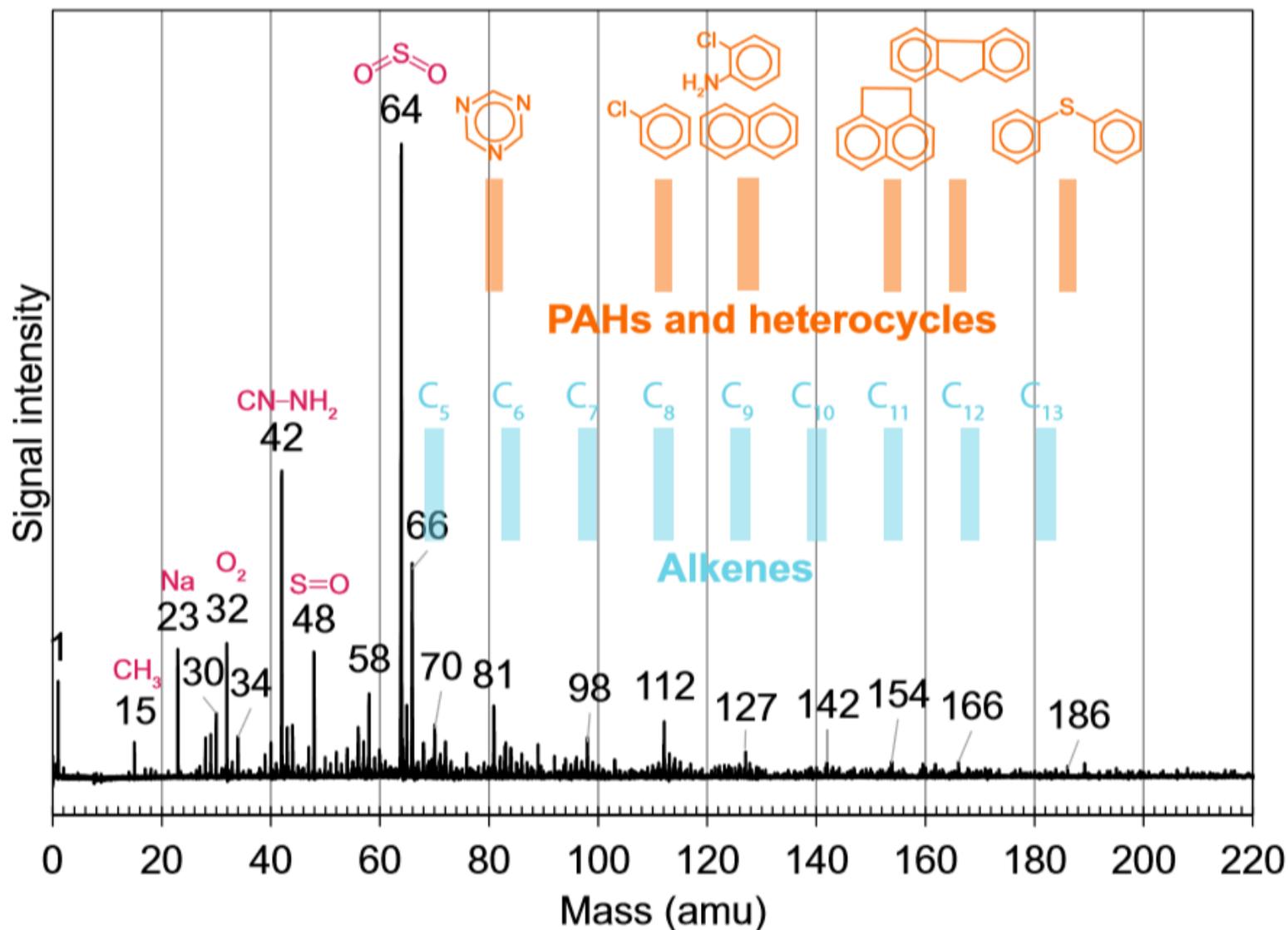


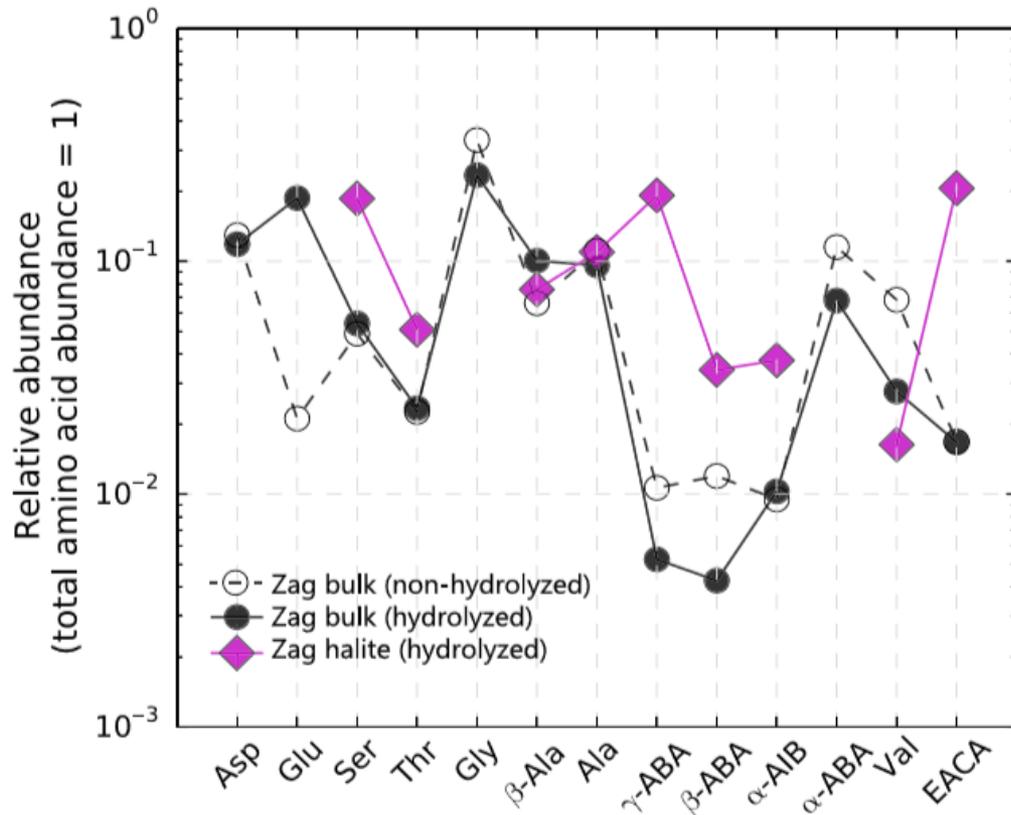
Figure 5 OPA/NAC amino acid derivative

UPLC: Ultra performance liquid chromatography

# $\mu$ -L2MS spectra of Zag Halite



## Organic Species in Zag Halite



### Abbreviations

Asp: aspartic acid

Glu: glutamic acid

Ser: serine

Thr: threonine

Gly: glycine

Ala: alanine

ABA: aminobutyric acid

AIB: aminoisobutyric acid

Iva: isovaline

Val: valine

EACA: ε-amino-n-caproic acid

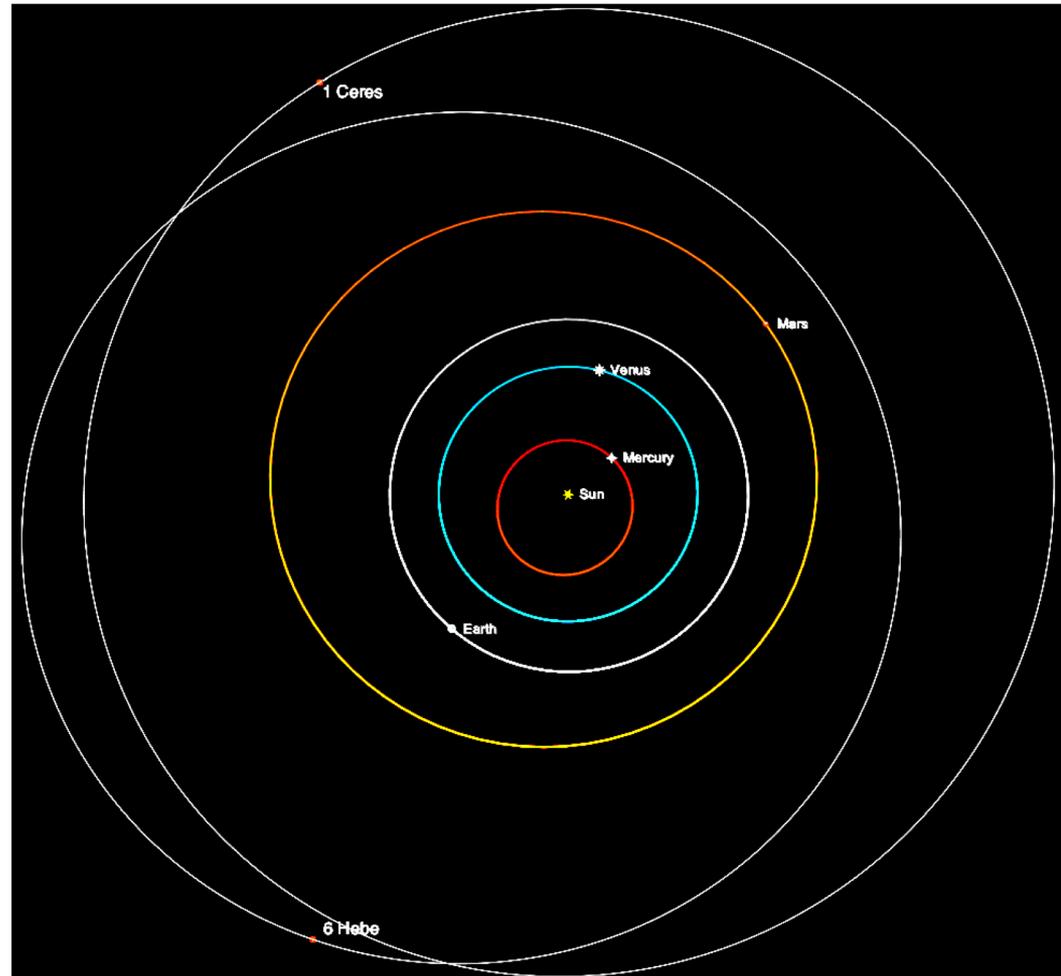
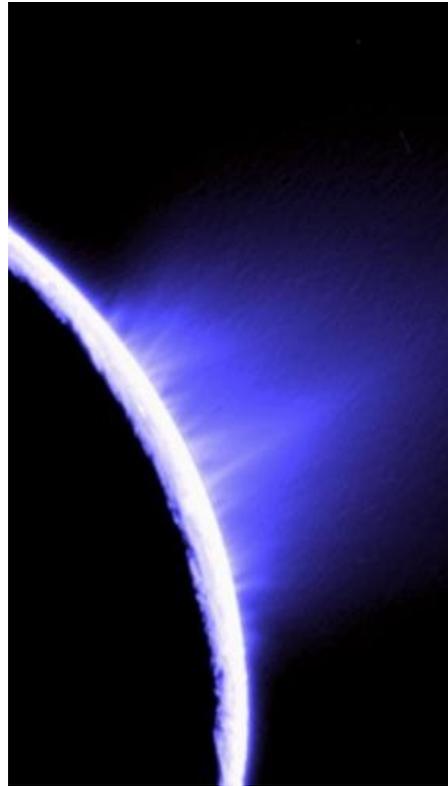
Ile: isoleucine

Leu: leucine

**Fig. 6. Relative amino acid abundances (total amino acid abundance = 1) of the 6 M HCl acid-hydrolyzed amino acid extract of the Zag matrix (●), the non-hydrolyzed amino acid extract of the Zag matrix (○), and the acid-hydrolyzed amino acid extract of the Zag halite (◆).** Although the Zag matrix is  $\gamma$ -ABA-,  $\beta$ -ABA-,  $\alpha$ -aminoisobutyric acid ( $\alpha$ -AIB), and EACA-deficient, the halite is shown to exhibit an opposite trend and is enriched in these amino acids. The marked difference in the amino acid contents between the halite and matrix indicates their separate synthetic origins. The abbreviations of the amino acids are defined in table S1.

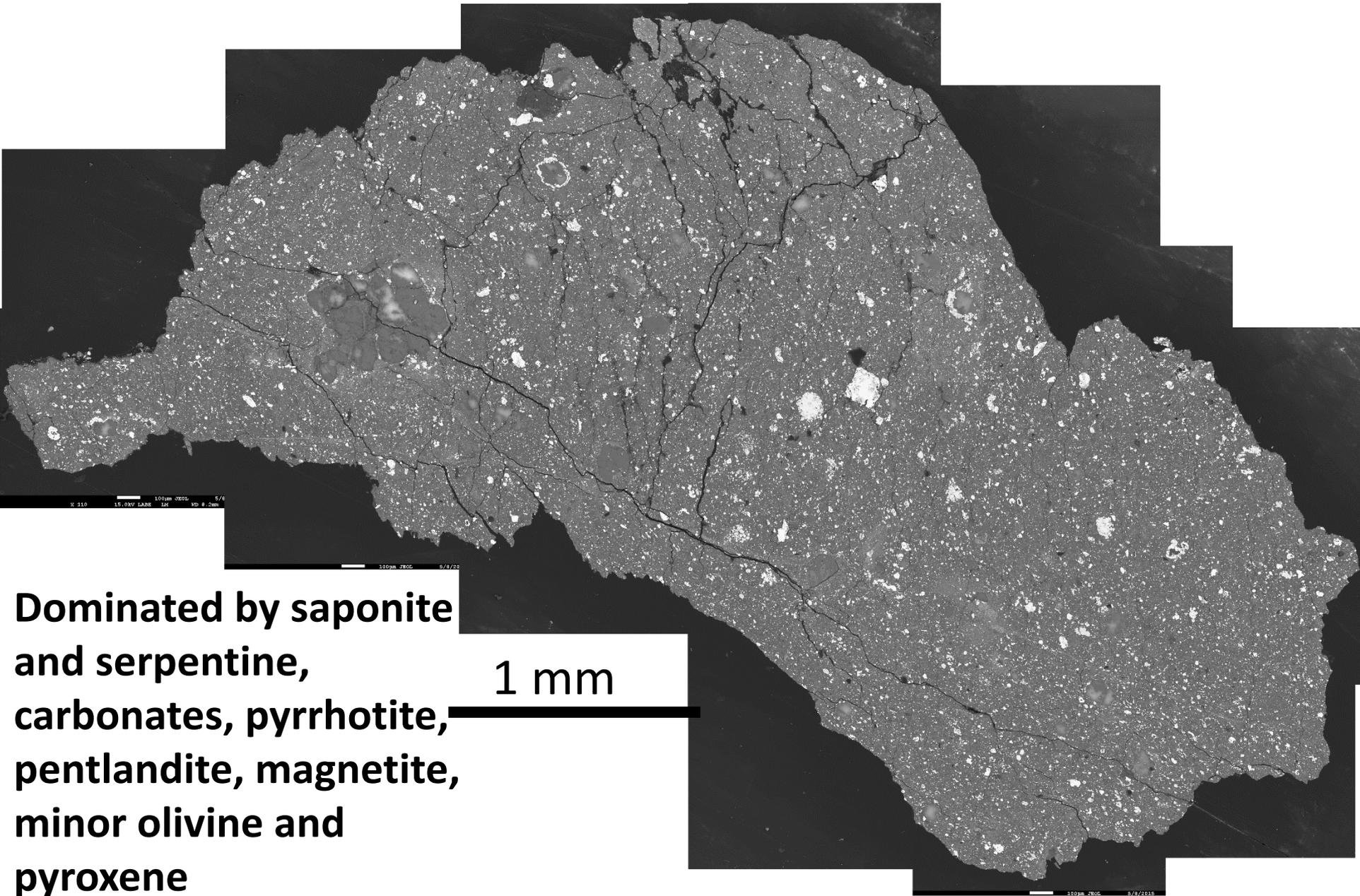
These materials originated on/in a hydrovolcanically active body : Ceres?

Or  
maybe a  
TNO –  
P or D  
asteroid



# Zag Clast (4 x 10 mm)

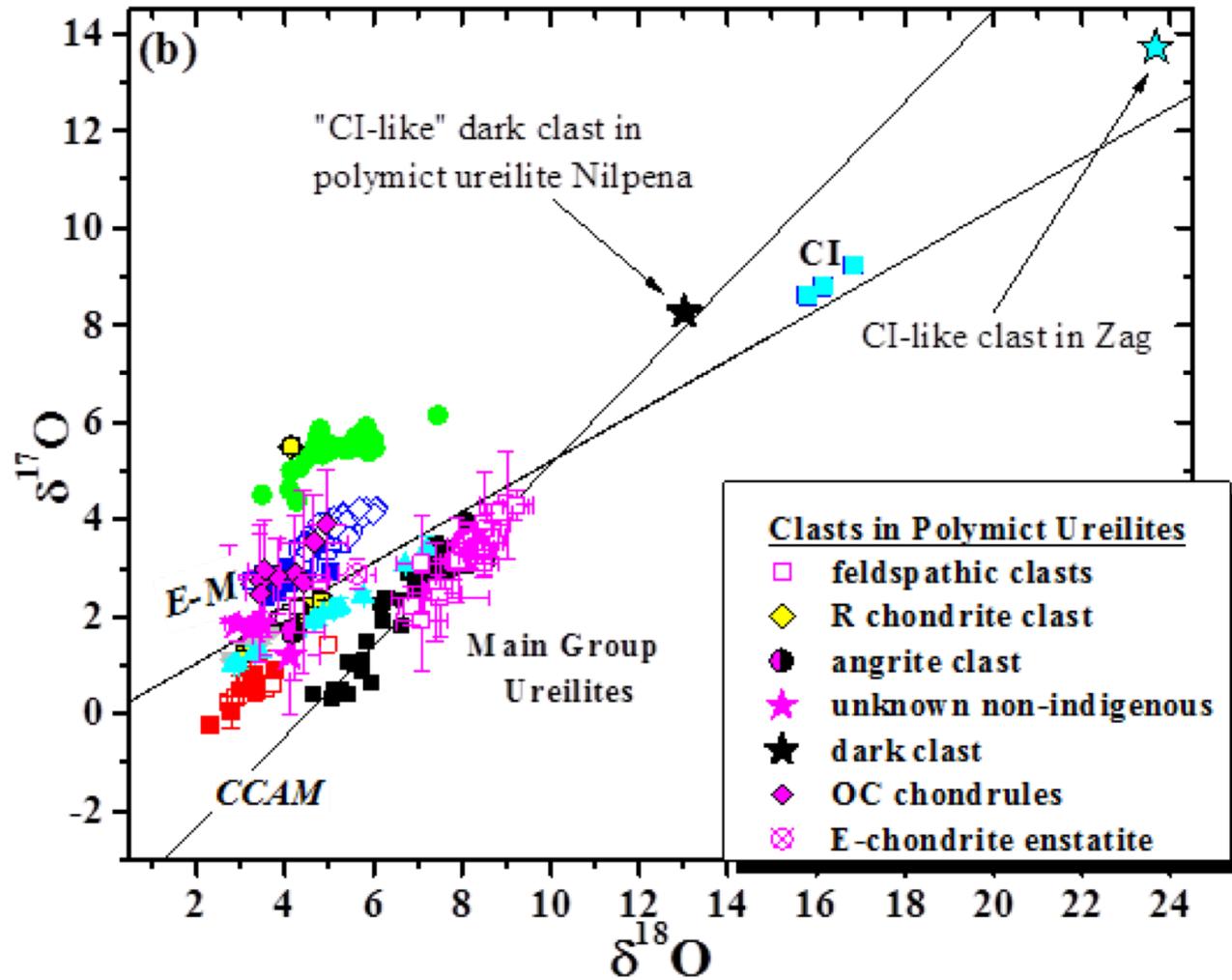




**Dominated by saponite  
and serpentine,  
carbonates, pyrrhotite,  
pentlandite, magnetite,  
minor olivine and  
pyroxene**

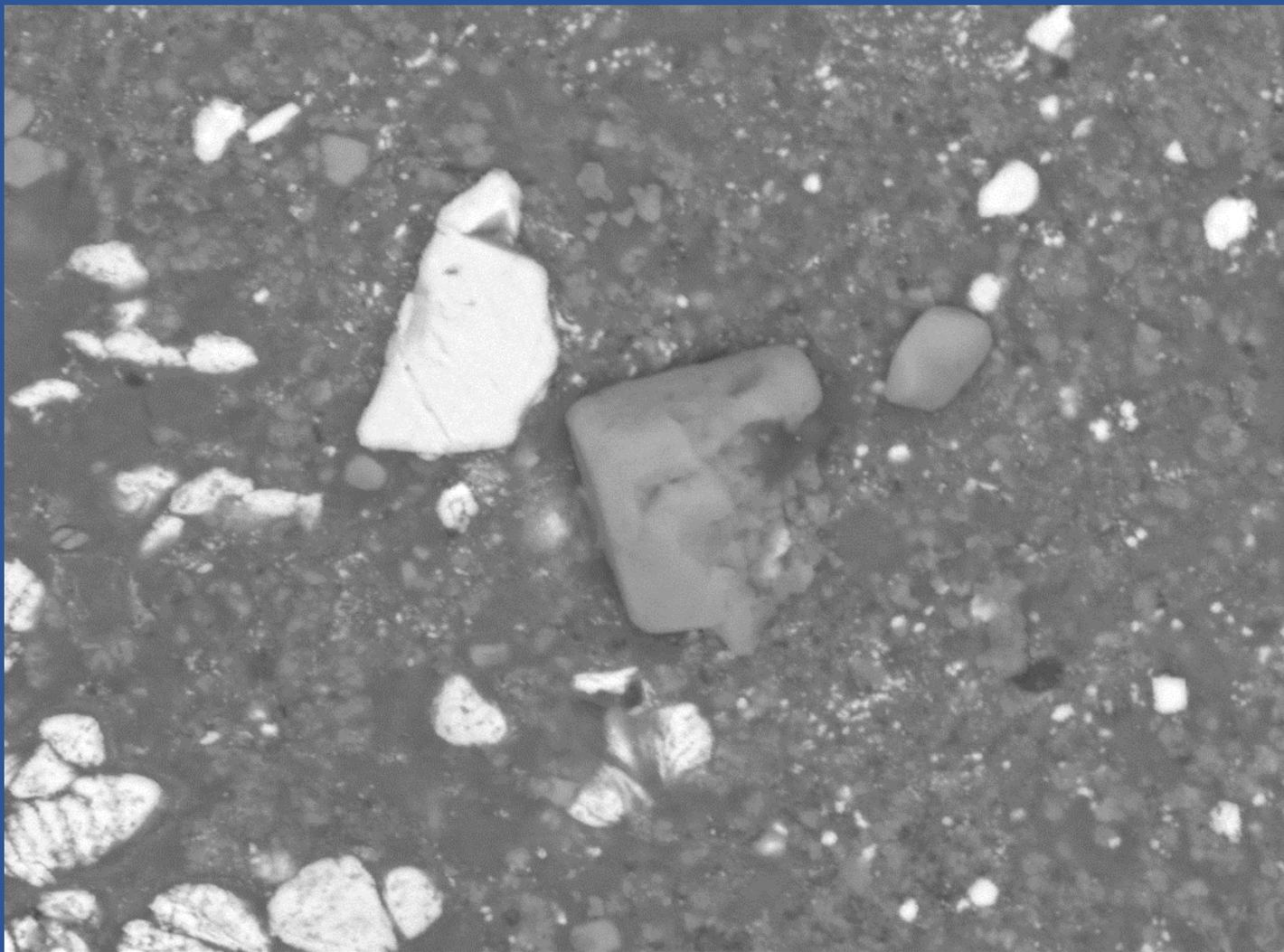
**1 mm**

Very large  $\Delta^{17}\text{O}$  : +1.41



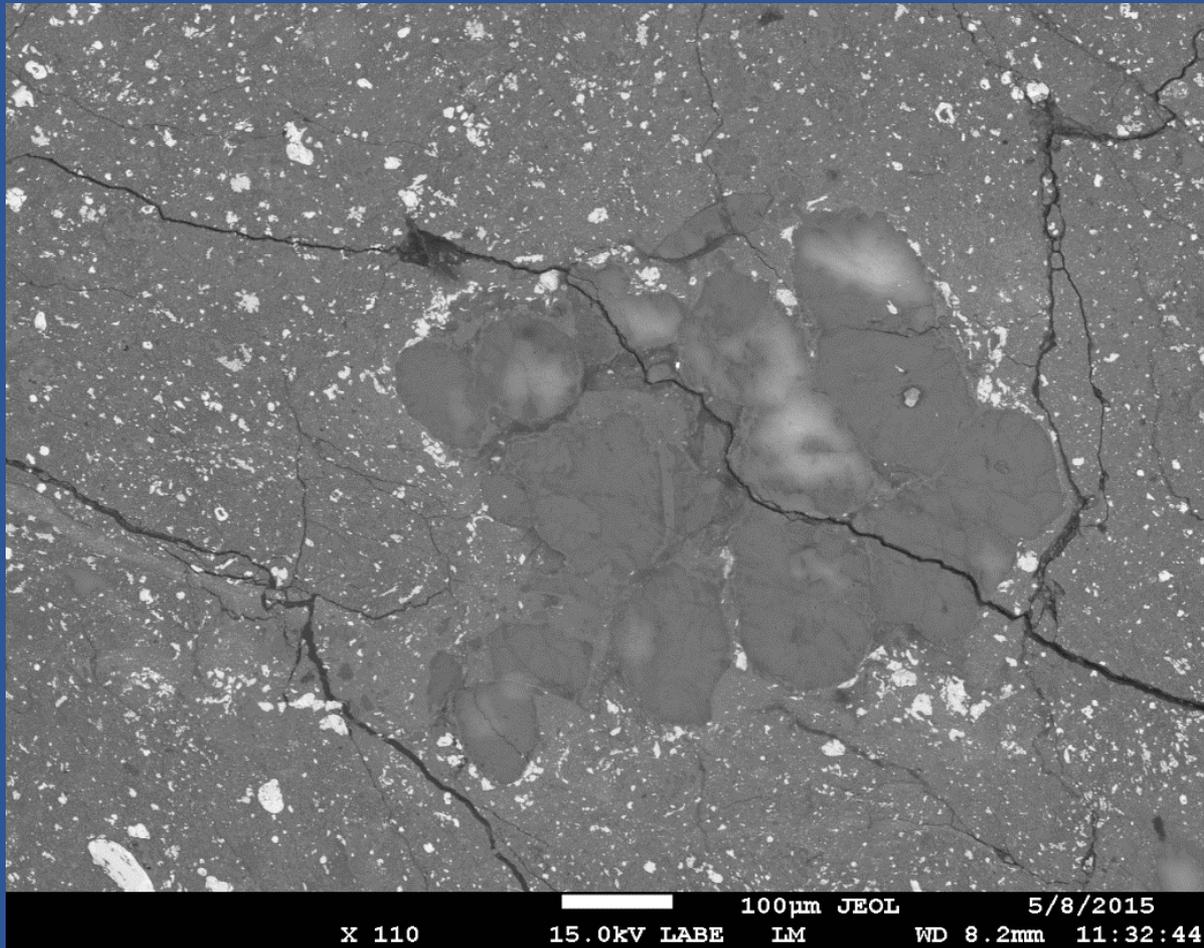
Bob Clayton and Tosh Mayeda, Richard Greenwood

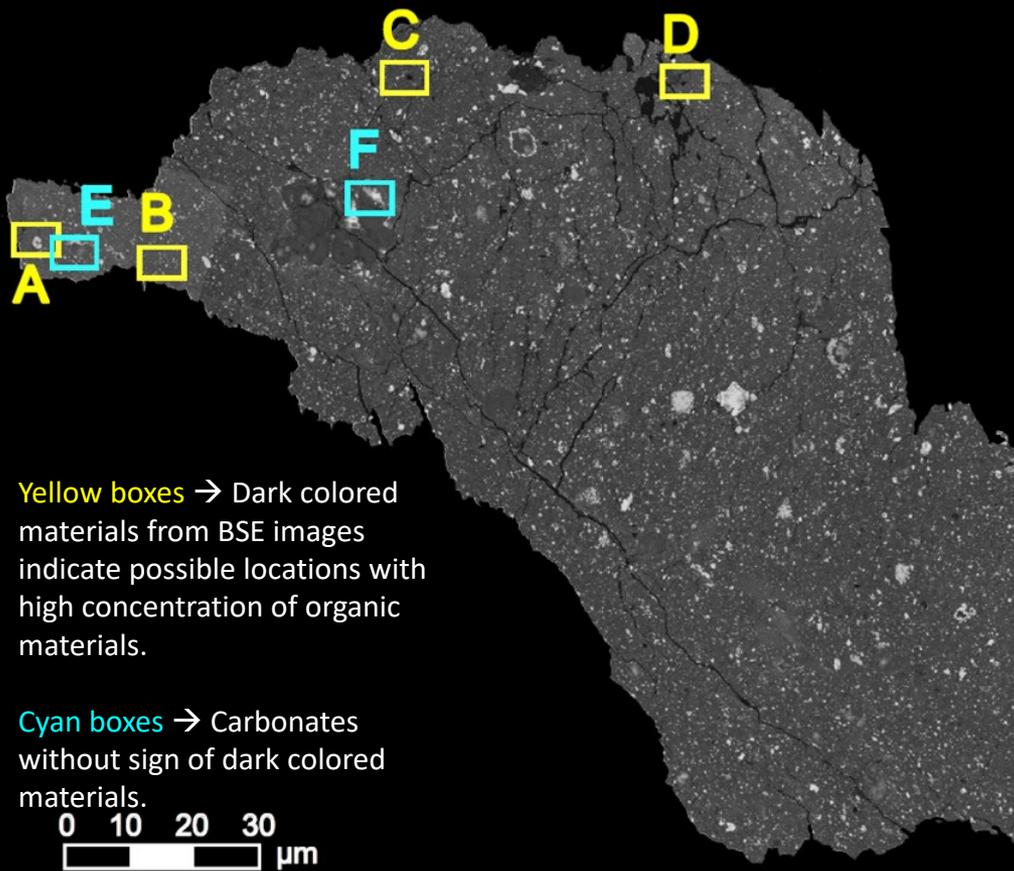
# Halite



X 2,300 15.0kV LABE SEM 10µm JEOL 5/8/2015 WD 8.0mm 10:59:32

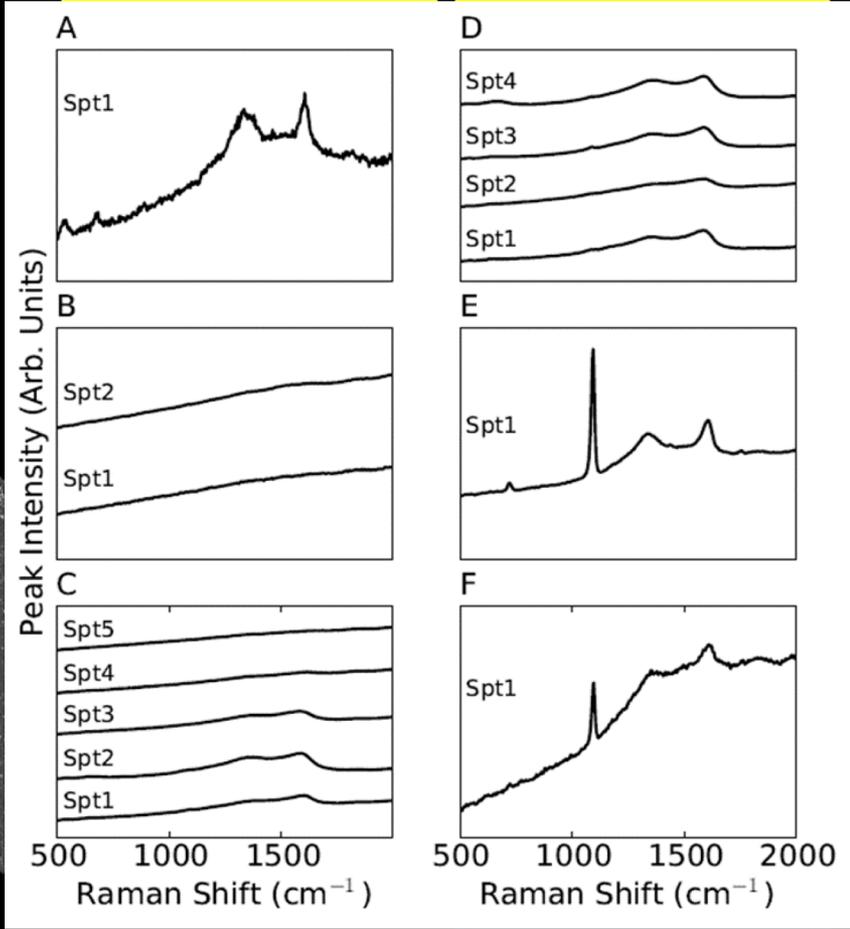
# Carbonates



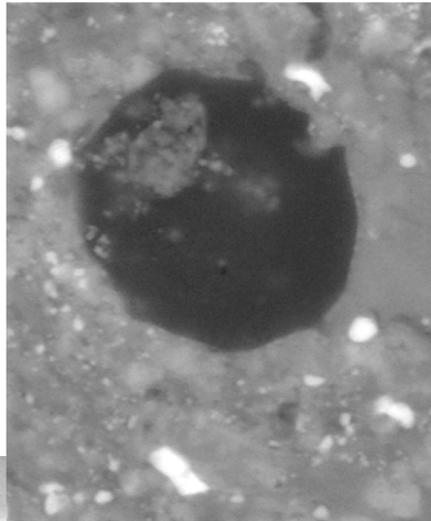


**Yellow boxes** → Dark colored materials from BSE images indicate possible locations with high concentration of organic materials.

**Cyan boxes** → Carbonates without sign of dark colored materials.

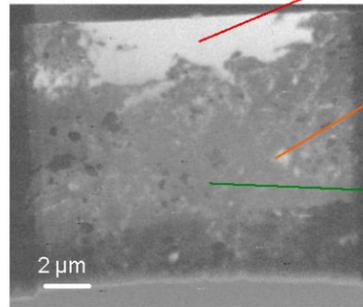


# Organic globule



**Zag clast 2 FIBed 9-17-15**

C-map 280/292 eV



C rich area

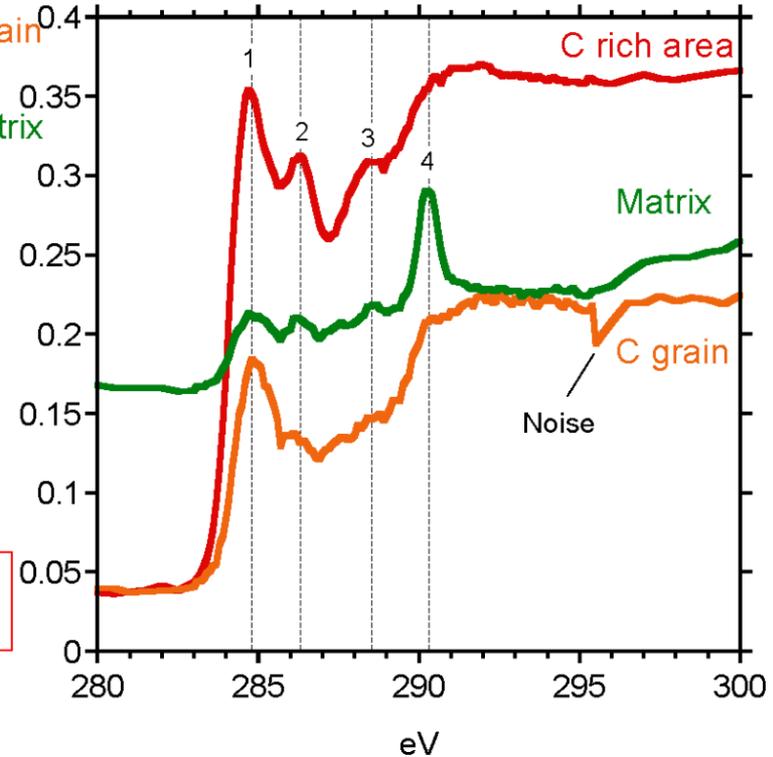
C grain

Matrix

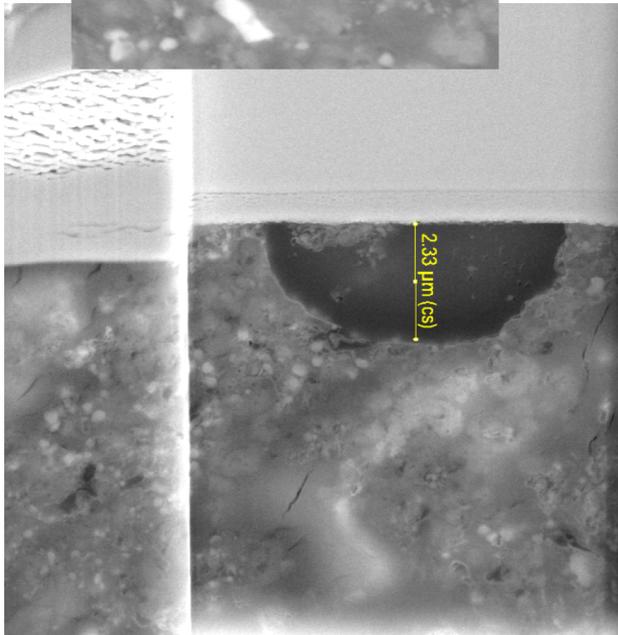
2 μm E = 292.000 eV dwell = 2.00 ms

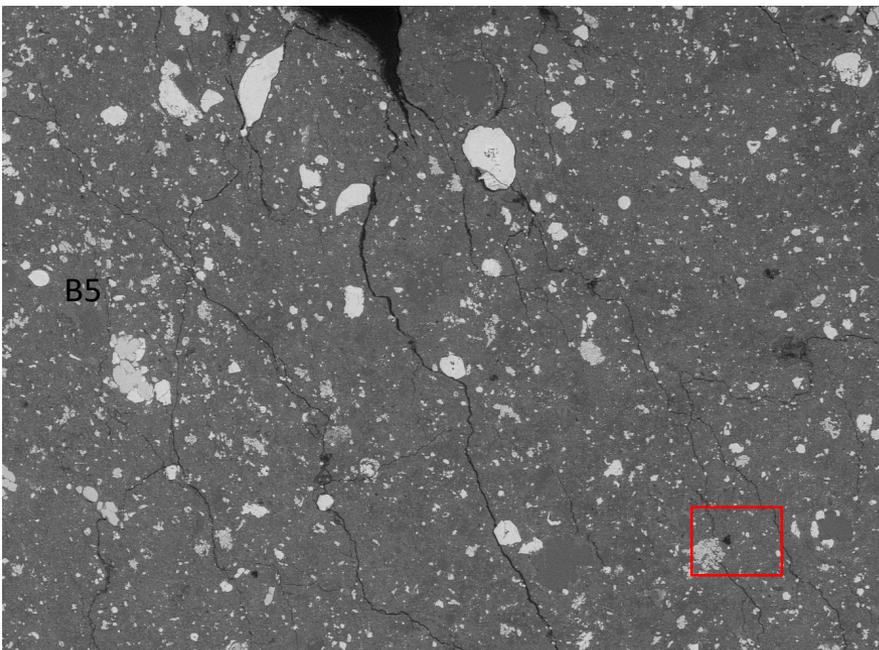
- 1: 284.8 eV C=C Aromatic/olefinic
- 2: 286.3 eV C=O Aryl/Vinyl-keto
- 3: 288.5 eV O=C=O Carboxyl
- 4: 290.3 eV CO<sub>3</sub> Carbonate

**C-XANES**



C rich area: Aromatic + C=O  
 → primitive IOM like?

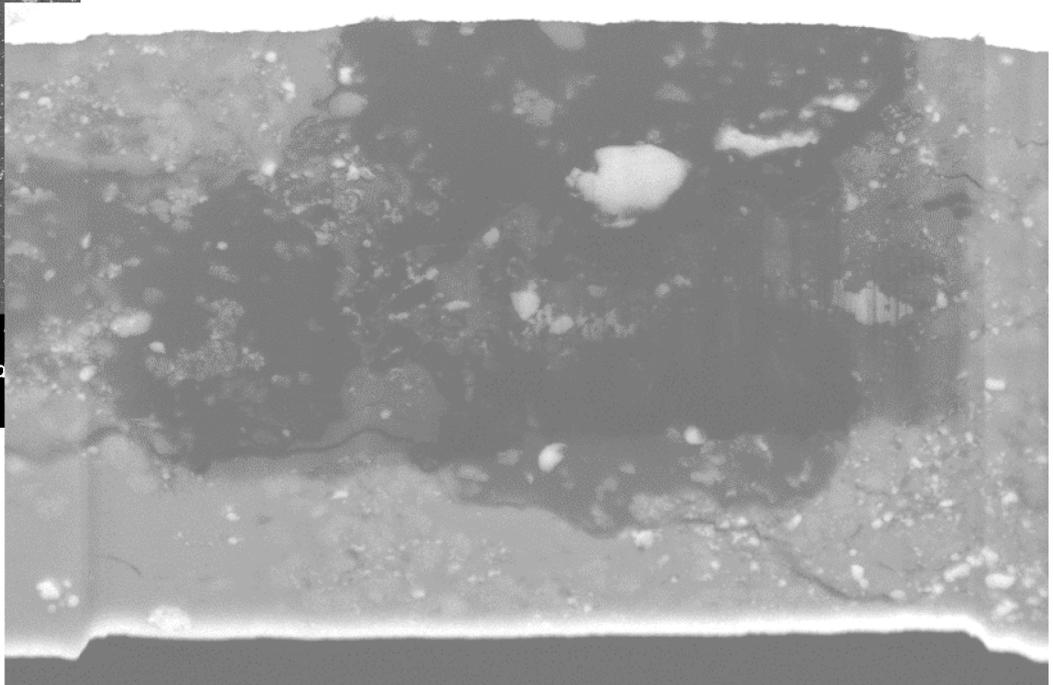




100  $\mu$ m

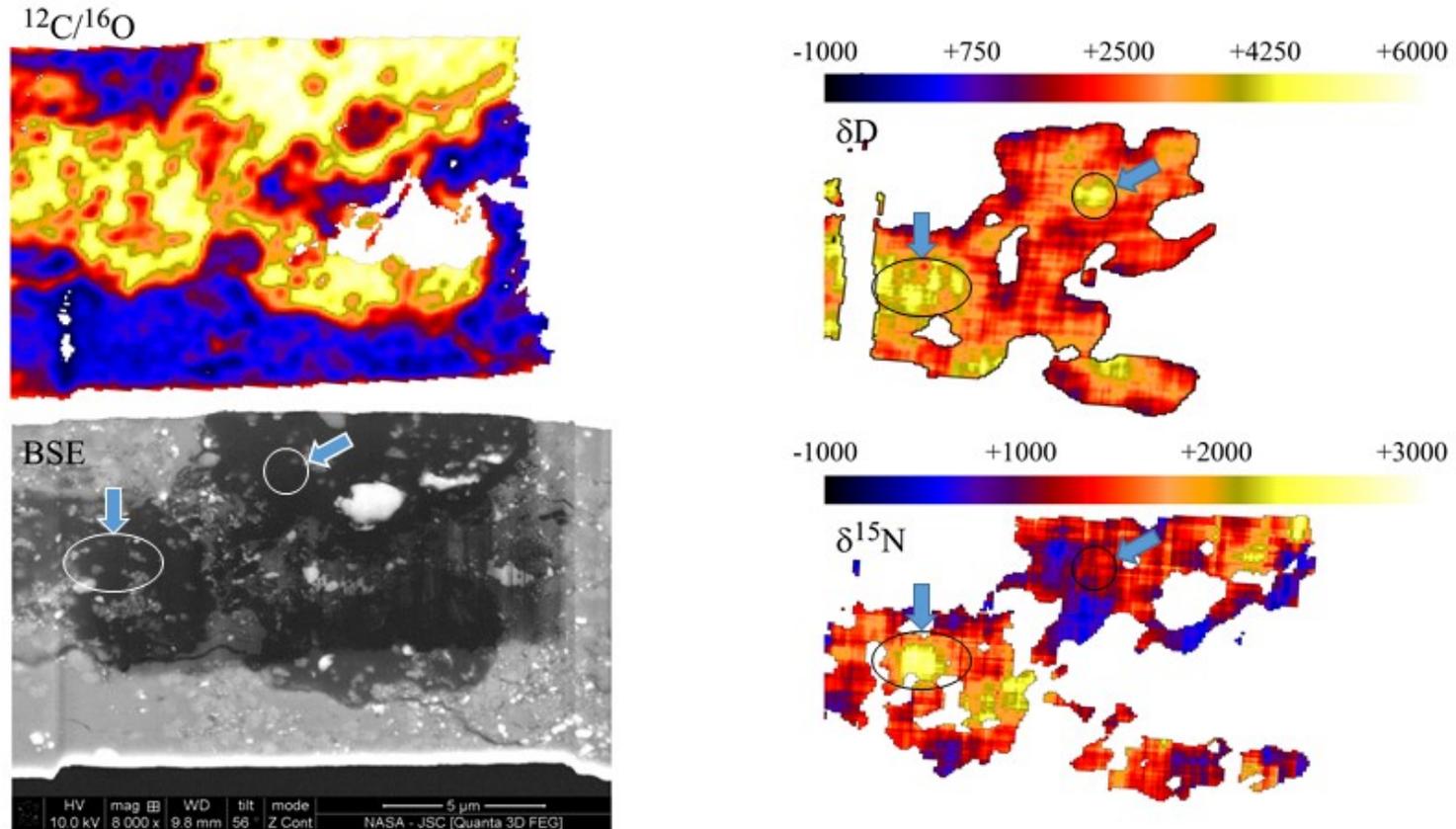
EHT = 15.00 kV  
WD = 5.9 mm  
Mag = 84 X

Signal A = AsB Width =  
Reference Mag = Polaroid  
1\_0406.tif

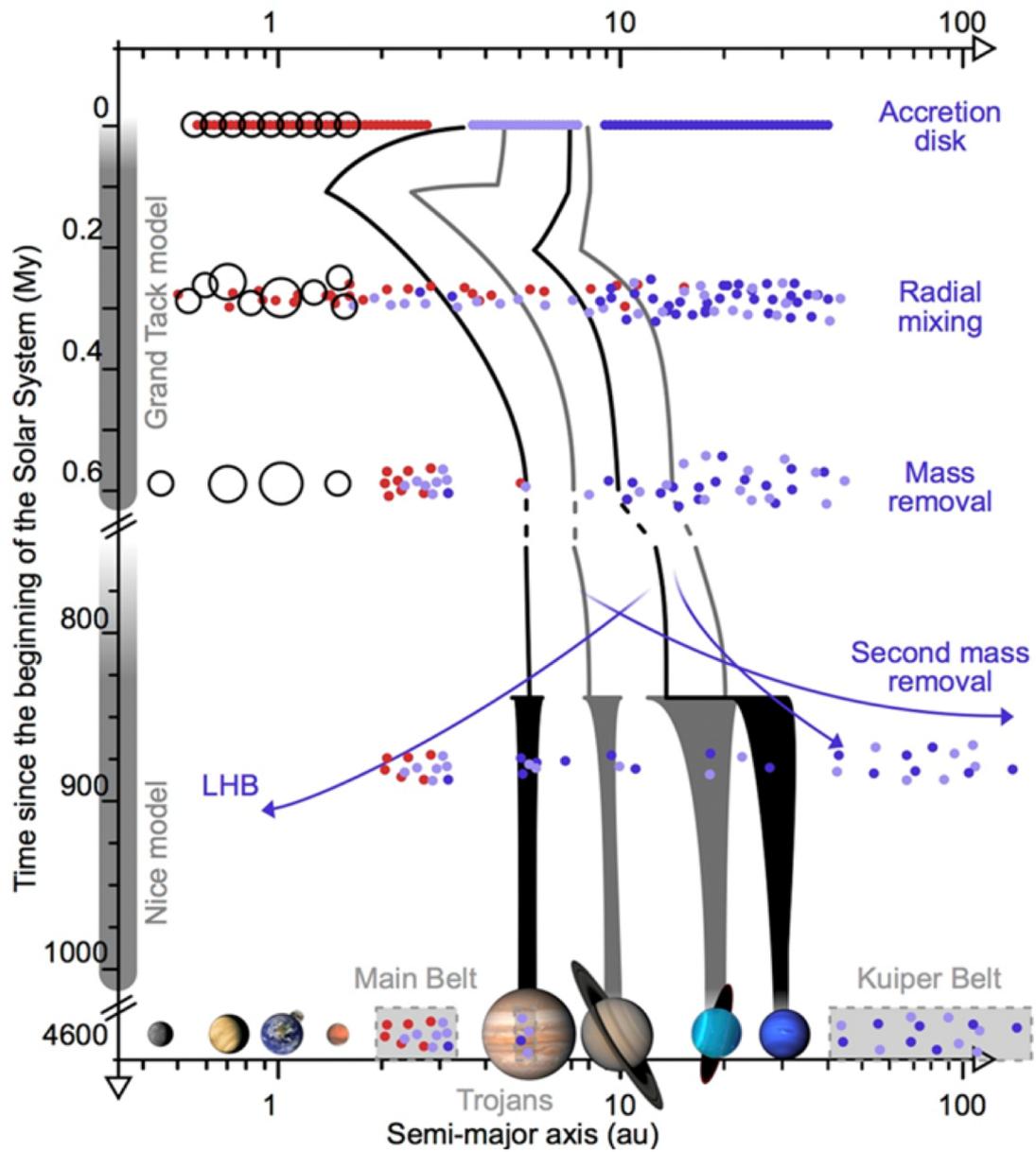


	HV	mag	WD	tilt	mode	5 $\mu$ m	
	10.0 kV	8 000 x	9.8 mm	56 °	Z Cont	NASA - JSC [Quanta 3D FEG]	

# Zag: NanoSIMS images ( $^{12}\text{C}/^{16}\text{O}$ , D and $^{15}\text{N}$ )

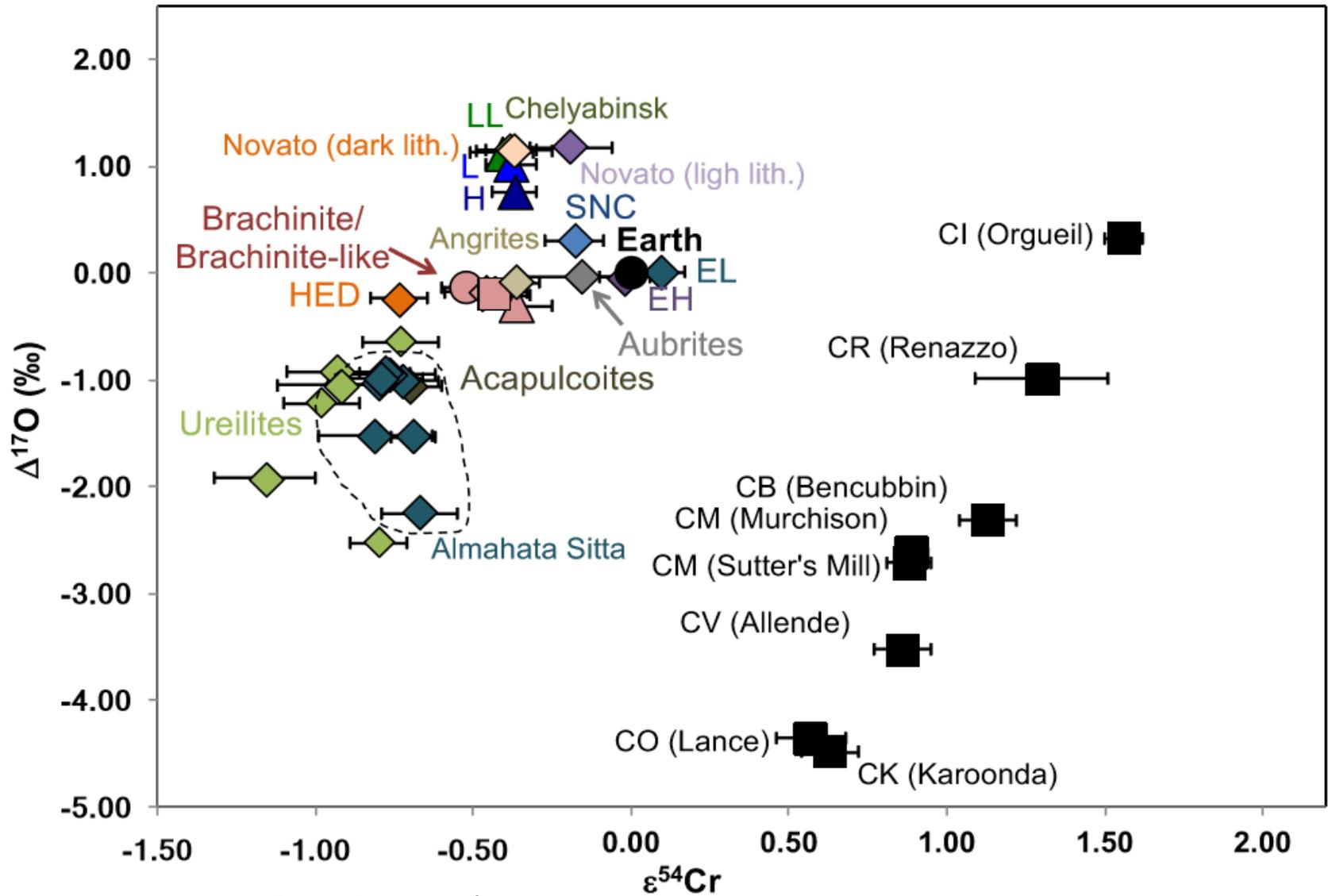


**Correlated High Concentrations of Deuterium,  $^{15}\text{N}$  and very heavy oxygen probably indicates very cold formation temperature**



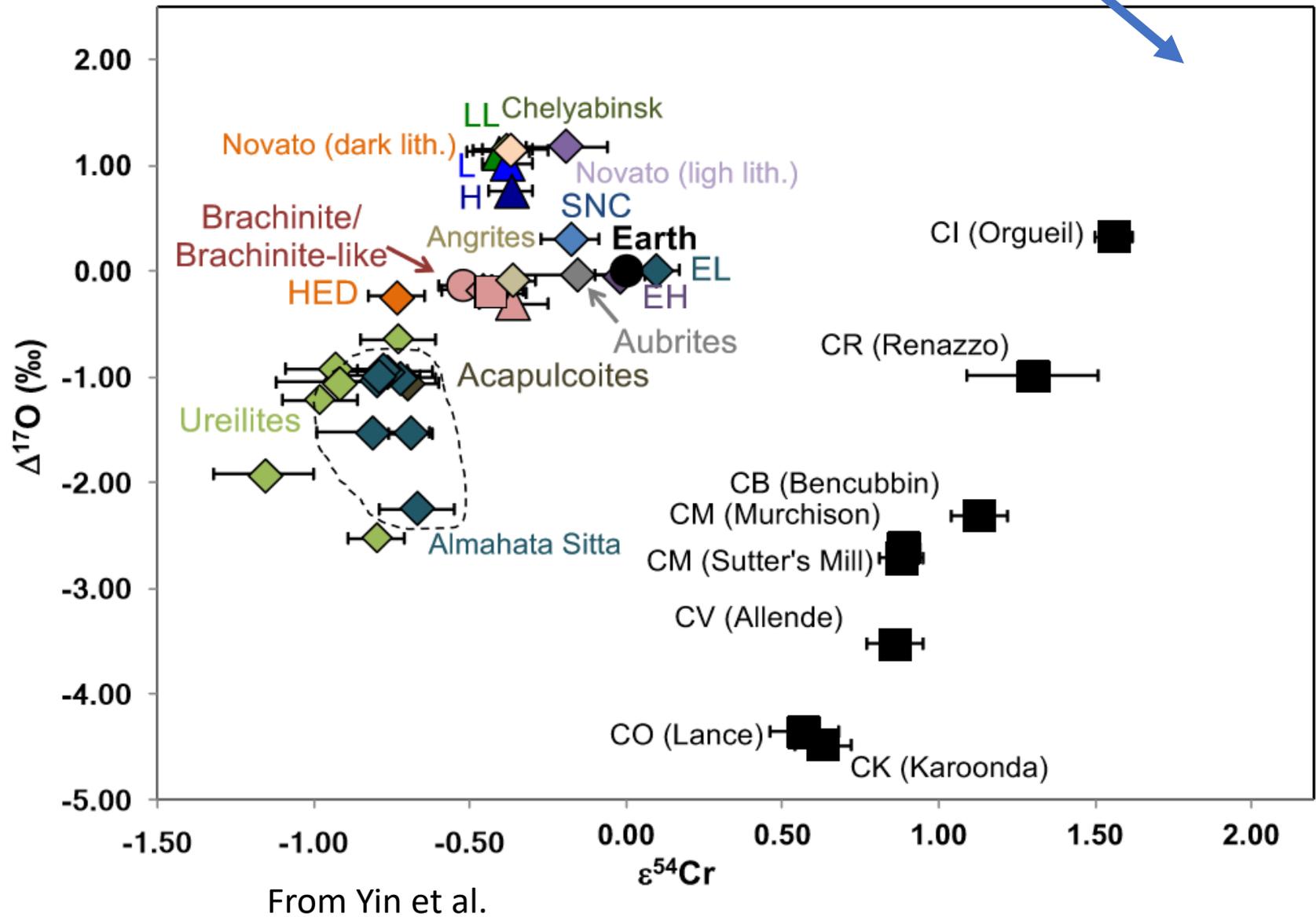
From DeMeo and Carry, 2014

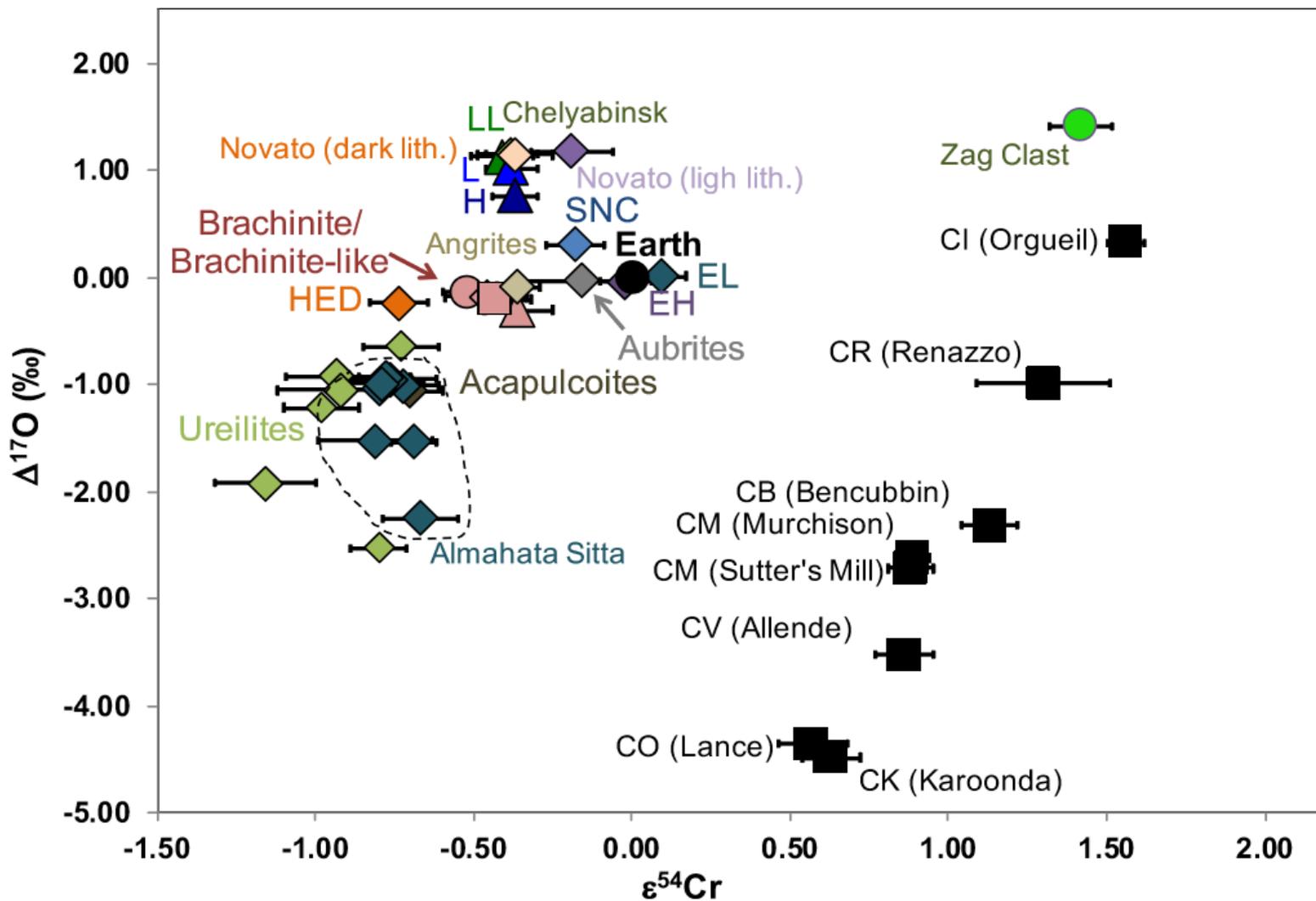
There are two distinct populations of meteorites, based on neutron-rich isotopes of Ti, Cr, Ni, Mo, when plotted with  $\Delta^{17}\text{O}$



From Yin et al.

# Can we find materials that formed farther outward from Jupiter?





Qin-Zhu Yin and Matt Sanborn

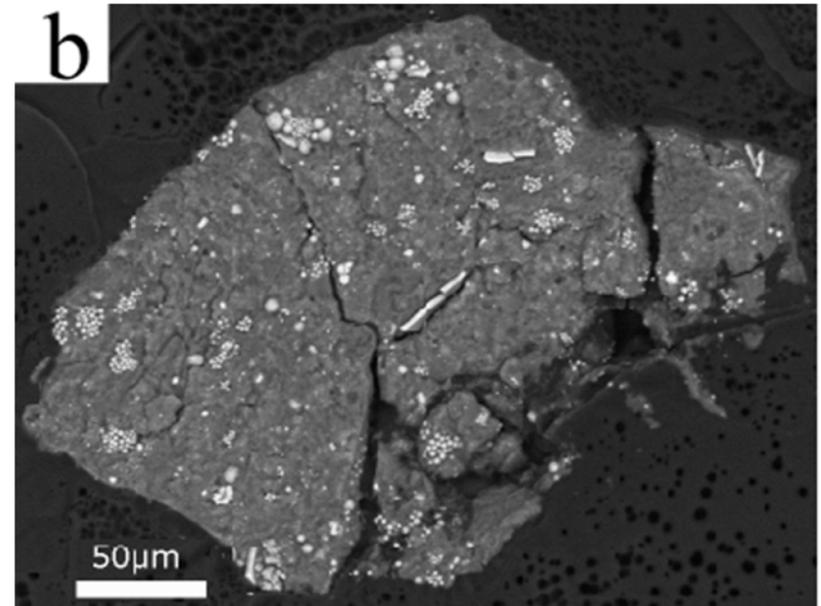
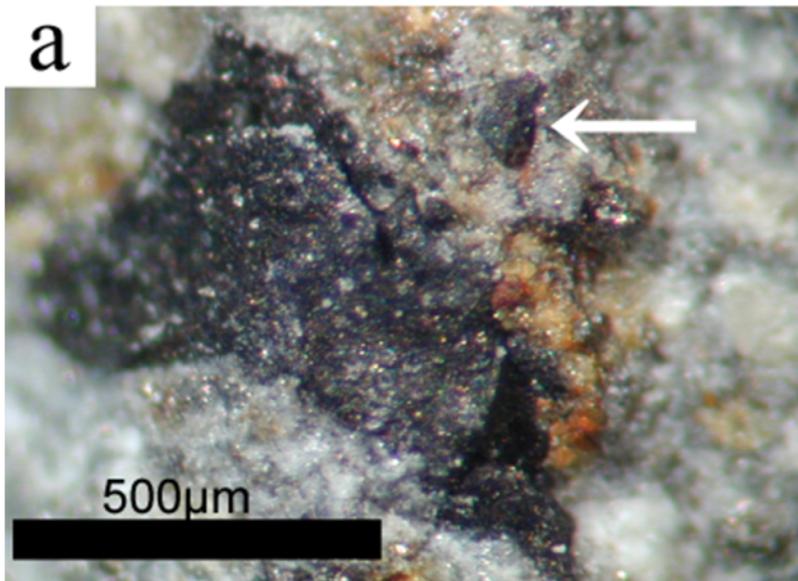
# Hydrous clasts

Tsukuba (H5)

Ebeam work published many years ago

No isotopes

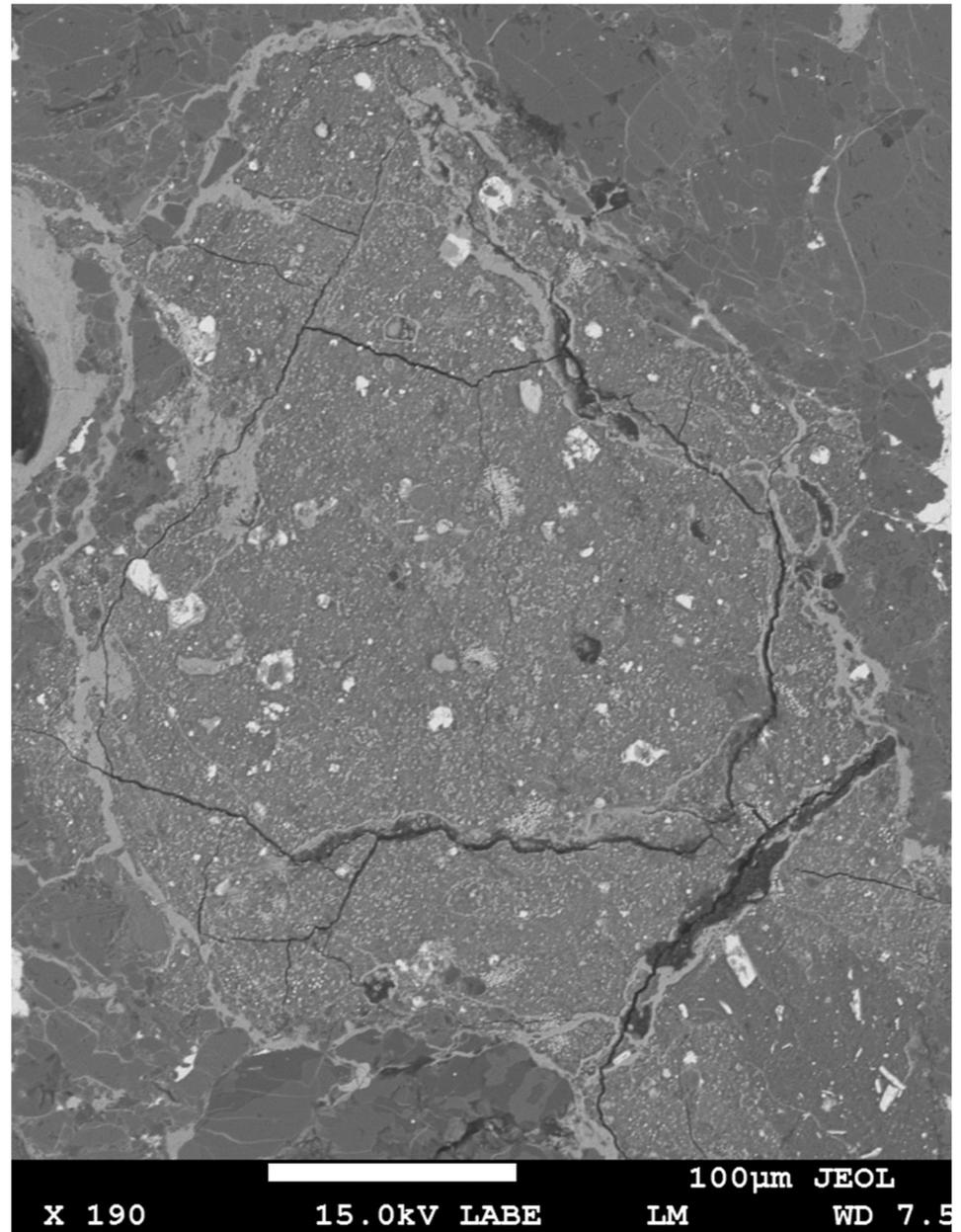
I have some tiny bits from Daisuke Nakashima



# Hydrous clasts

**NWA 8369 H5**

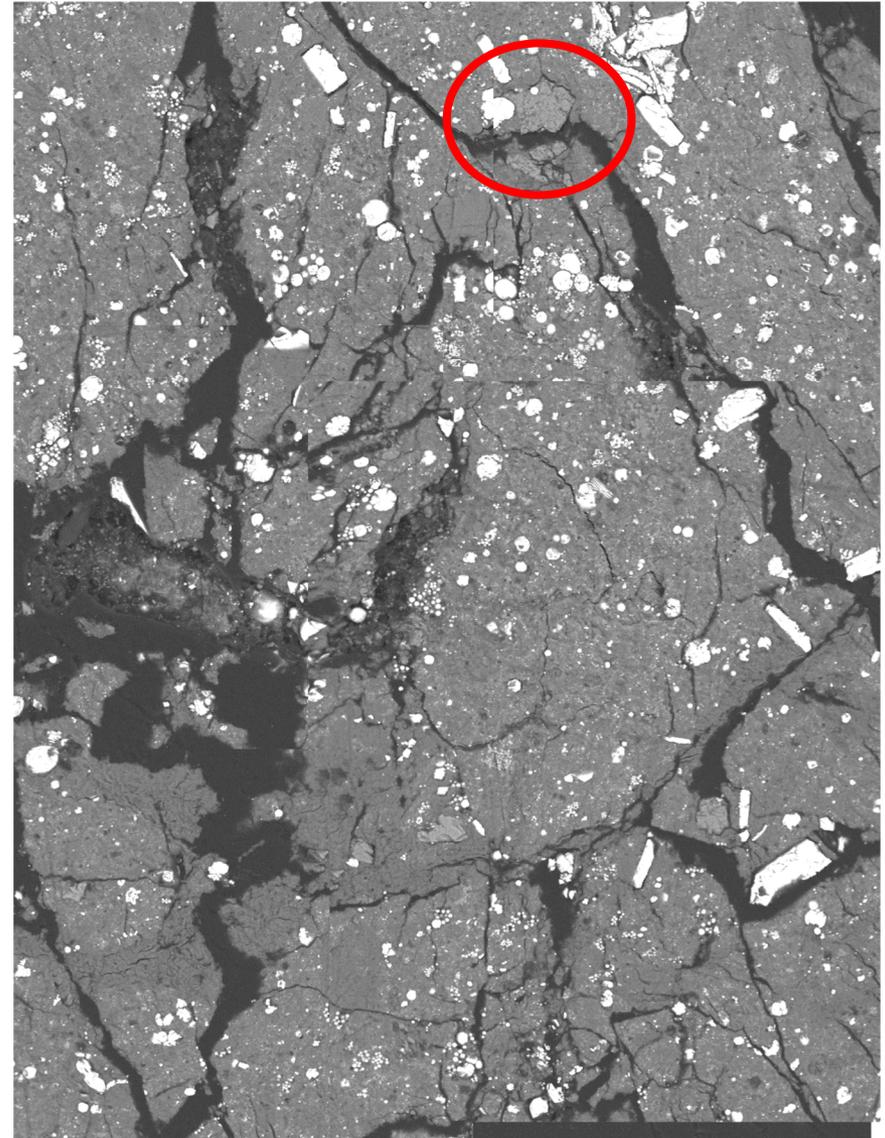
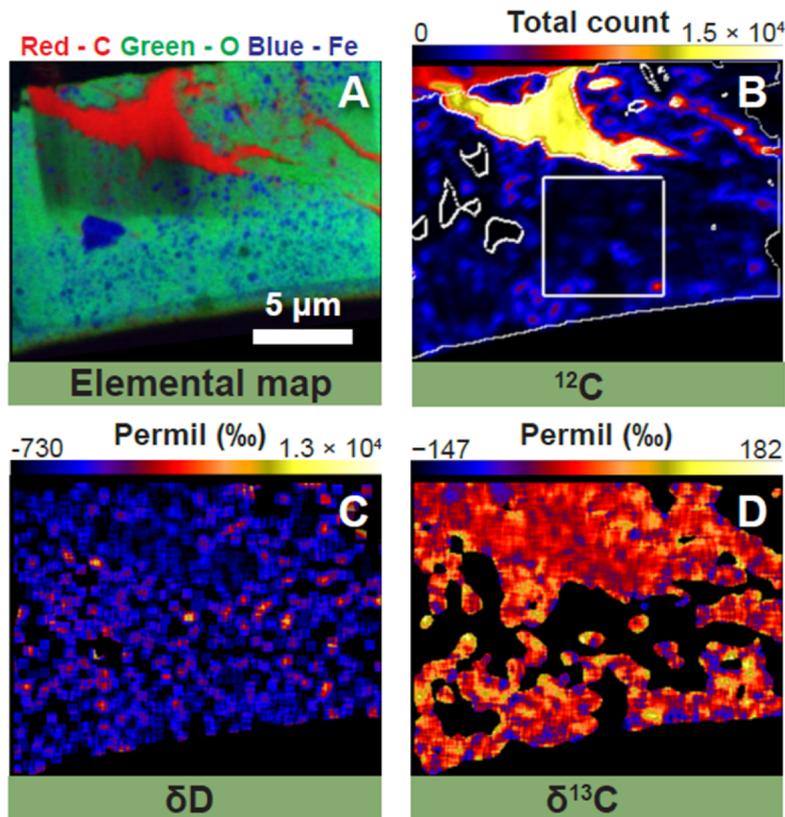
**Microprobe work  
only so far**



# Hydrous clasts

Carancas (H4/5) – small clast in a sample from Jason Utas

Queenie Chan and Yoko Kebukawa did some analyses of organics from a FIB slice

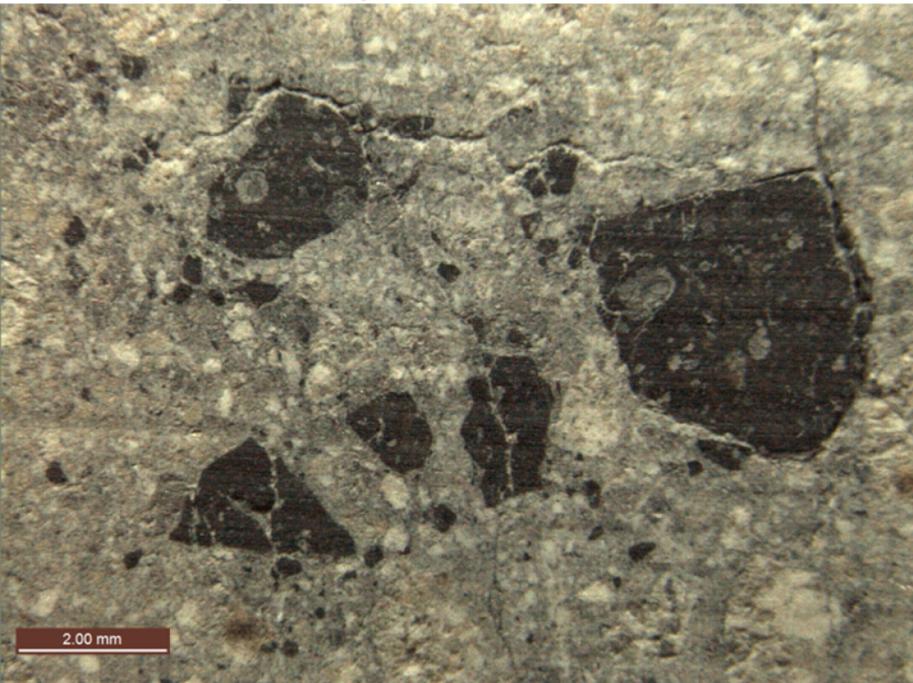


# Carancas crater

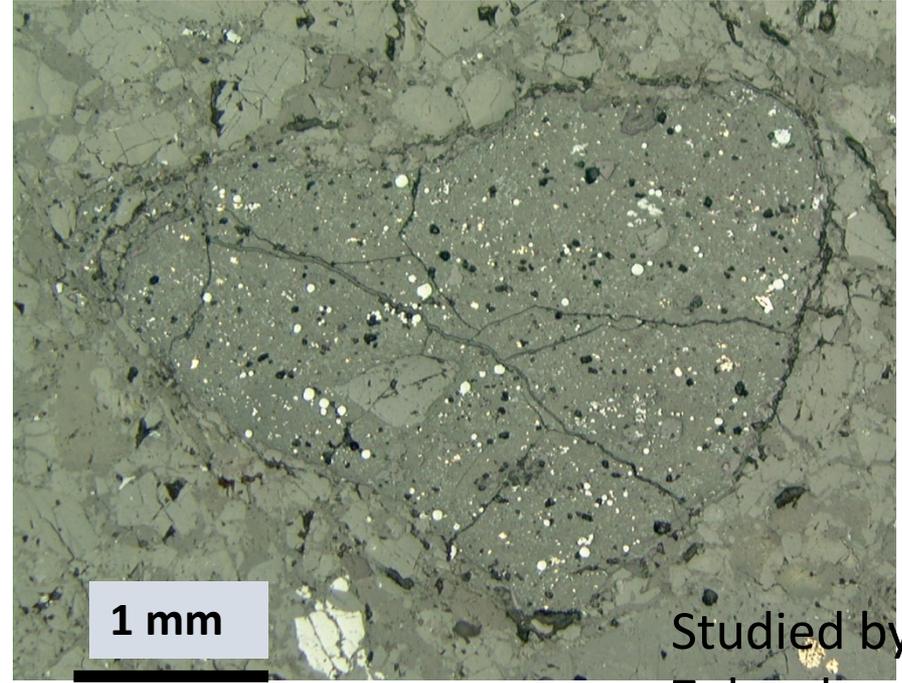
**September 15, 2007, near Lake Titicaca in Peru**



# CR/CI/MM like clasts in HEDS



NWA 6695  
(Howardite)



Y-791834  
(Eucrite)

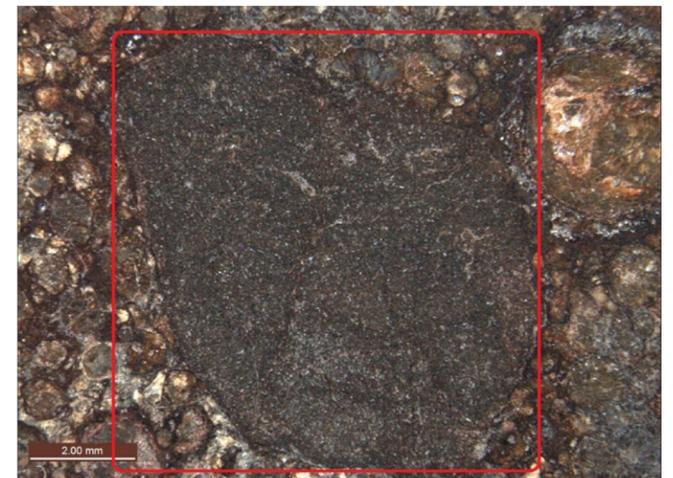
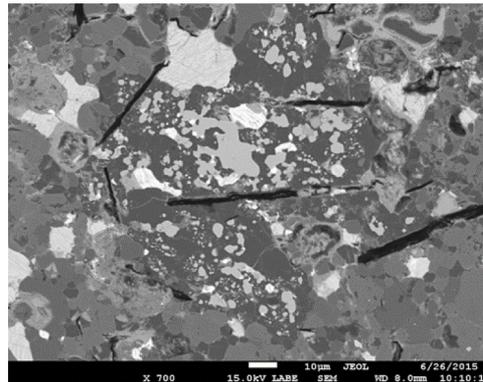
Studied by  
Zolensky,  
Gounelle,  
Briani,  
Buchanan,  
etc

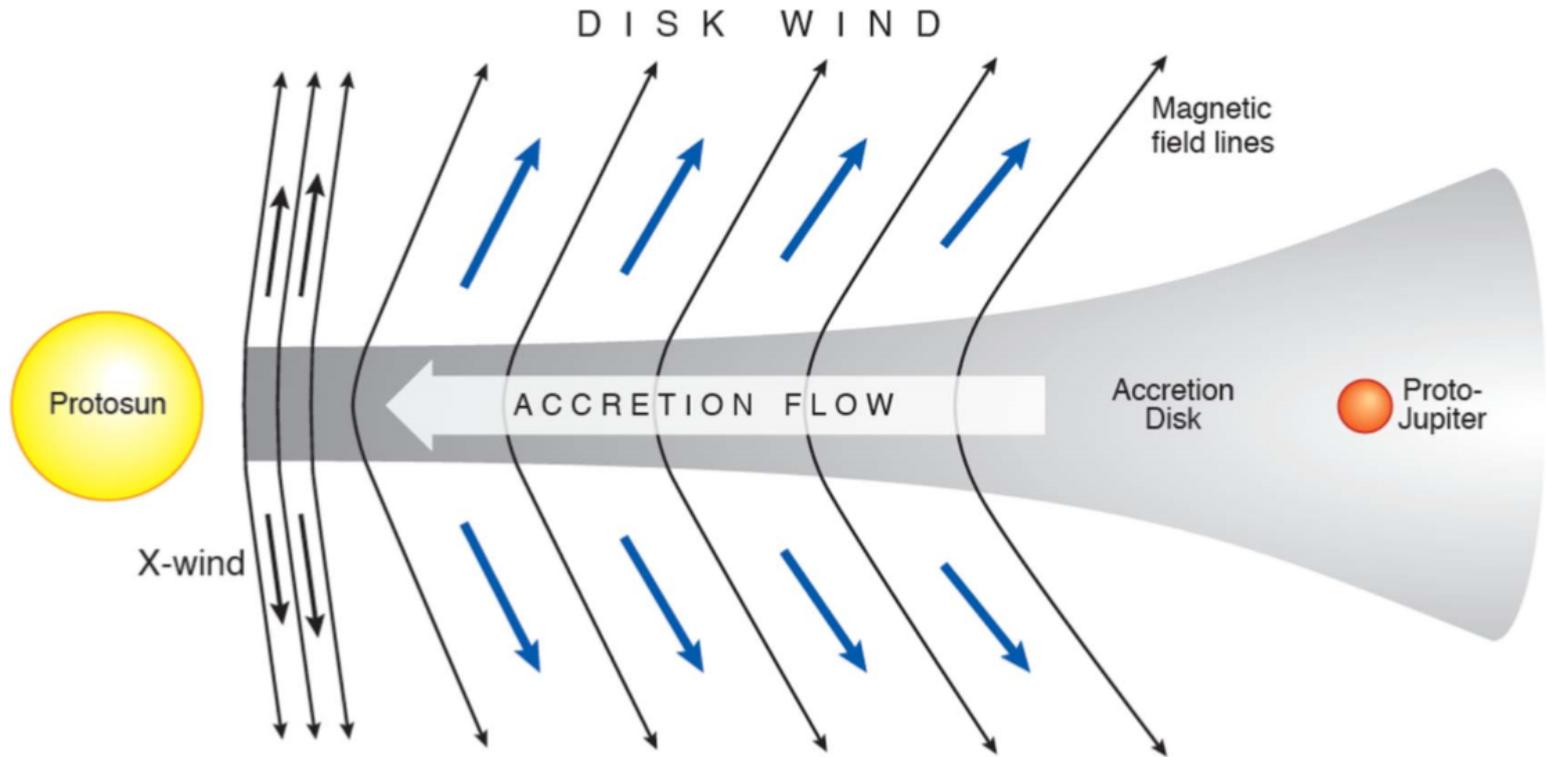
**Our idea is that these hydrous clasts are identical to P and D class asteroid material**

**We plan to date the carbonates to try to determine when they altered**

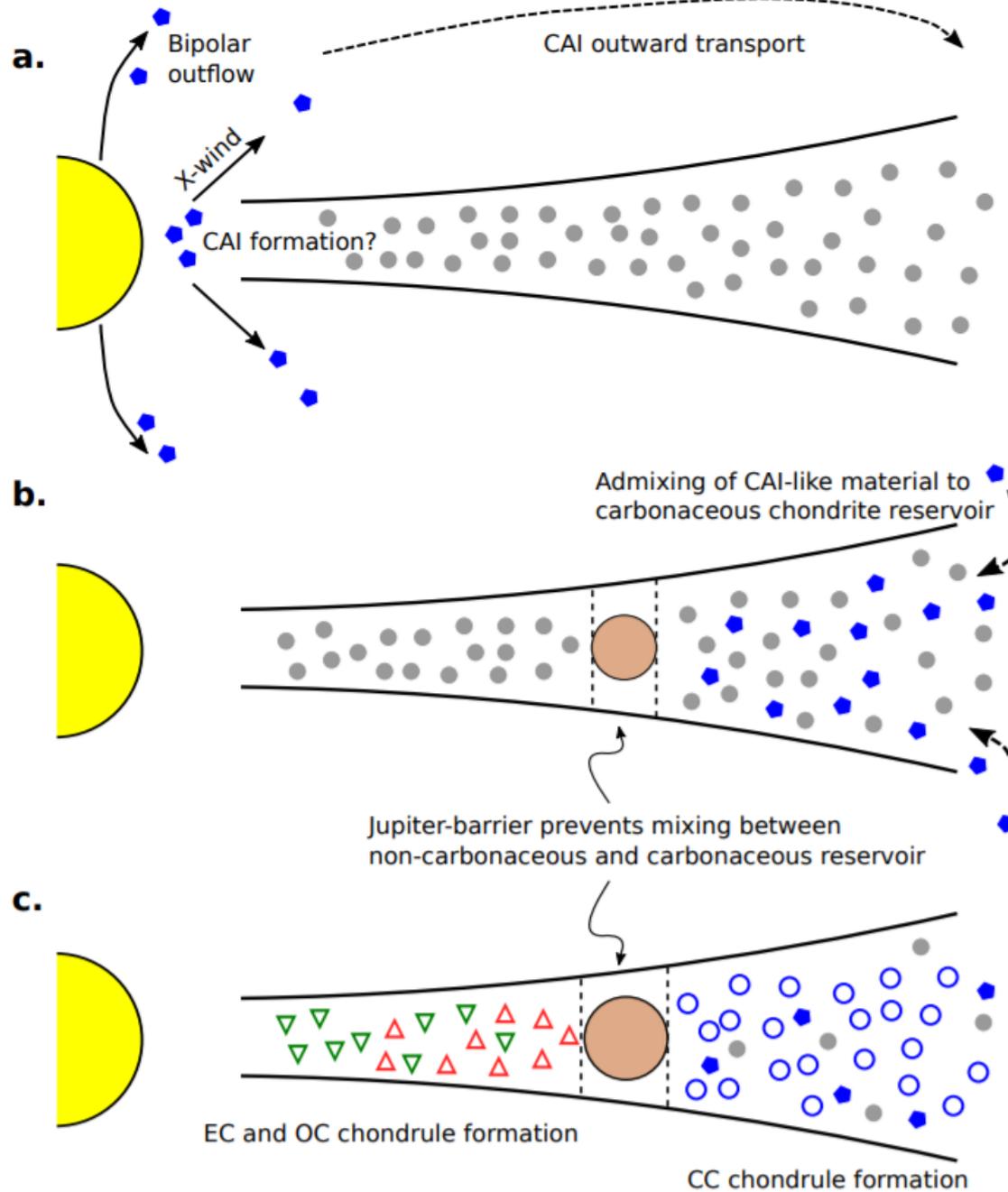
**There are associated carbon-rich anhydrous clasts that we propose to be the products of impacts of the outer ss materials into the inner ss asteroids**

**We plan to date these by Ar-Ar**





**Figure 4.** Cartoon showing the protosolar disk, which surrounds the young Sun, and two mechanisms that have been proposed to accelerate ionized gas along magnetic field lines and launch refractory inclusions and chondrules to the outer part of the disk: the X-wind from close to the protostar (Shu et al. 1996) and disk winds (Salmeron & Ireland 2012). The X-wind model has many problems (Krot et al. 2009; Desch et al. 2010). However, ALMA observations suggest that disk winds, which are responsible for removing



From Gerber et al., 2016