# Ultracarbonaceous Antarctic Micrometeorites (UCAMMs)

*« Samples from the external regions of the protoplanetary disk »*

Cécile Engrand[1] and colleagues[2]…

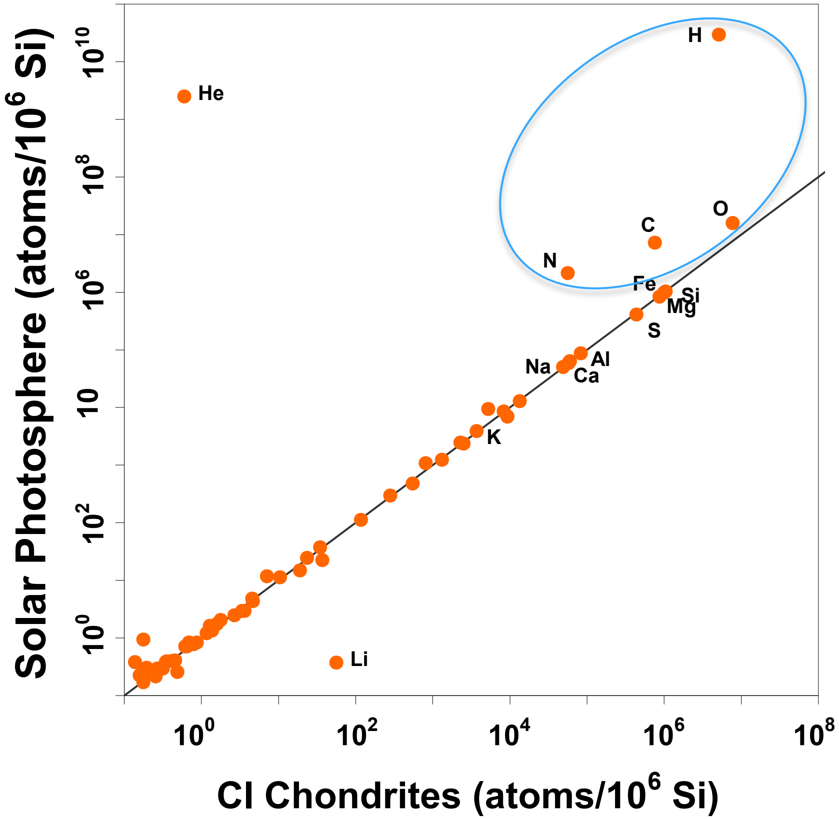
[1]CSNSM, Bât. 104, CRNS/Univ. Paris-Sud, Université Paris-Saclay
Bat. 104, F-91405 Orsay, France (cecile.engrand@csnsm.in2p3.fr)

[2]next slide…

# …colleagues

- CSNSM: E. Charon, J. Duprat, N. Bardin, G. Slodzian, L. Delauche, M. Godard
- IAS: E. Dartois
- Institut Curie: T.D. Wu, J.-L. Guerquin-Kern
- UMET: H. Leroux
- IMPMC: K. Benzerara, L. Remusat
- IPAG: E. Quirico, L. Bonal, F.R. Orthous-Daunay, V. Vuitton
- GANIL: B. Augé et al.
- Univ. New Mexico: E. Dobrica
- Univ. Hawai’i: J.P. Bradley, H. Ishii

# Composition of the solar nebula?


(Lodders 2010)

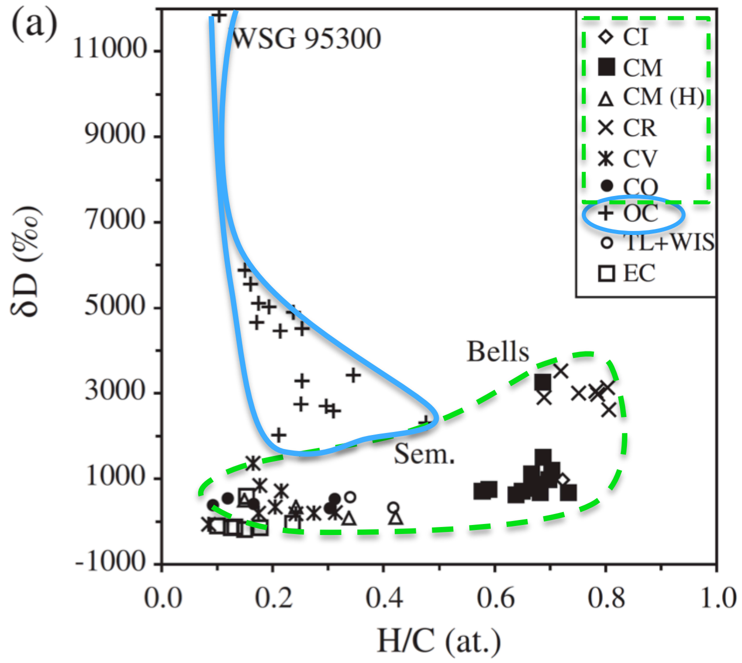
- Carbonaceous chondrites have the solar photosphere's composition
- They only represent ~ 5% of the meteorites
- The light elements are depleted wrt solar values
- Organic matter in extraterrestrial material?
- Comets?

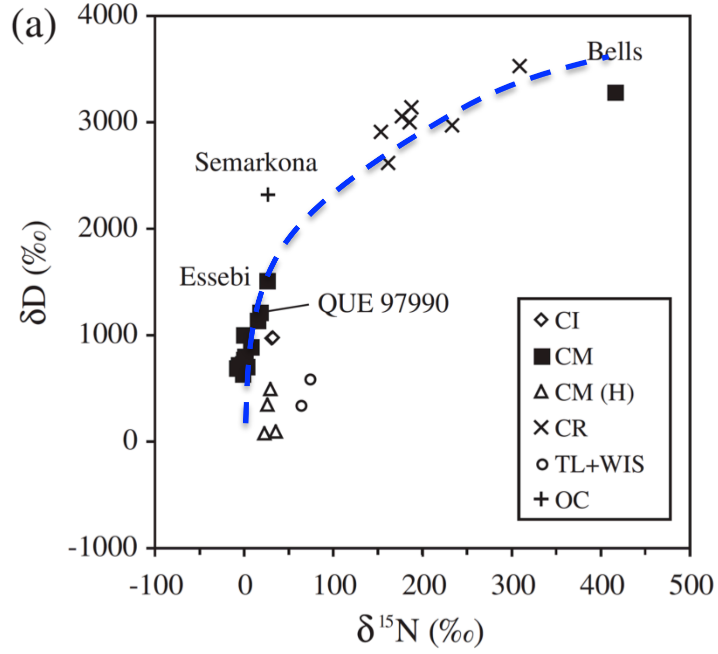
# Primitive organic matter in the Solar System

⇒« insoluble organic matter »

- OM in meterites
  - Origin in Solar nebula vs ISM (presolar molecular cloud)
- OM in comets
  - remote sensing and in situ measurements (Stardust, Rosetta)
- OM in cometary* dust : IDPs and UCAMMs
  - Laboratory measurements of samples collected on Earth

# IOM in meteorites

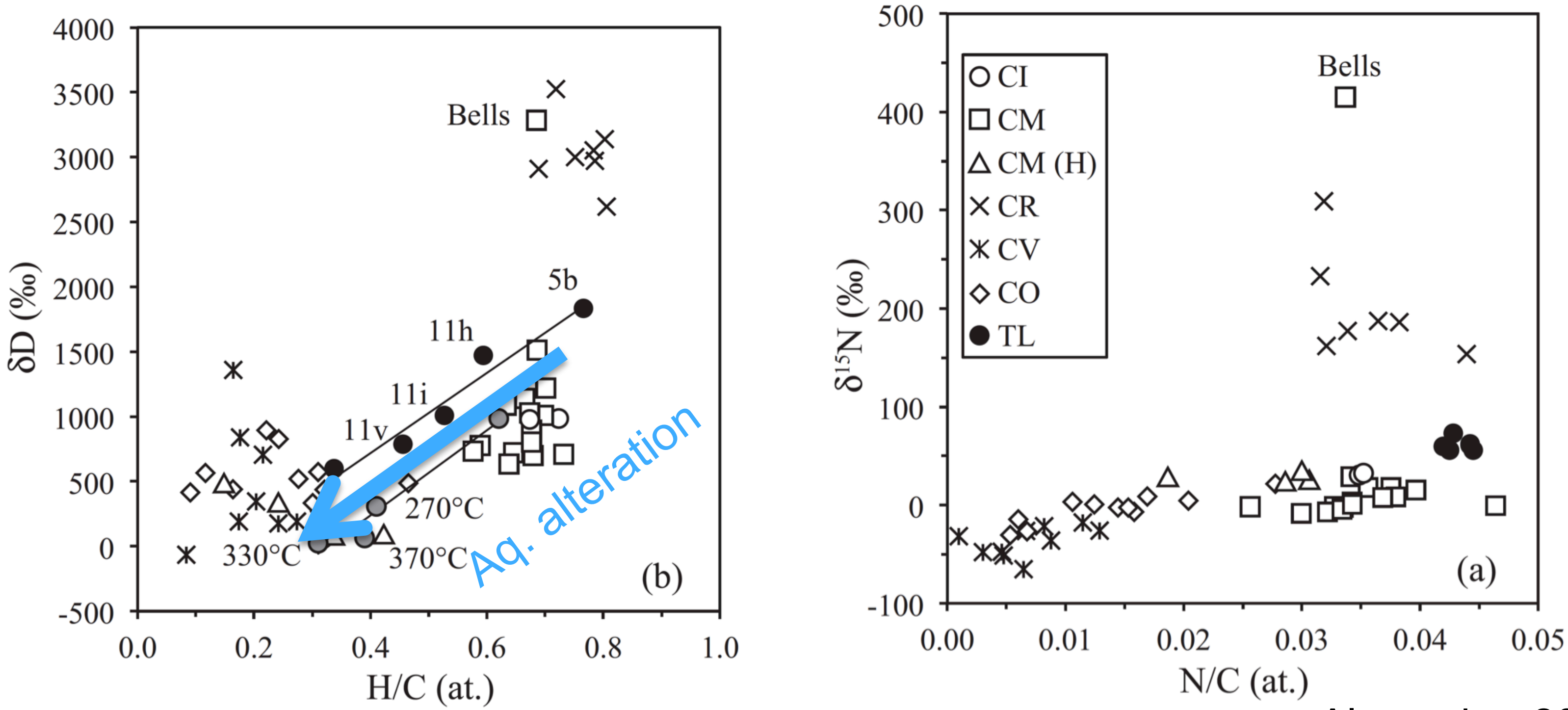



Alexander+2007, 2010, 2014

- CCs : <u>decrease</u> of δD with thermal metamorphism
- UOCs: <u>increase</u> of δD with thermal metamorphism
- Correlation δD - $\delta^{15}$N?

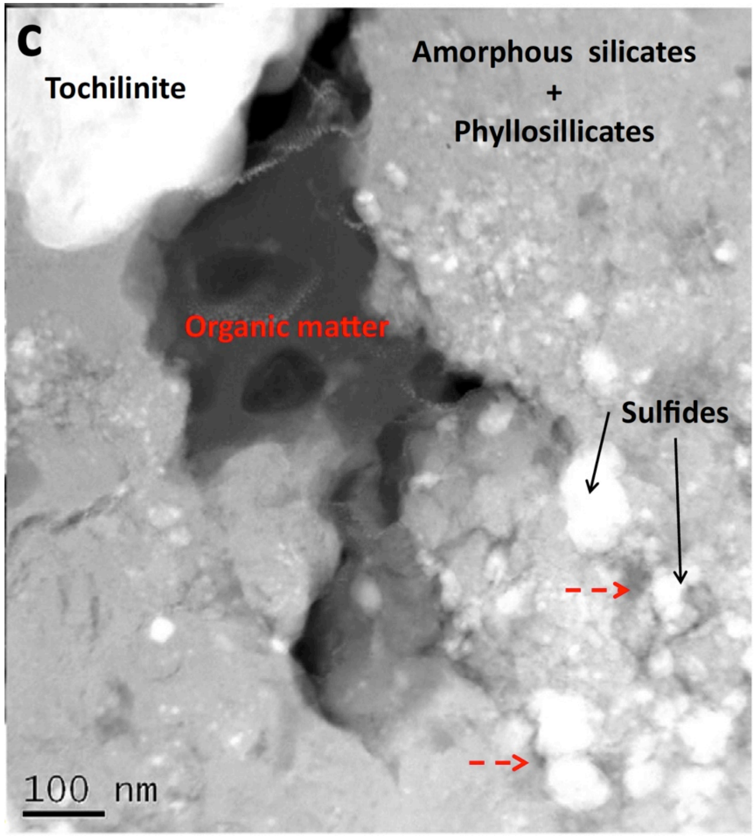
# A unique IOM precursor?



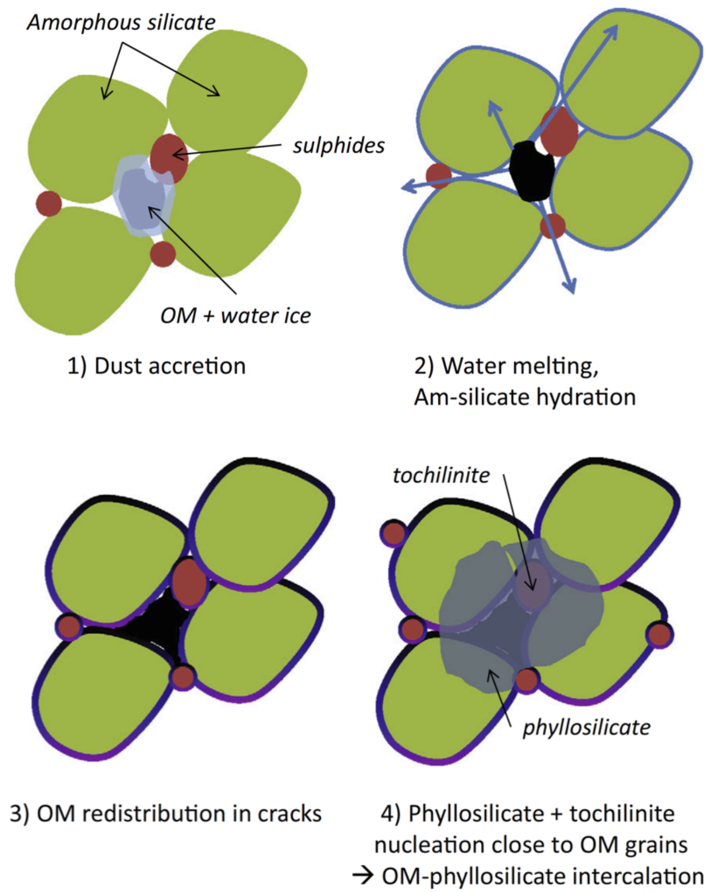

Alexander+2014
Oba &Naraoka2009

- CR-like IOM precursor + aqueous alteration? (Alexander+2014)
- D fractionation from reduction of $H_2O$ by Fe ?

# Ice-OM accretion? (CR meteorite)

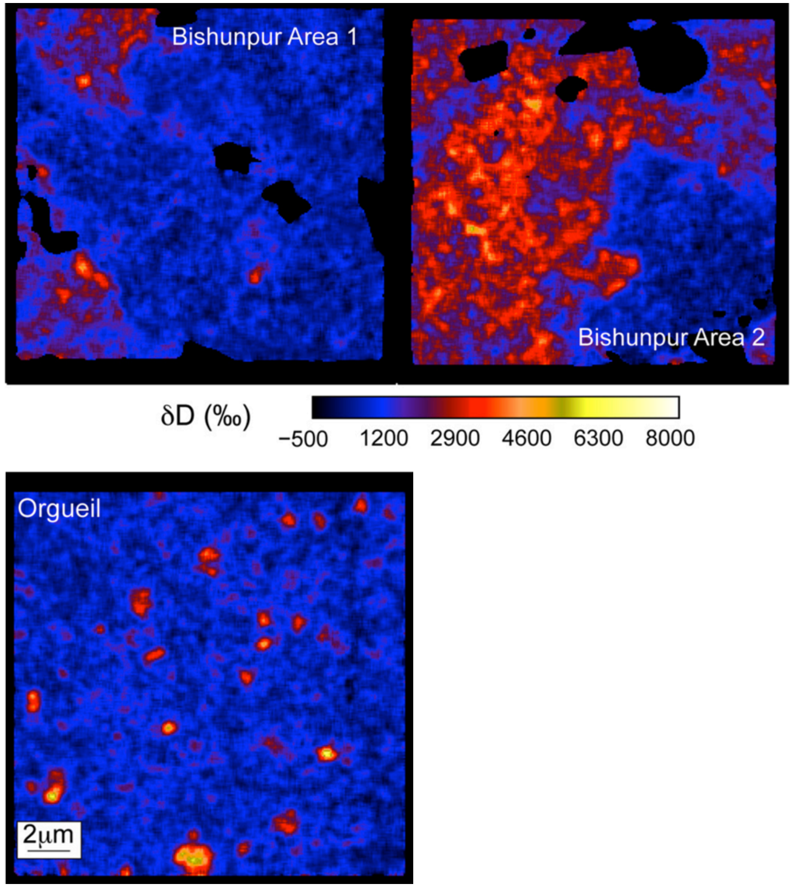



Le Guillou+2014 GCA

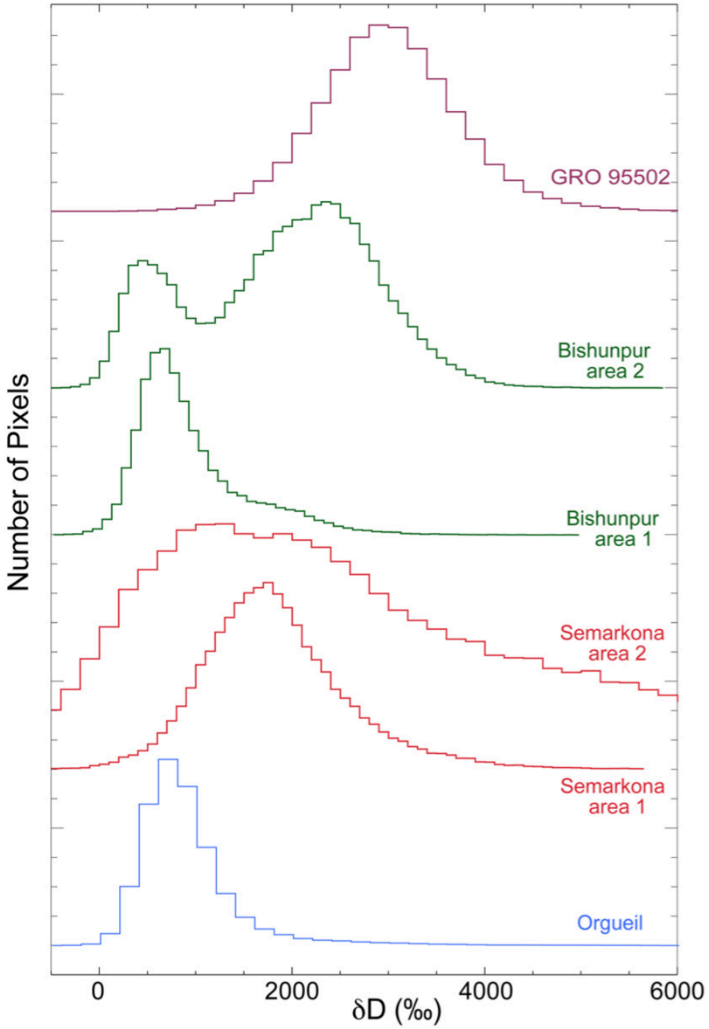



- Link OM – water? (OM – hydrated minerals association)

# Two IOM phases in UOCs

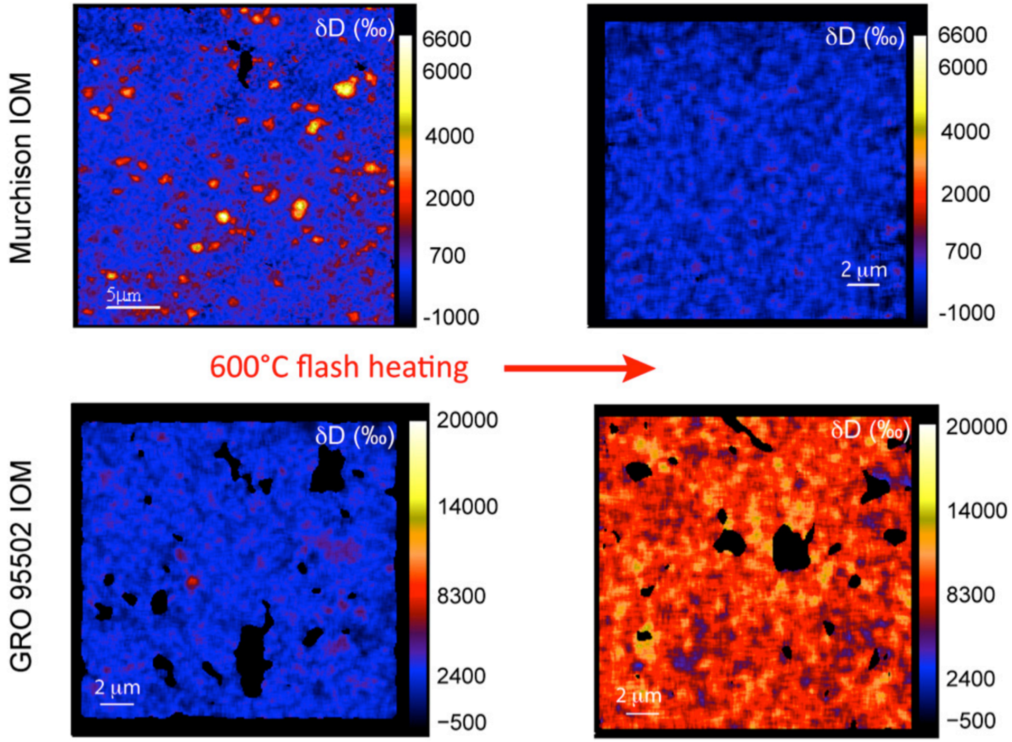



Remusat+2016




- Bimodal distribution of D/H in UOCs

# D/H and thermal metamorphism



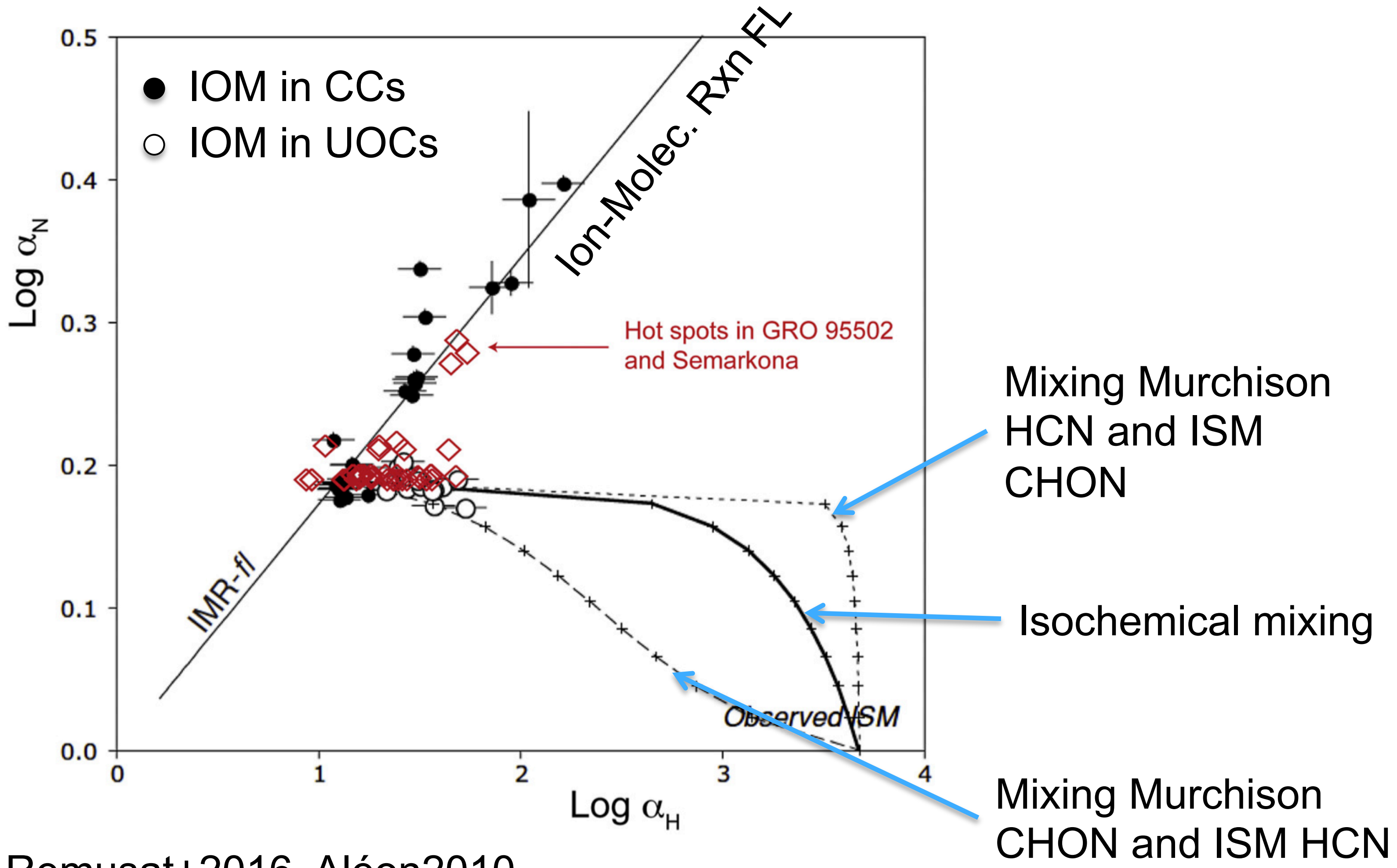

Remusat+2016

- Heating : Similar structural and molecular evolution for UOC and CC IOMs (structural reorganization and increase of aromatic/aliphatic carbon ratio).
- Heating : increase D/H for UOC; decrease D/H for Murchison (CC)
- **Not the same IOM precursor?**
- **ISM component in UOC IOM? (or preferential H loss?)**

# Origin of N isotopic anomalies

- interstellar or cold molecular cloud origin via low-temperature ion–molecule reactions (Terzieva & Herbst 2000, Rodgers & Charnley 2008, Aléon 2010)
  - $^{15}N$ enhancements in two dense prestellar cores (Hily-Blant+2013)
  - variations in N isotopic ratio across the Galaxy (Adande &Ziurys 2012)
- solar system origin via photochemical self-shielding (Clayton 2002; Lyons+2009)
  - Experimental reproduction of $^{15}N$ enrichements by VUV photolysis (Chakraborty+2013)

# Mostly solar origin for CC and UOC IOM




Remusat+2016, Aléon2010

- UOCs: Mixing at the molecular level? (no hotspot with D/H = 0.1 > 0.1μm)
- Some hotspots for 2 UOCs on the IMR-fl (presolar cloud or outer regions)

# IOM in meteorites

- UOC IOM :
  - only D-rich organics
  - homogeneous $\delta^{15}N \sim 0$
  - very few $^{15}N$ anomalies w/ large D-enrichments (IMR)
  - 2 origins? (solar system + ~ 1% presolar cloud?)
- CC IOM:
  - Accretion and mixing of both D- and $^{15}N$-rich organics
  - Ion–molecule or grain surface chemistry in cold environments could explain both D- and $^{15}N$-enrichments
- Comets?

# Spatial exploration of comets

**1986** — **Halley** (*Giotto/ Vega*)

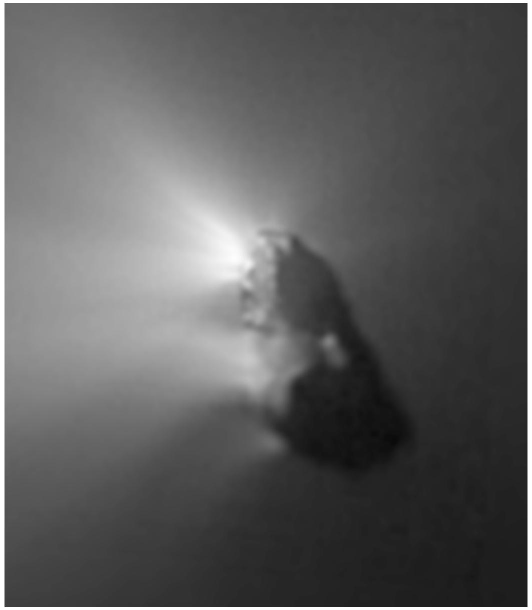
**1992** — **Grigg-Skjellerup** (*Giotto*)

**2001** — **Borelly** (Deep Space 1)

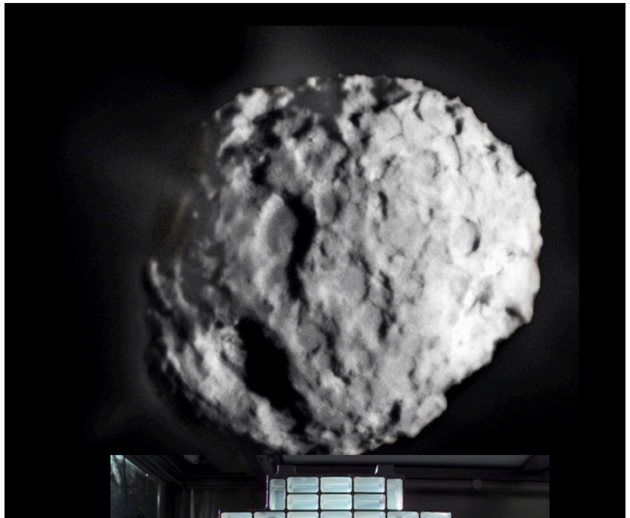
**2004** — **Wild 2** (*Stardust*)

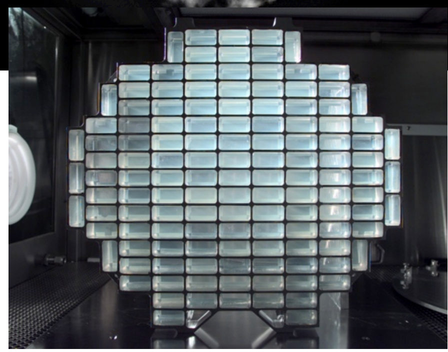
**2005** — **Tempel 1** (Deep Impact)

**2014-16** — **67P/C-G** (Rosetta)

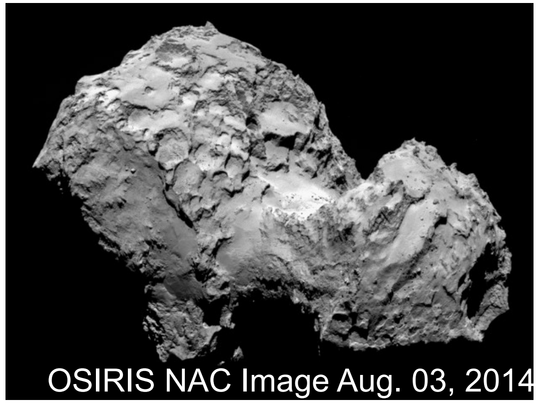


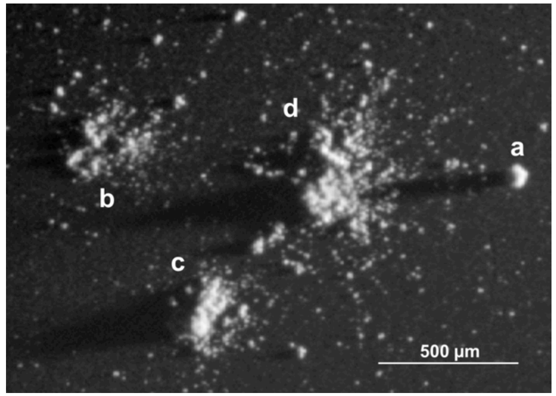
Comet 1P/Halley
1986
Giotto/ESA





Comet 81P/Wild 2
(6 jan. 2004)
Distance 500 km
Stardust/NASA

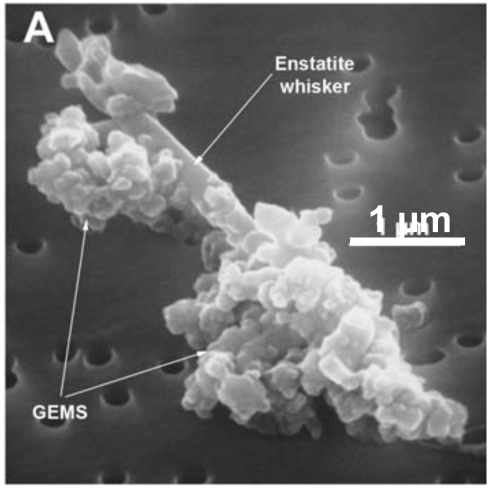



Langevin+2016

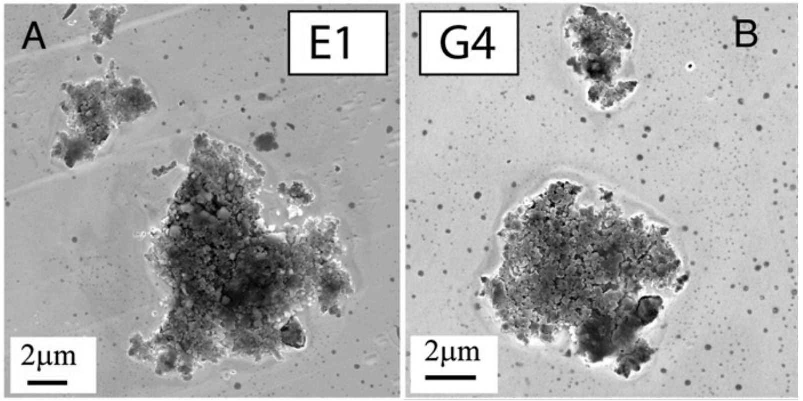
# Cometary dust collected on Earth?

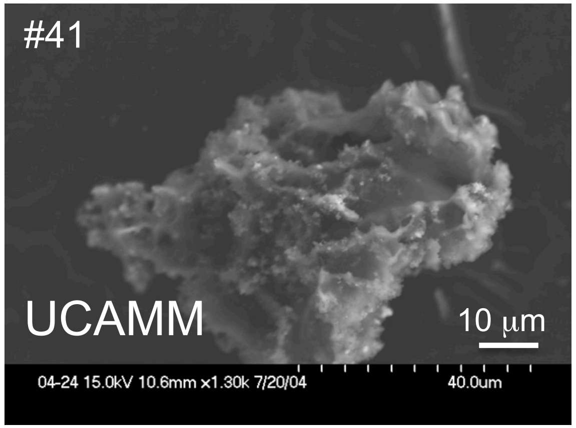
- Cosmic Dust flux ~ 30 000 ton/year
  - (Mass max ~ 200 µm)
- Theorical dual origin : comets and asteroid
- … ~ 90% from JF comets (Nesvorny+2010, Poppe2016…)
- Collection in stratosphere (IDPs) and Antarctica (MMs)
- Cometary dust:
  - IDPs : CP-IDPs & Timed collection (26P/G-S, 21P/G-Z)
  - UCAMMs



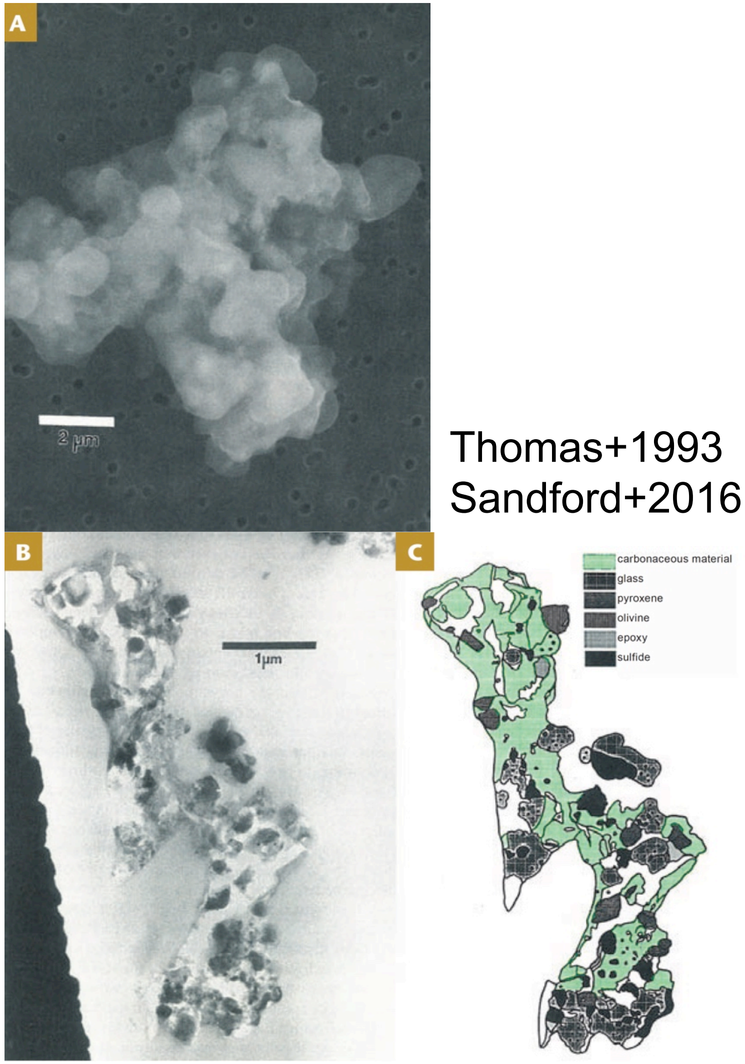

Ishii+2008

Grigg-Skjellerup IDP

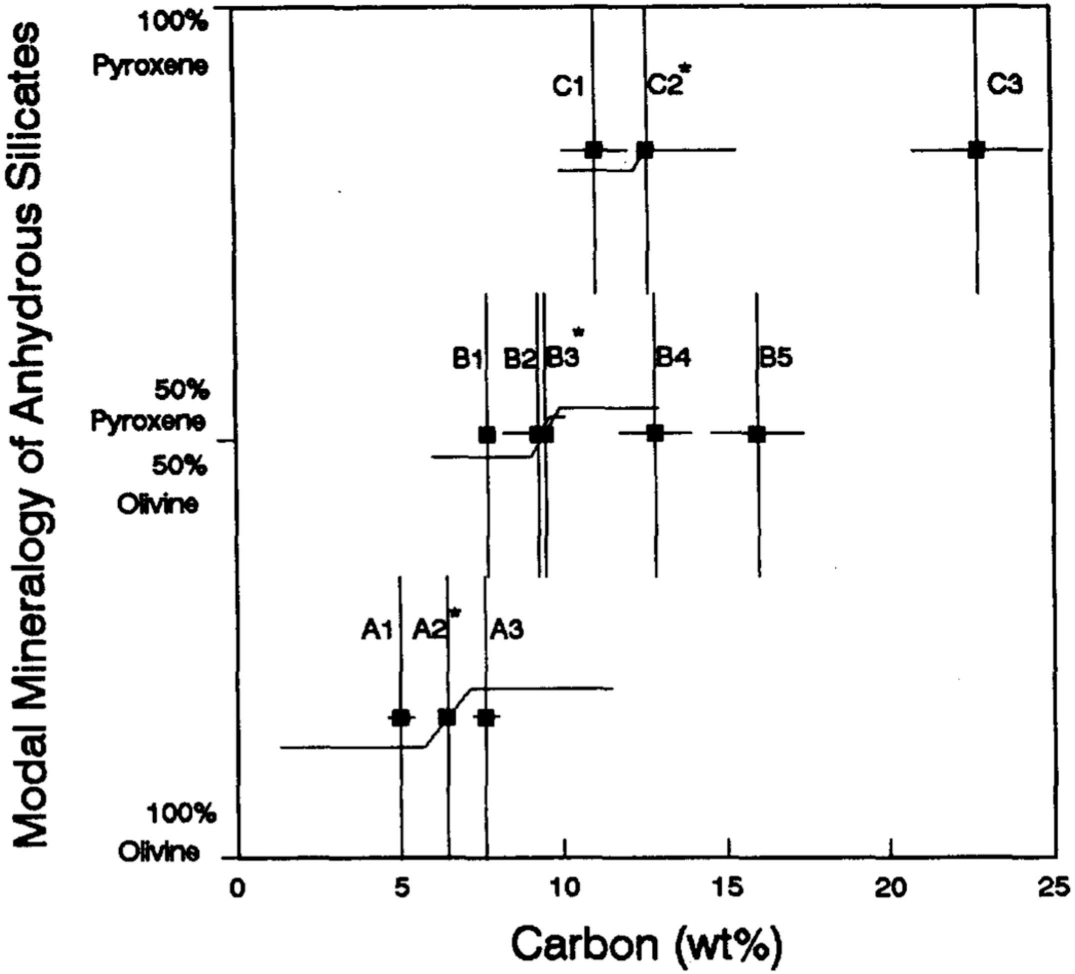


# CP-IDPs are C-rich & Px-dominated



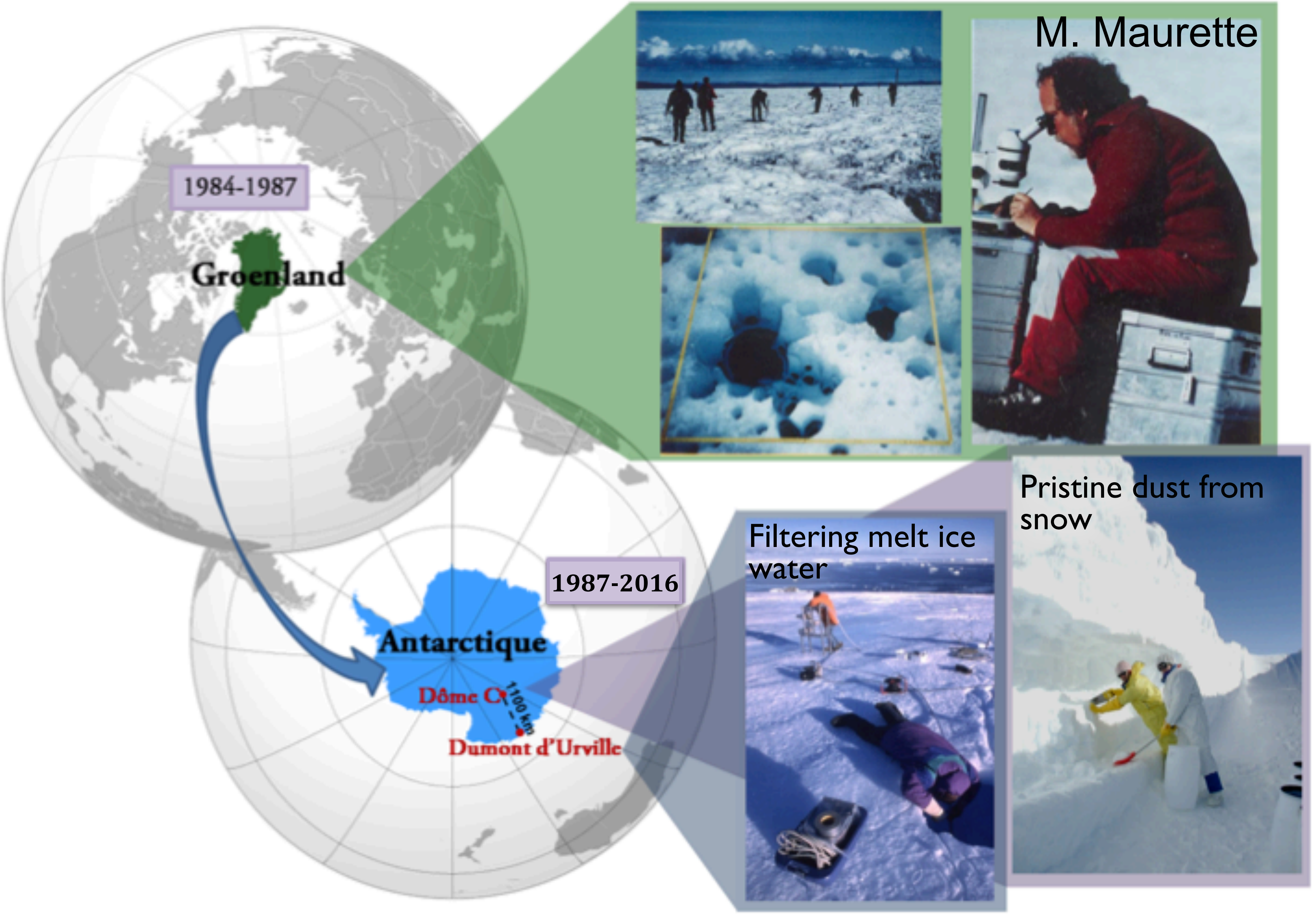

Thomas+1993
Sandford+2016




Thomas+1993

- A cometary origin of CP-IDPs is proposed

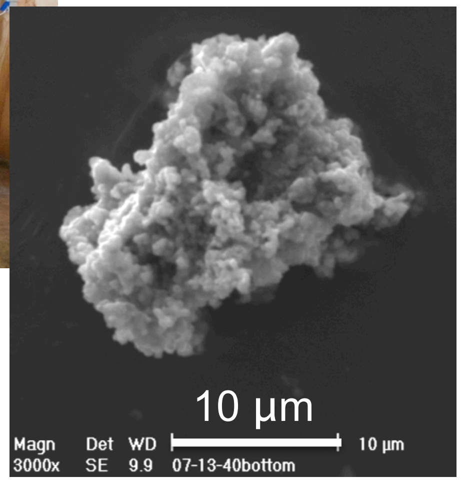
# French Micrometeorite collections



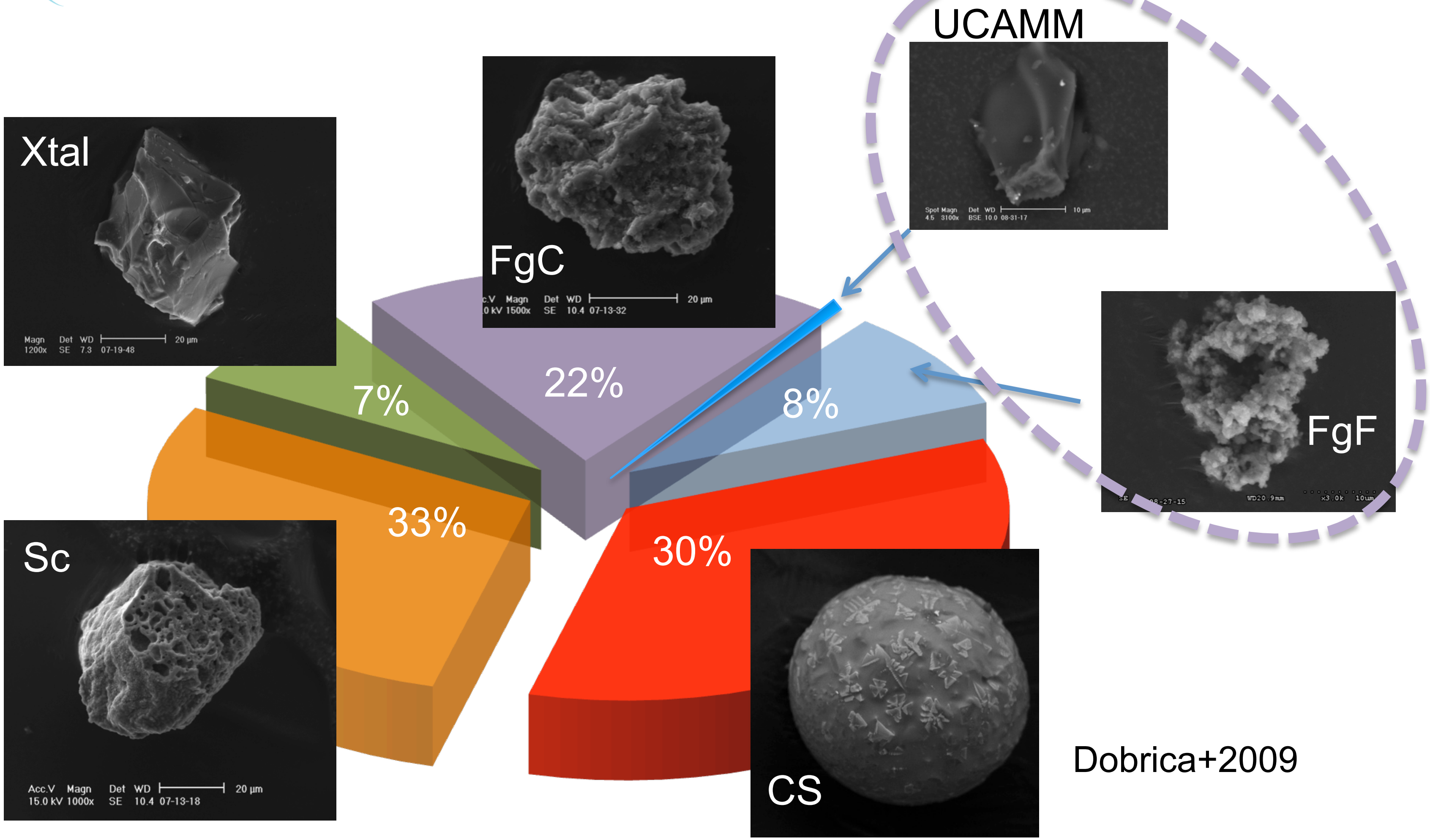

Maurette+ Nature 1987, 1991
Duprat+ ASR 2007

# Micrometeorites @ CONCORDIA
# Micrometeorites from central Antarctic snow

- **CONCORDIA Collection (CSNSM)**
  - **> 5000 interplanetary dust particles** CONCORDIA (75°S, 123°E) (IPEV-CNRS)
  - **Very good preservation**
  - **2000, 2002, 2006, 2014 & 2016 field campaigns**



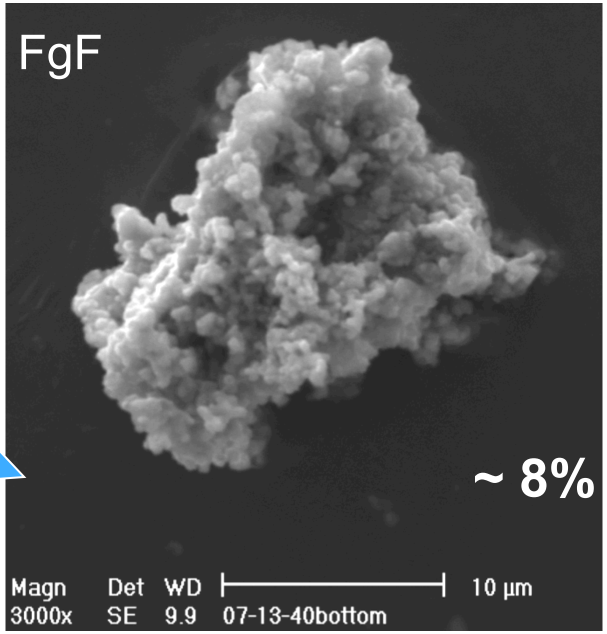
# Concordia micrometeorites

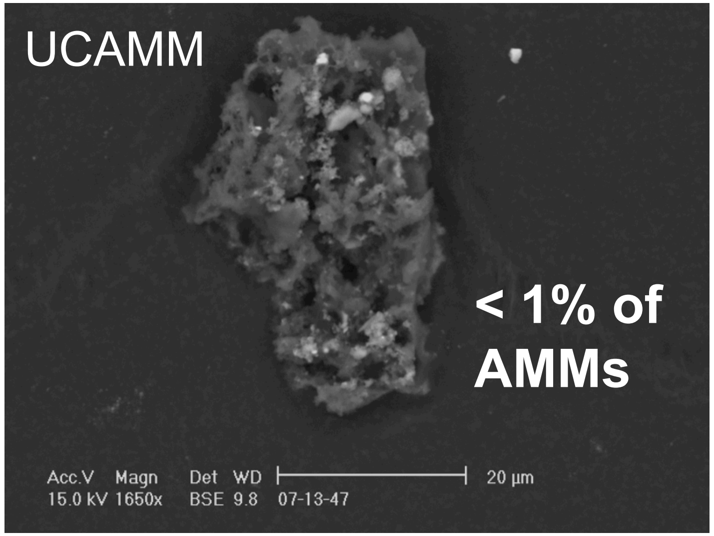



- size range: 20-250 μm
- Average size ~45 μm

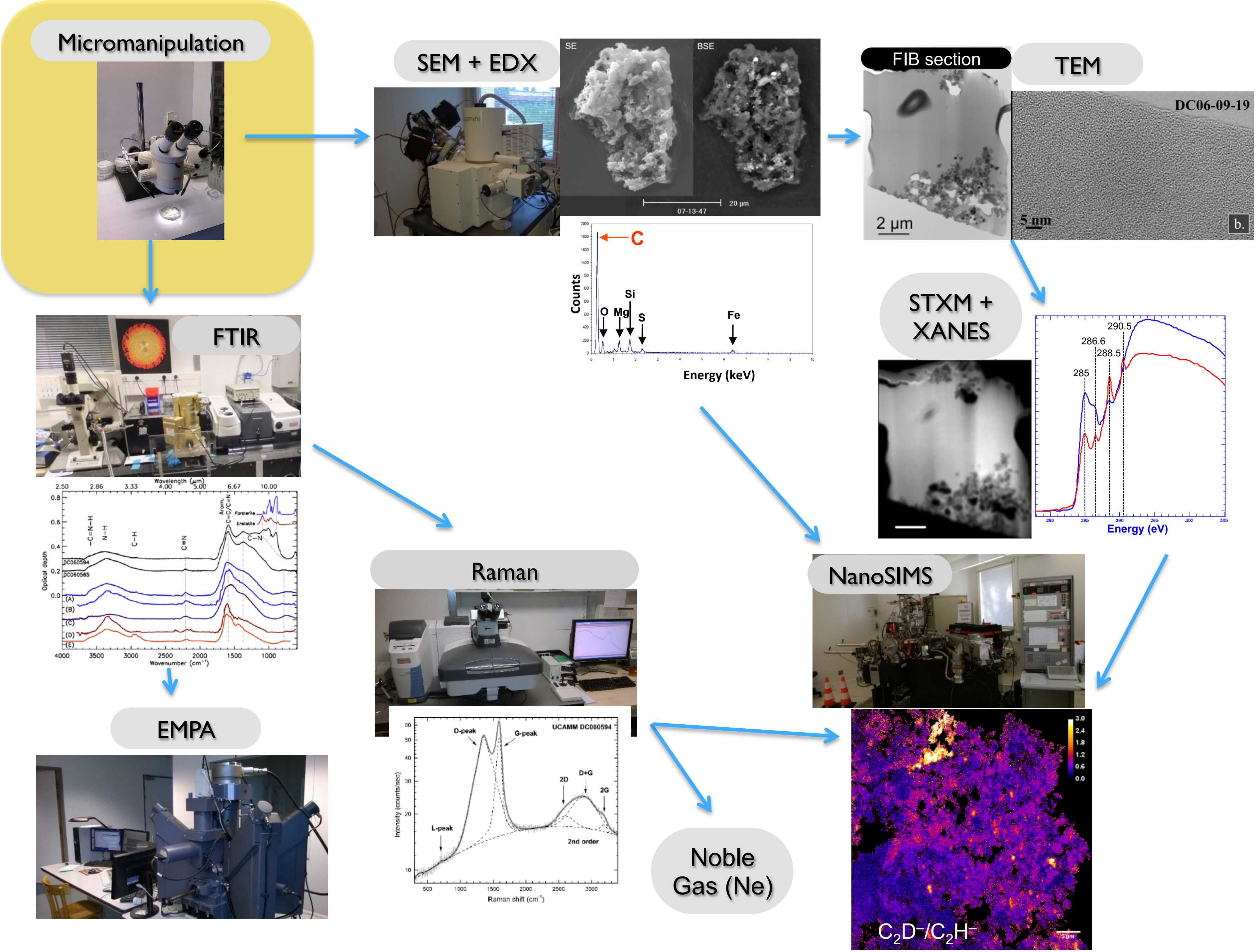
# The CONCORDIA MM collection

- Two new families of particles:
  - Friable MMs (FgF, Fine-Grained Fluffy) = CP-IDPs?
  - Ultracarbonaceous Antarctic MMs (UCAMMs)

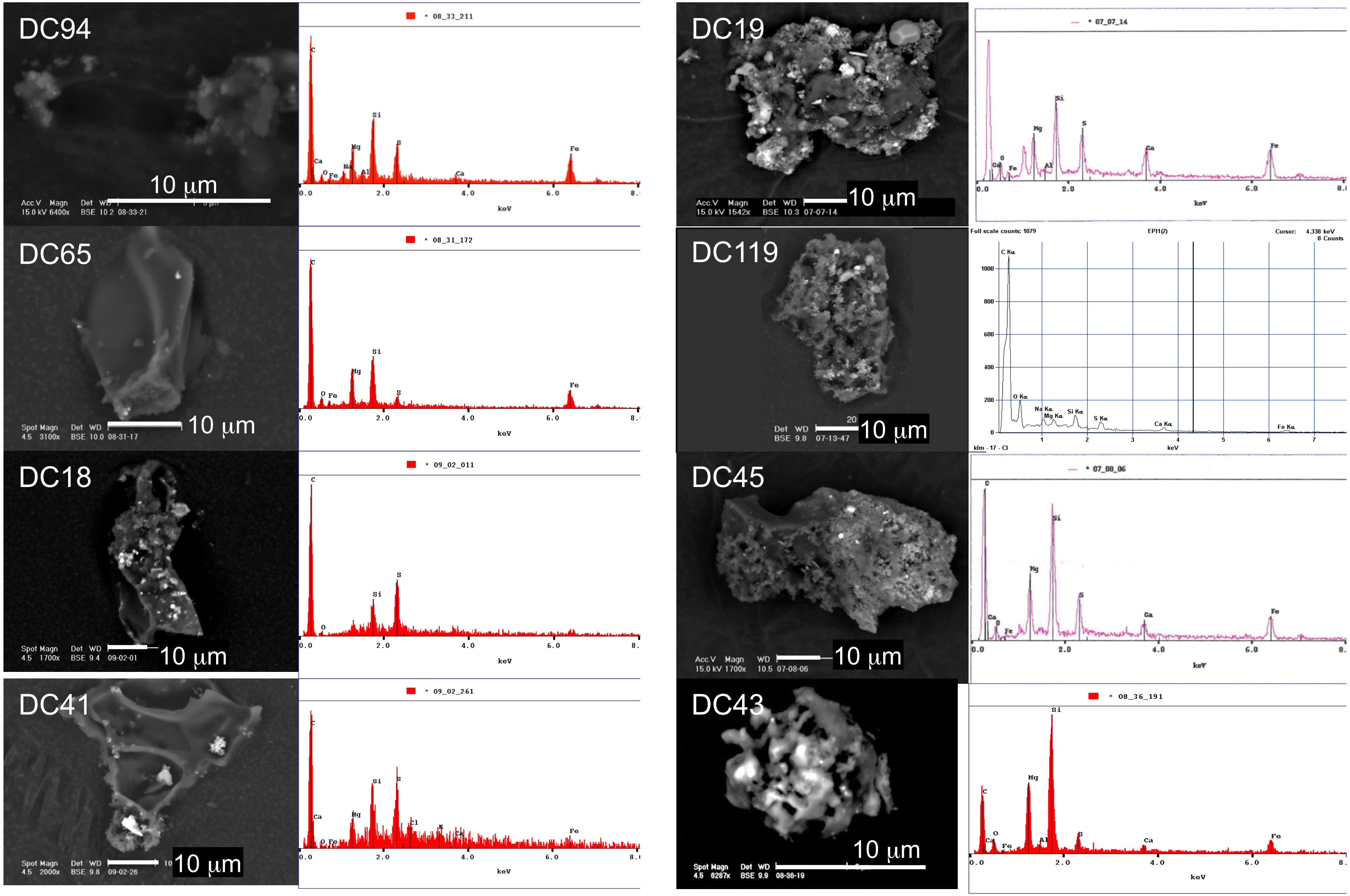


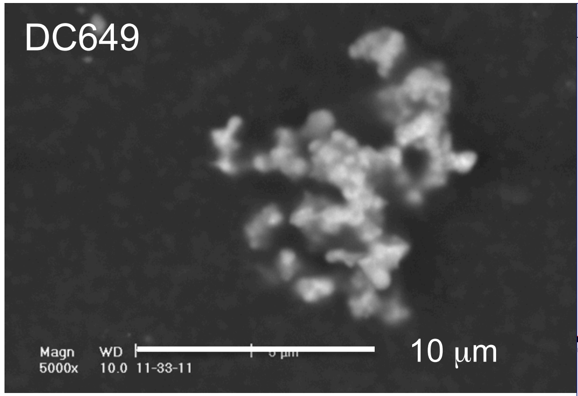

Nakamura+2005, Dobrică+2009, 2011, 2012, Duprat+ Science 2010

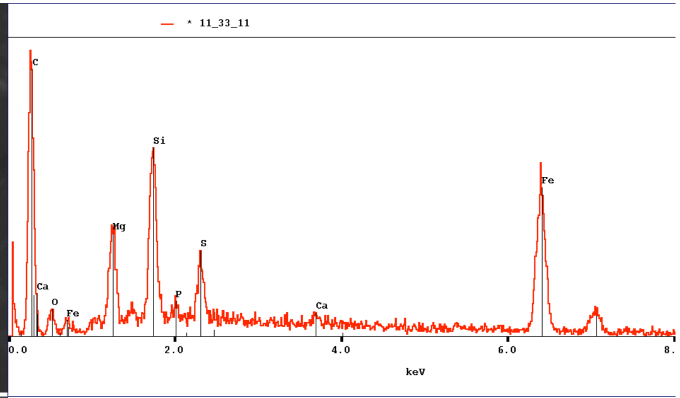

Micromanipulation
SEM + EDX
SE
BSE
07-13-47
20 µm
C
Counts
O
Mg
Si
S
Fe
Energy (keV)
FIB section
2 µm
TEM
DC06-09-19
5 nm
b.
STXM +
XANES
290.5
286.6
288.5
285
Energy (eV)
FTIR
Wavelength (µm)
Optical depth
Wavenumber (cm⁻¹)
Forsterite
Enstatite
DC060594
DC060565
Raman
D-peak
G-peak
UCAMM DC060594
2D
D+G
2G
L-peak
2nd order
Raman shift (cm⁻¹)
NanoSIMS
$C_2D^-/C_2H^-$
EMPA
Noble
Gas (Ne)

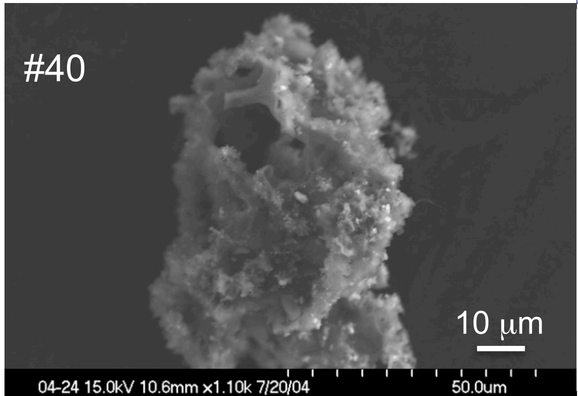
# 11 CONCORDIA UCAMMs

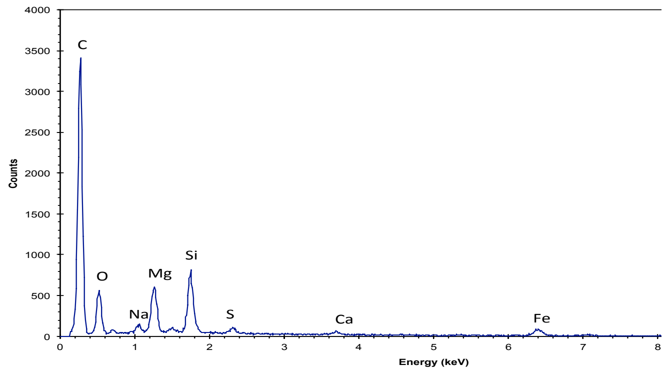


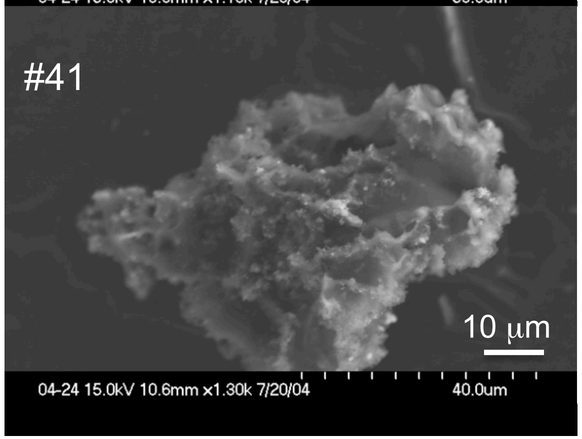
# 11 CONCORDIA UCAMMs (cont'd)

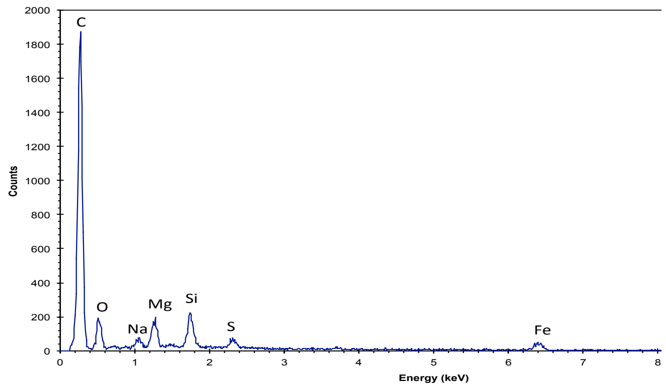


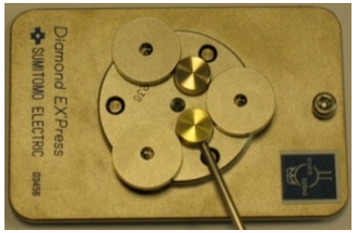



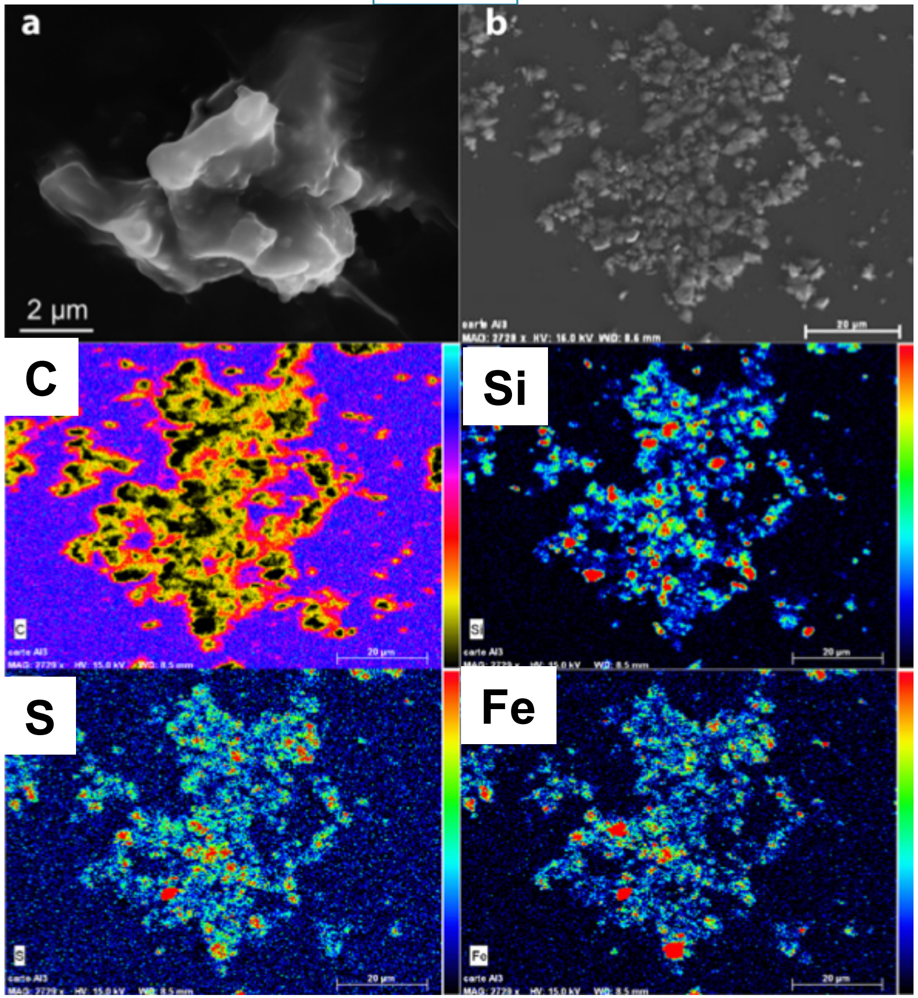




And still searching…

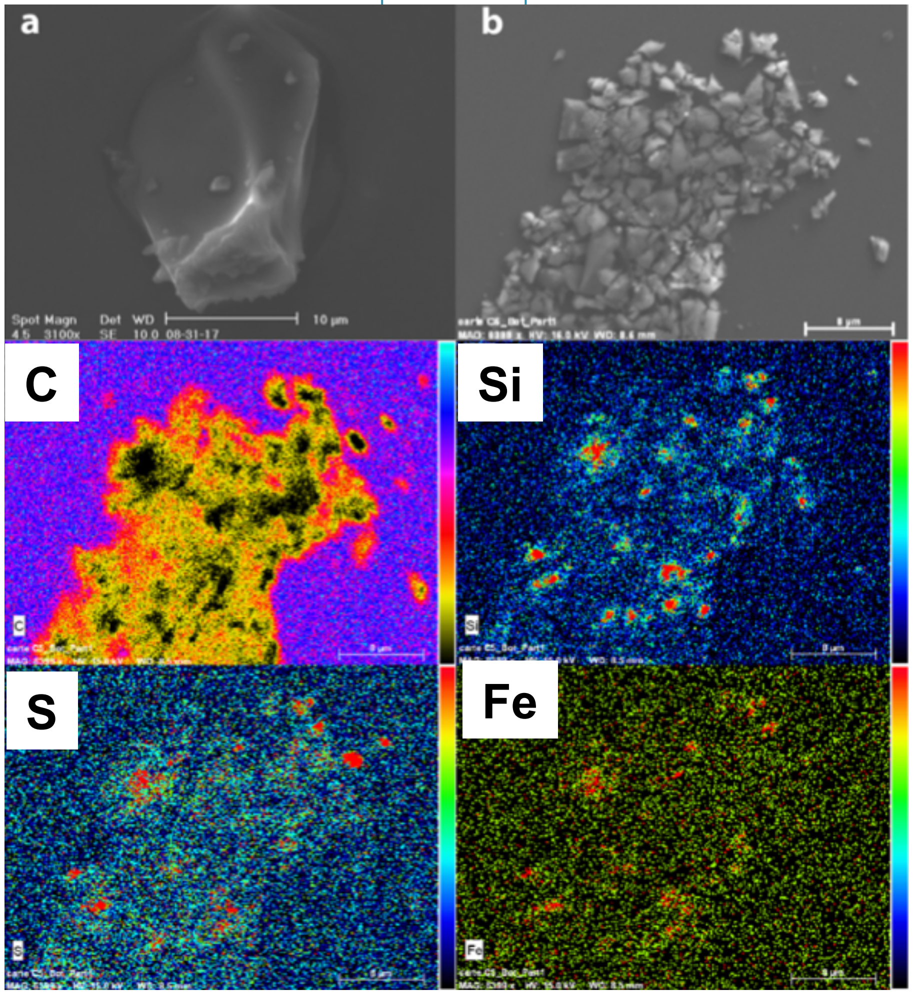
# UCAMMS for IR and SIMS



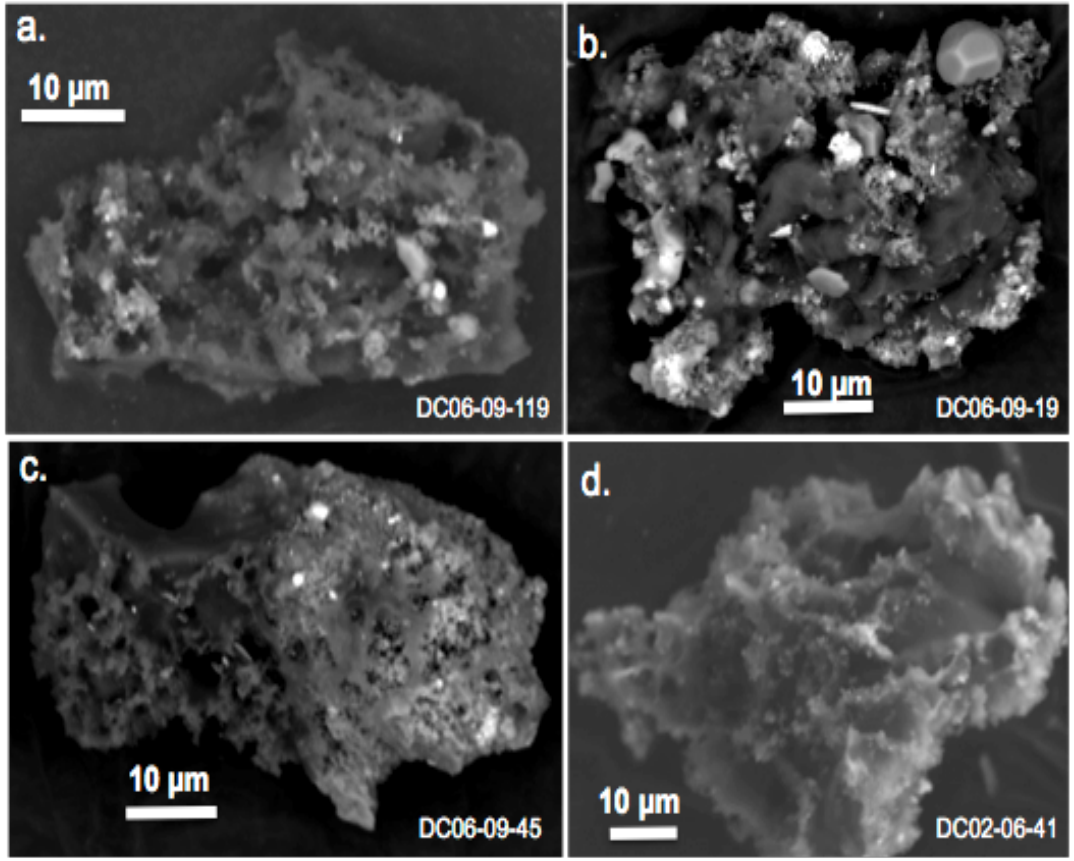

DC94

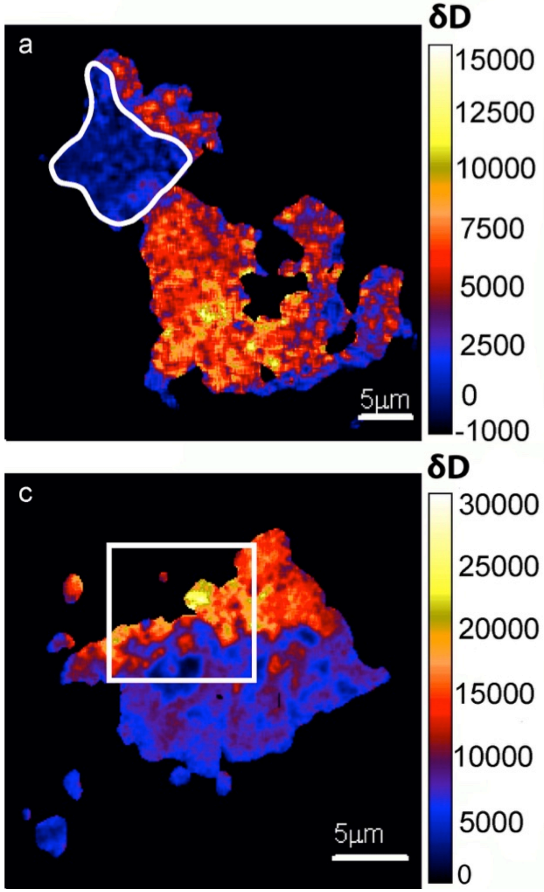



DC65



# UCAMMs – Hydrogen isotopes (NanoSIMS)



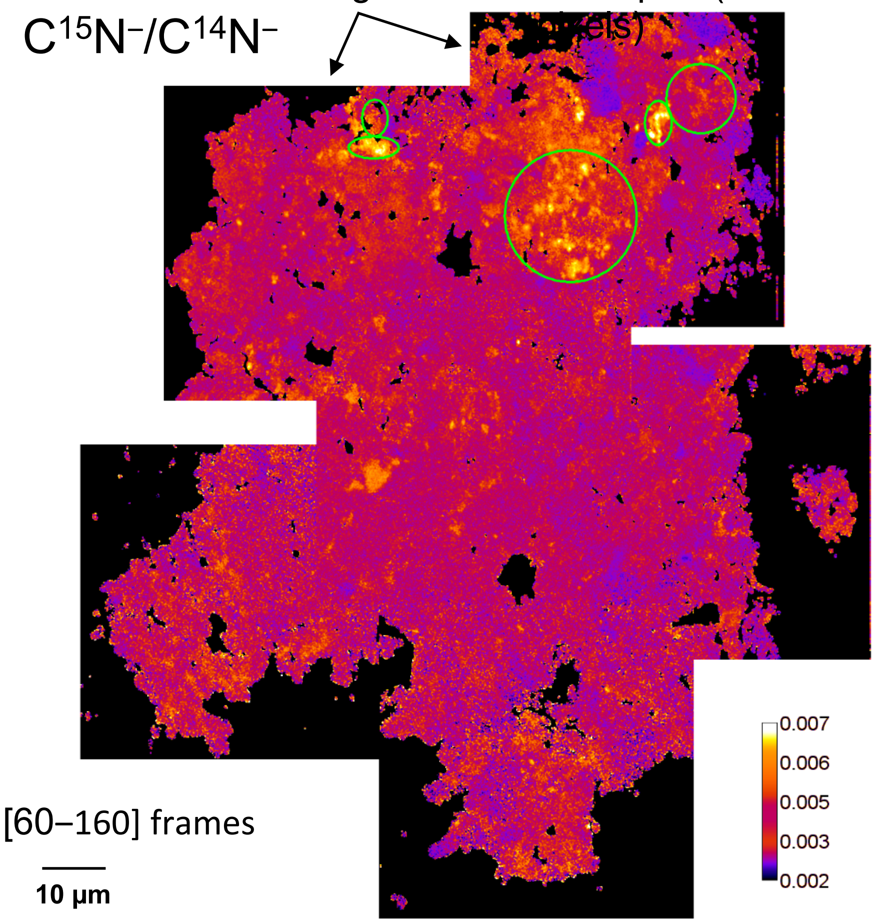

Duprat+2010 Science

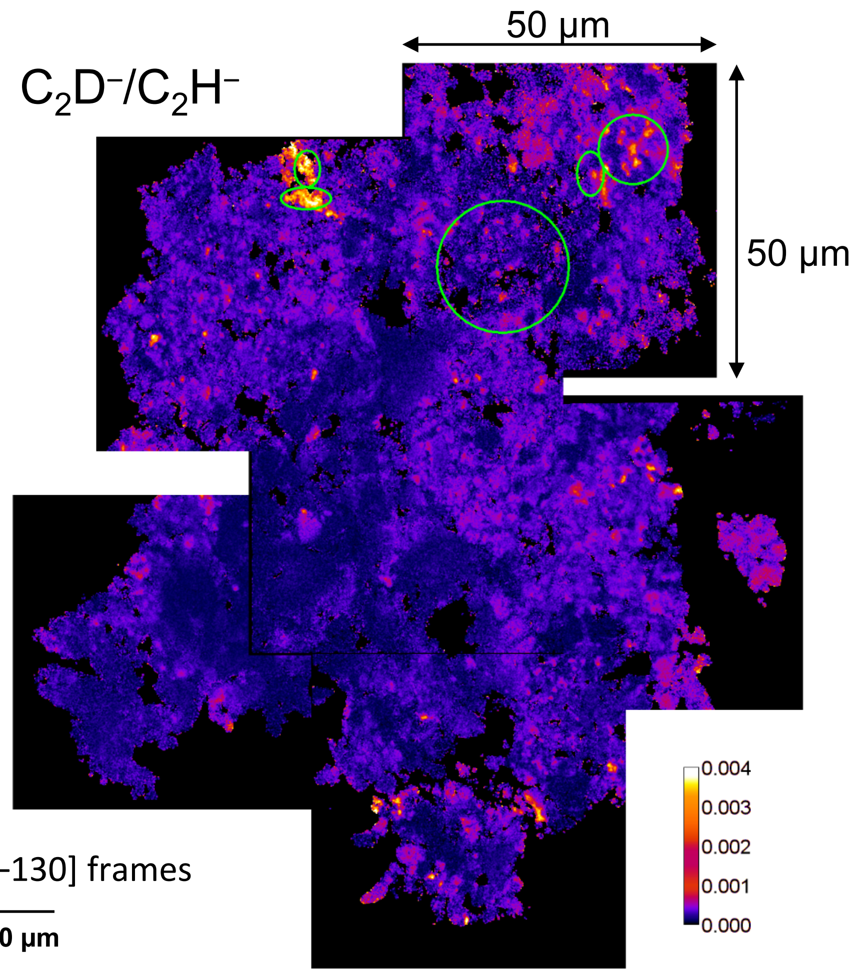
- A globally D-rich carbonaceous phase (D/Hbulk ~ 5 to 10 times SMOW)
- Maximum D/H ratios up to 30x terrestrial value (i.e. $4.6 \pm 0.5 \times 10^{-3}$)

# $C^{15}N^-/C^{14}N^-$ and $C_2D^-/C_2H^-$ isotopic ratio images on DC94

It is possible to compare the $C^{15}N^-/C^{14}N^-$ and $C_2D^-/C_2H^-$ isotopic ratio images

Image size : 50 × 50 µm² (512 × 512

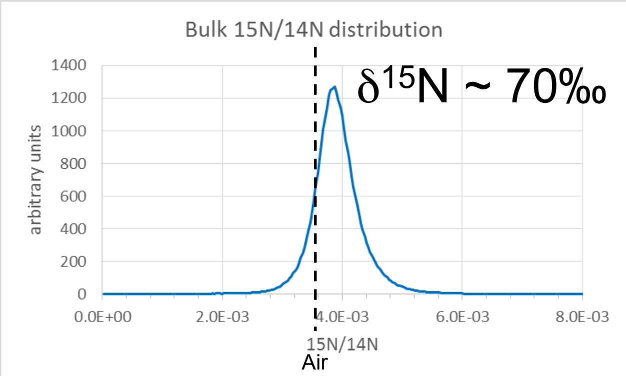


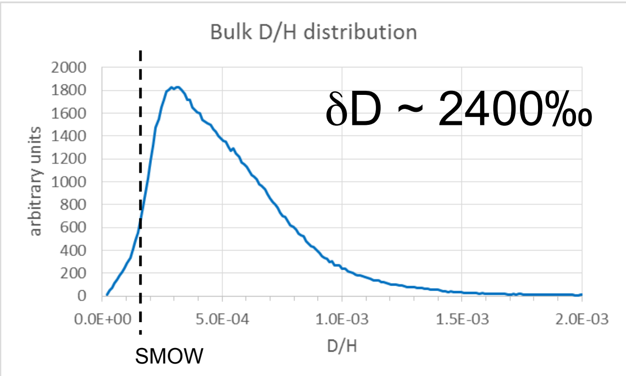



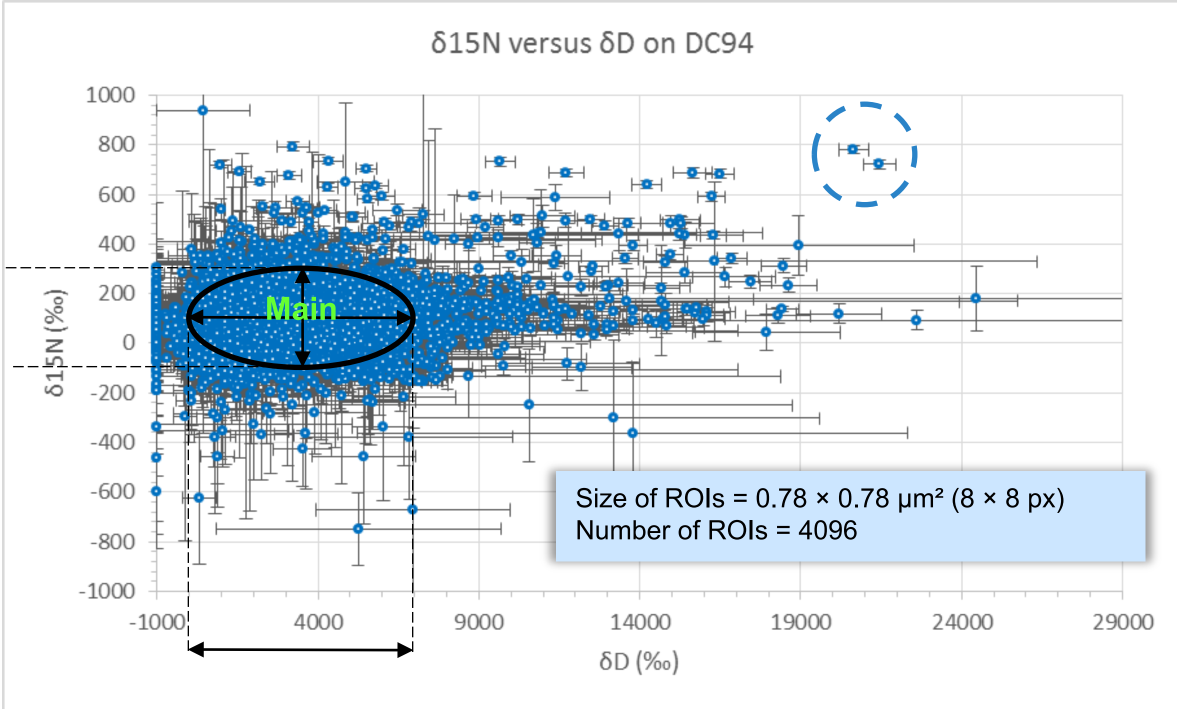

(Bardin+ MetSoc 2015)

- DC94 fragment has heterogeneous N and H isotopic compositions

# Search for spatial correlations between $\delta^{15}N$ and $\delta D$



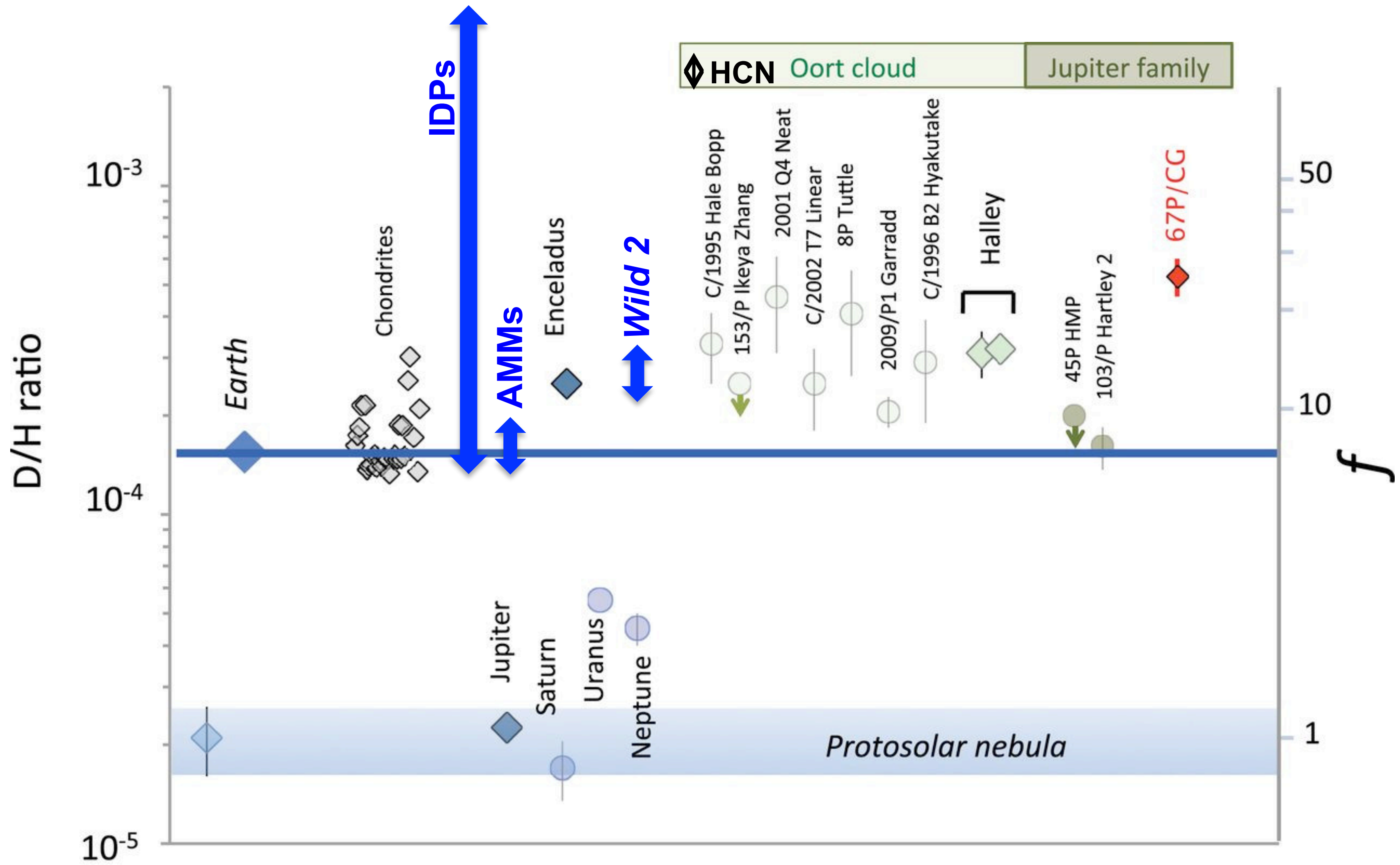




(Bardin+ MetSoc 2015)

- main OM : large variations in $\delta D$ and moderate variations in $\delta^{15}N$
- No clear correlation between $\delta D$ and $\delta^{15}N$ for most of the grain

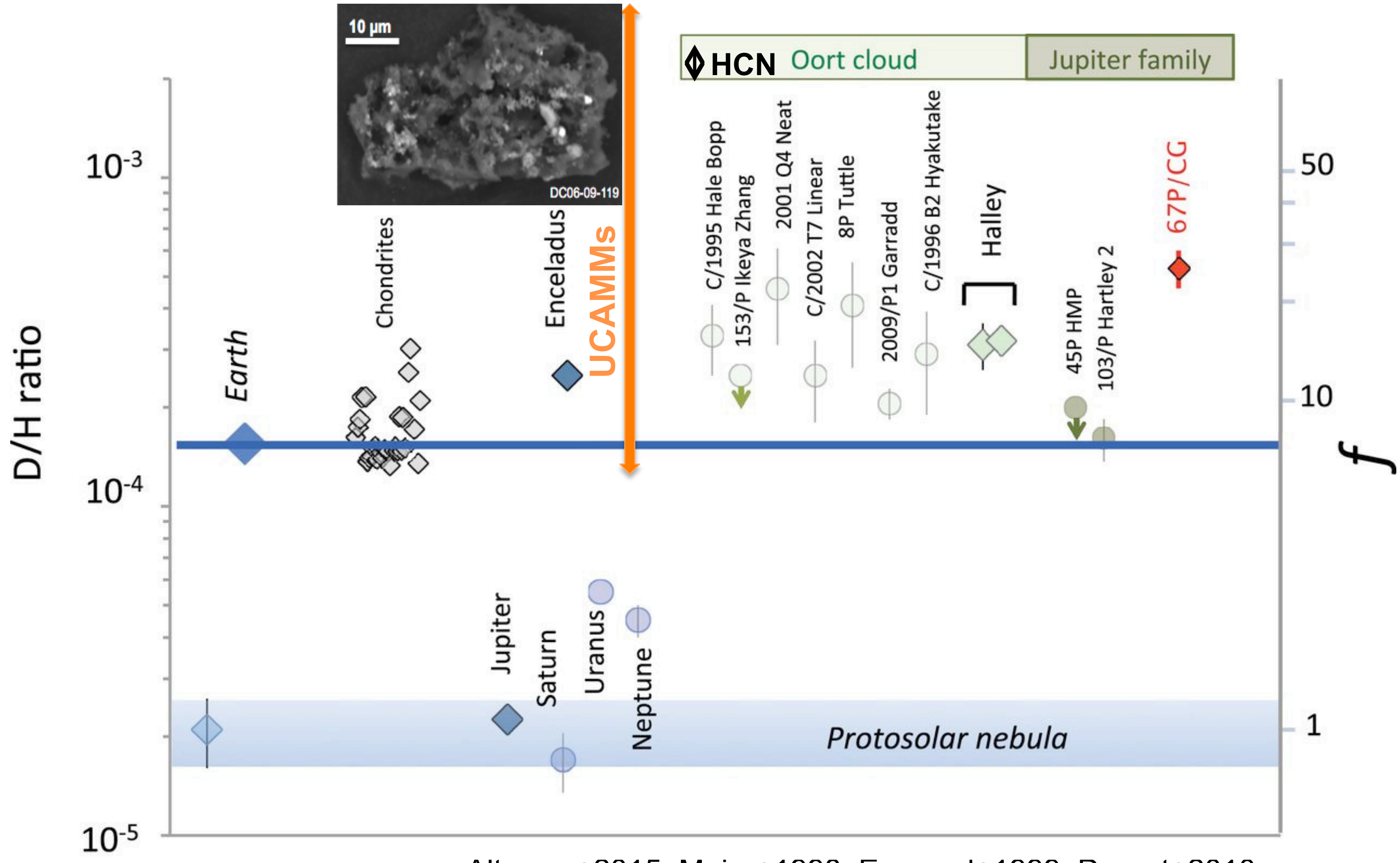
# D/H ratios




Altwegg+2015, Meier+1998, Engrand+1999, McKeegan+2006

- Caveat : comparing D/H in water and organics

# D/H ratios



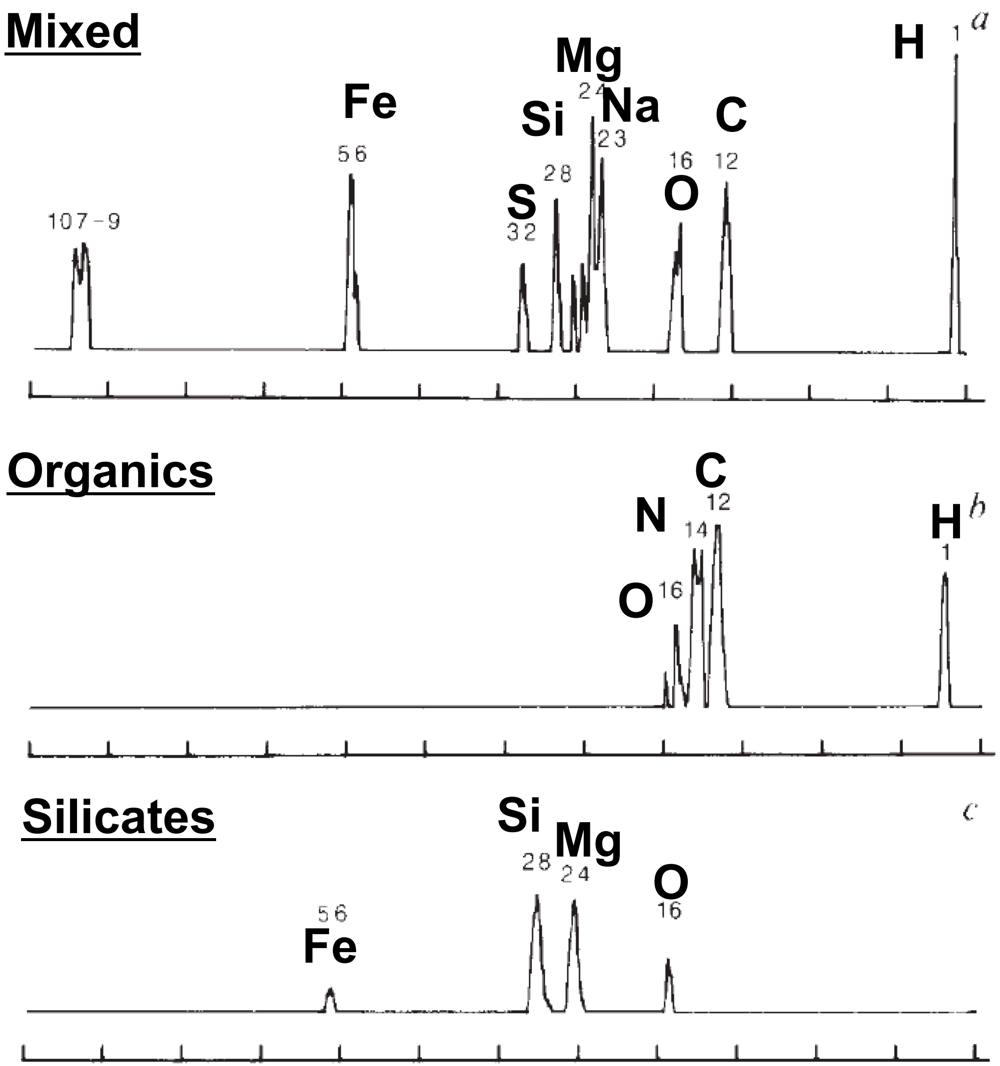

Altwegg+2015, Meier+1998, Engrand+1999, Duprat+2010

- Caveat : comparing D/H in water and organics

# 1986

Comet Halley

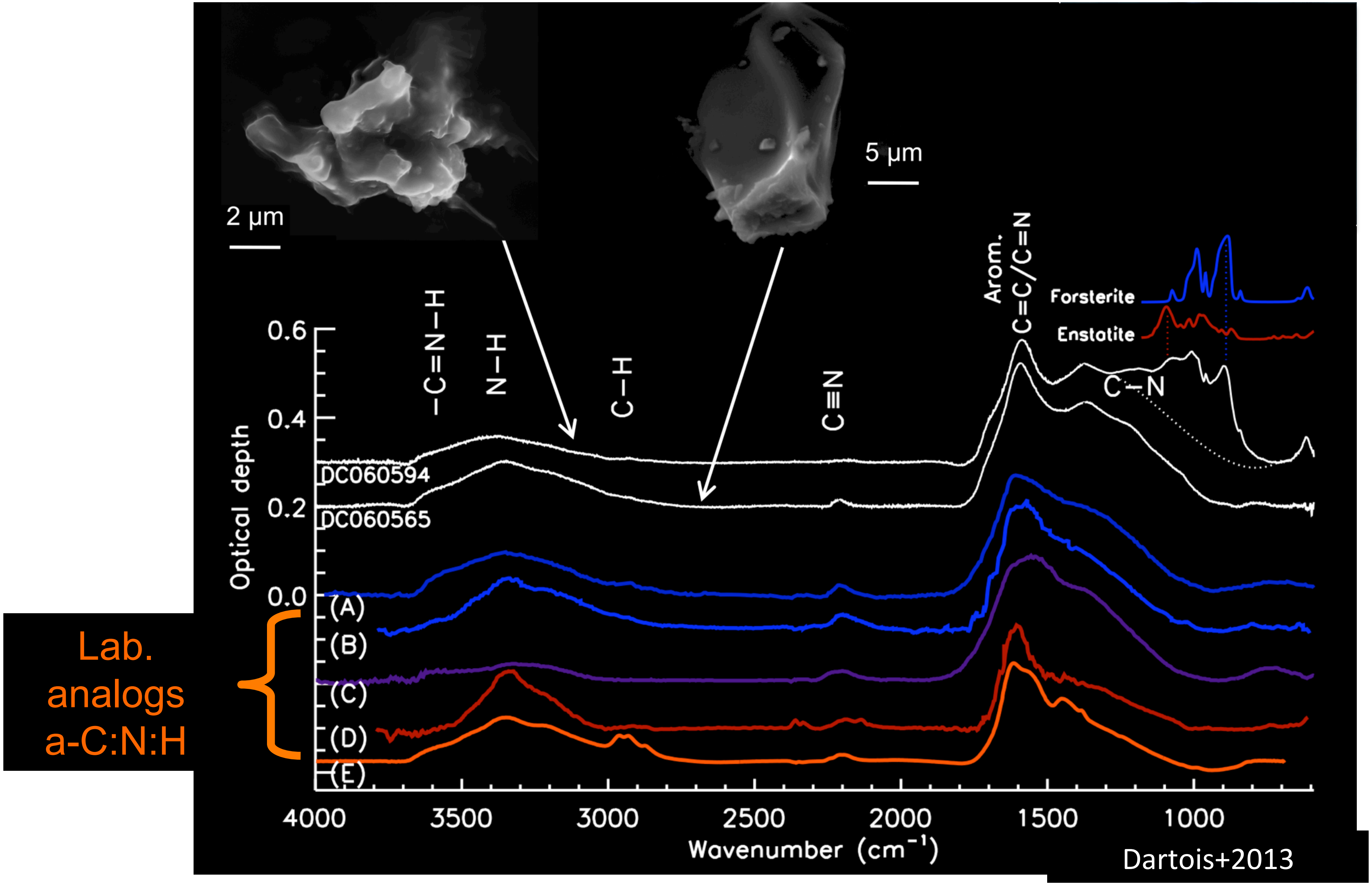
80% of the spectra



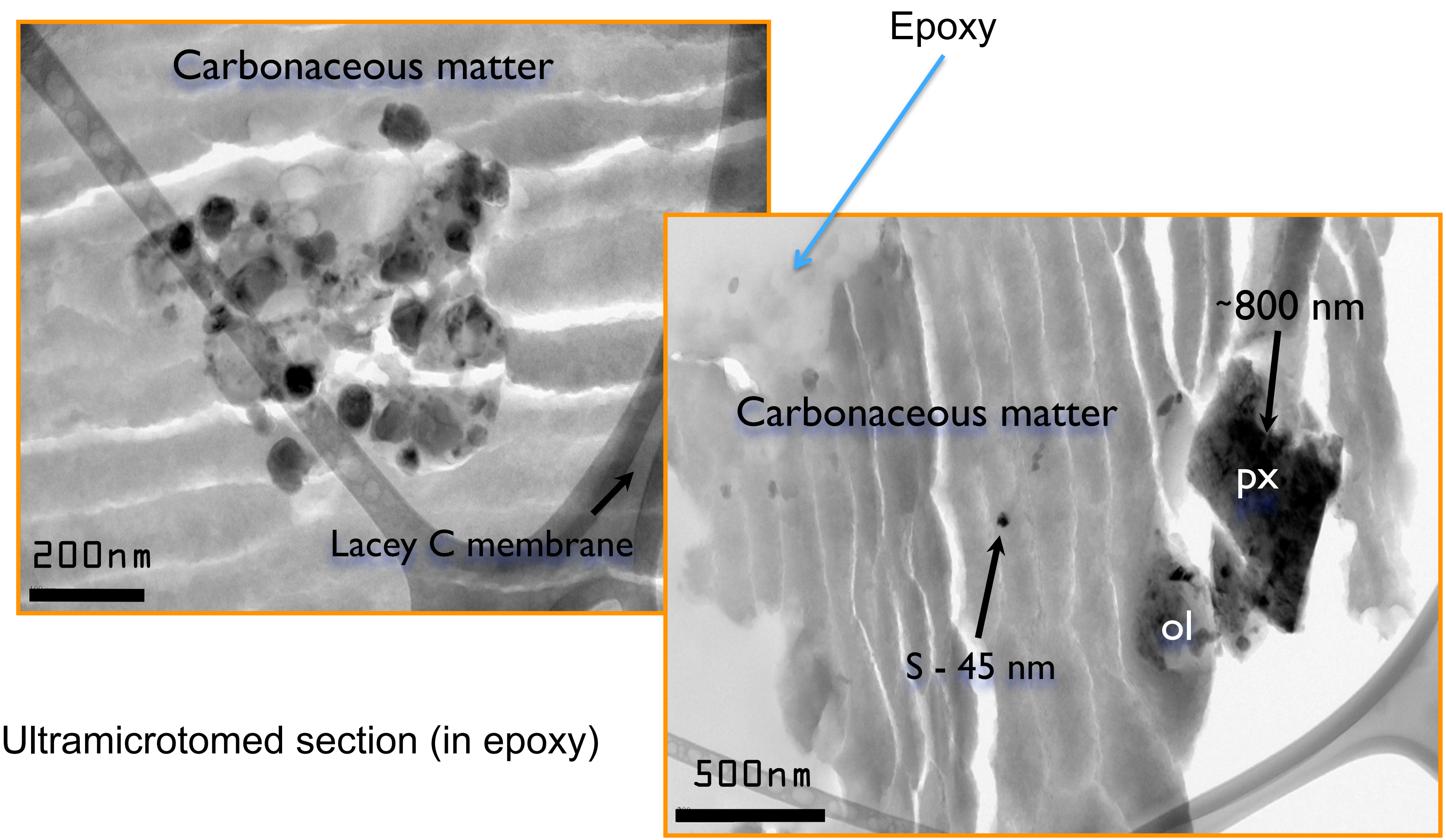

(PIA data)

(Kissel et al. 1986)

# UCAMMs : a N-rich « CHON »…



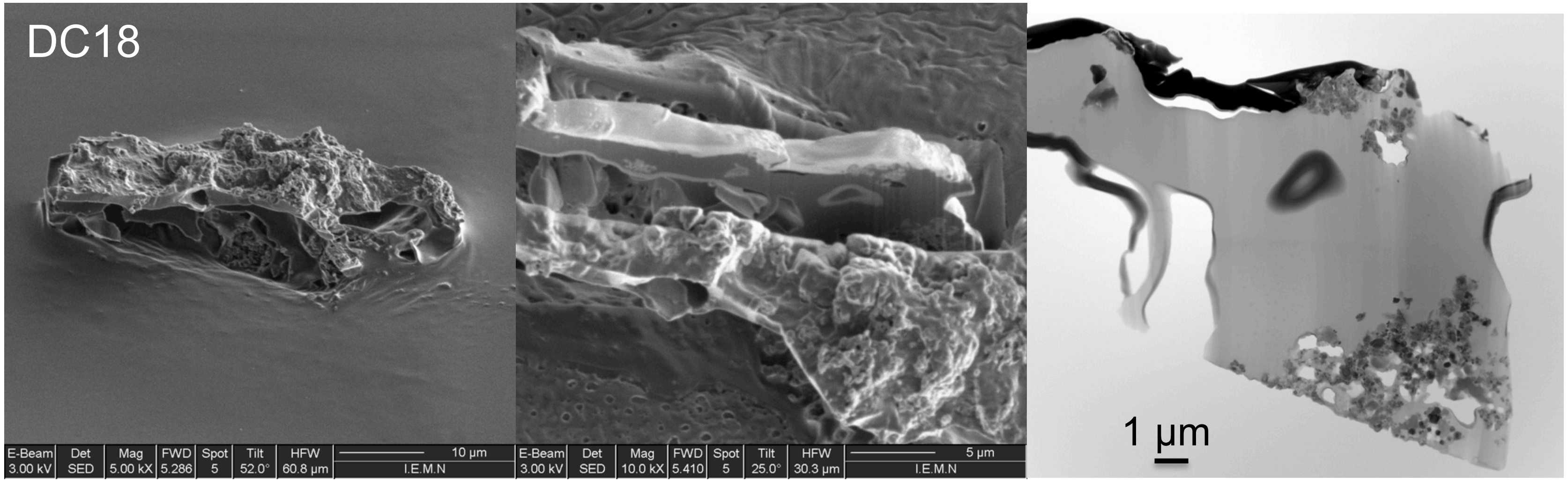
# Intimate OM-minerals mixing in UCAMMs

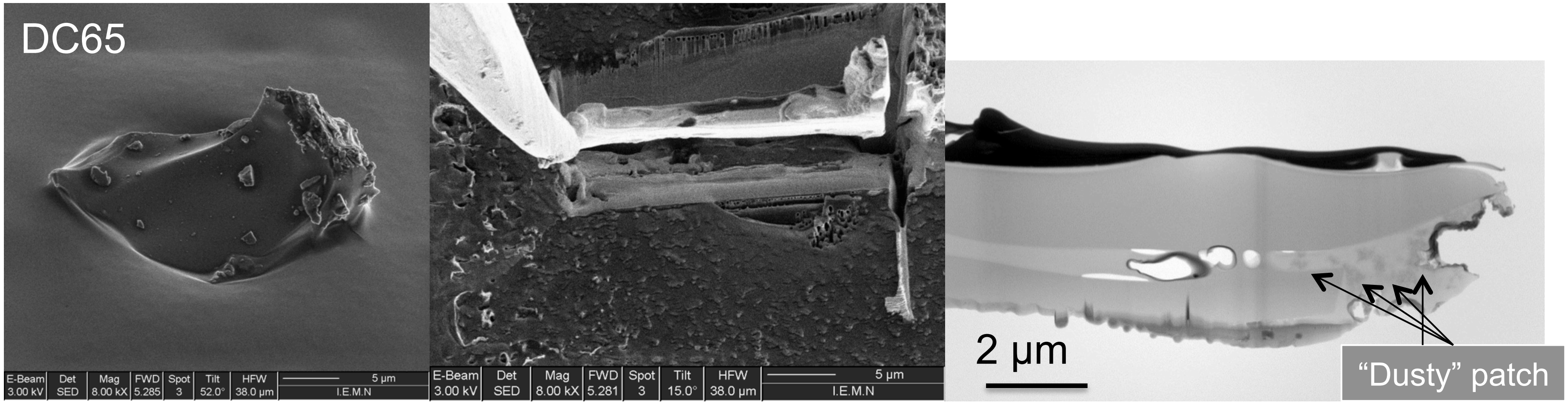



Ultramicrotomed section (in epoxy)

Dobrică+2012

# 100 nm FIB sections – no epoxy

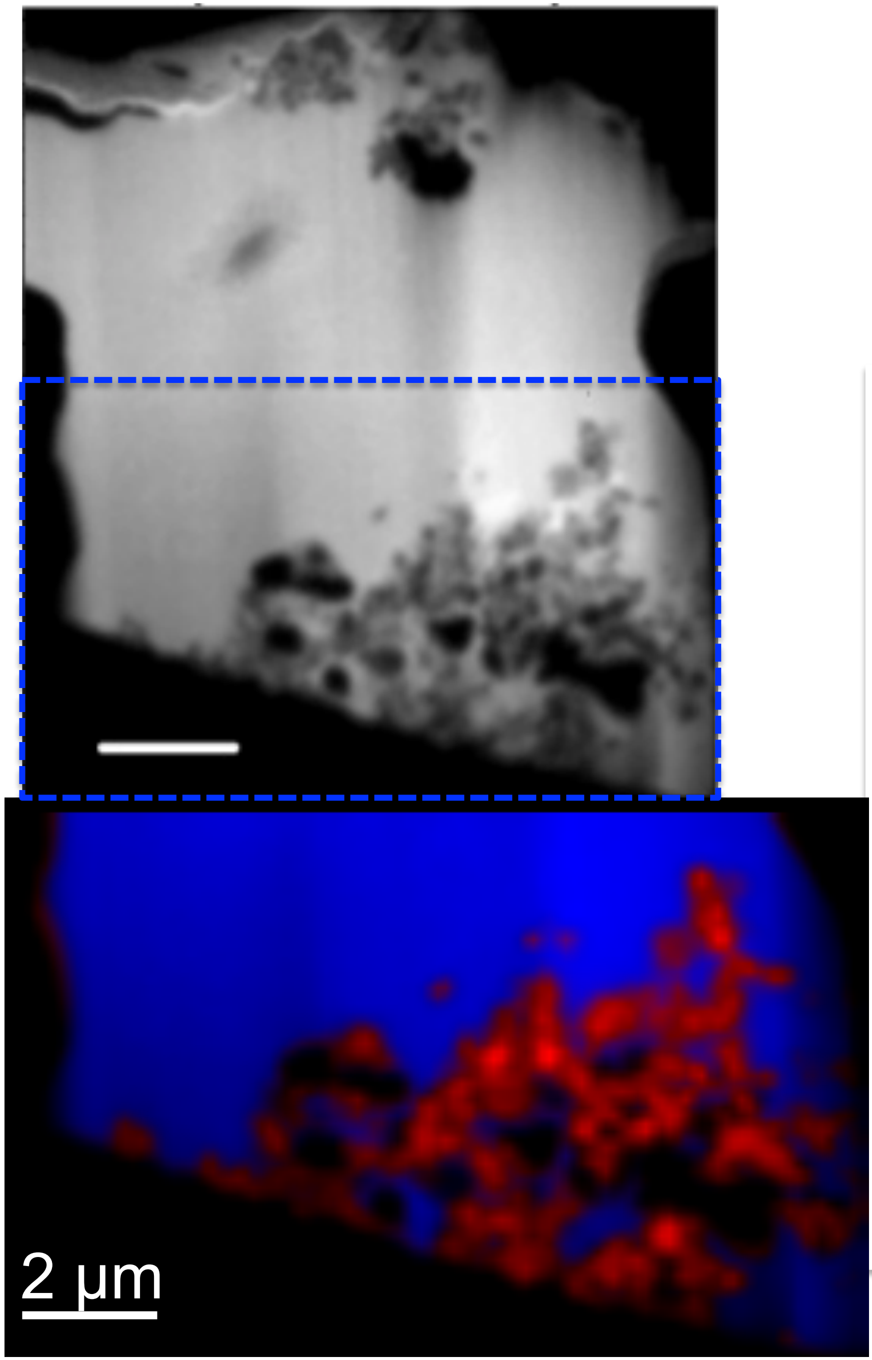


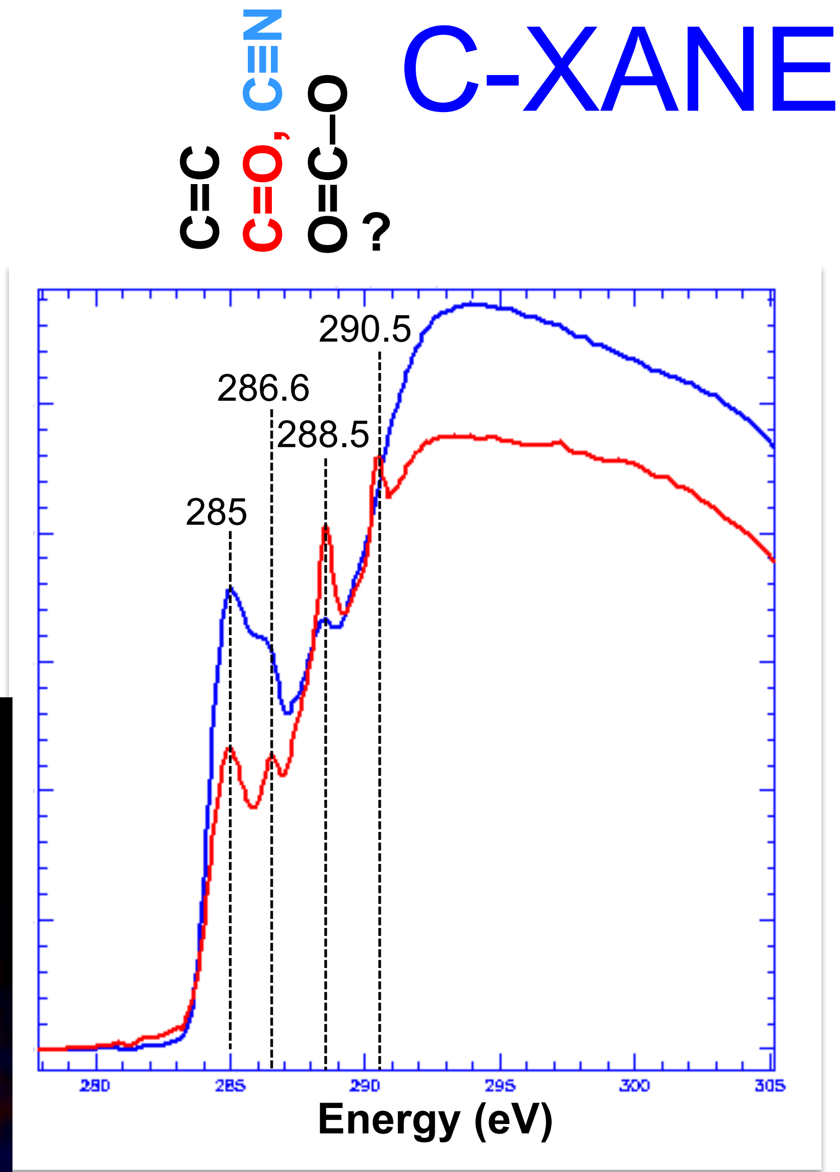




Engrand+2015 LPSC

(FIB Sections : D. Troadec IEMN Lille)

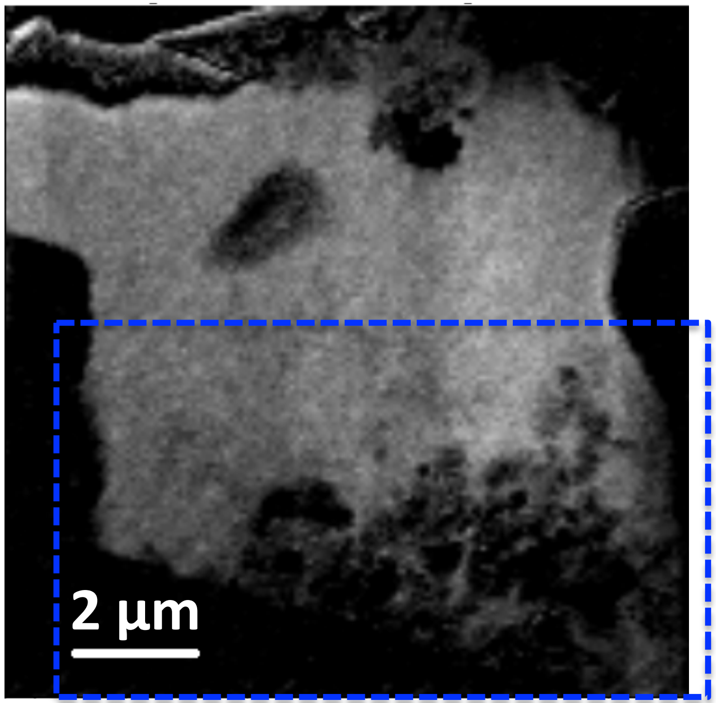
# DC18
# C-XANES

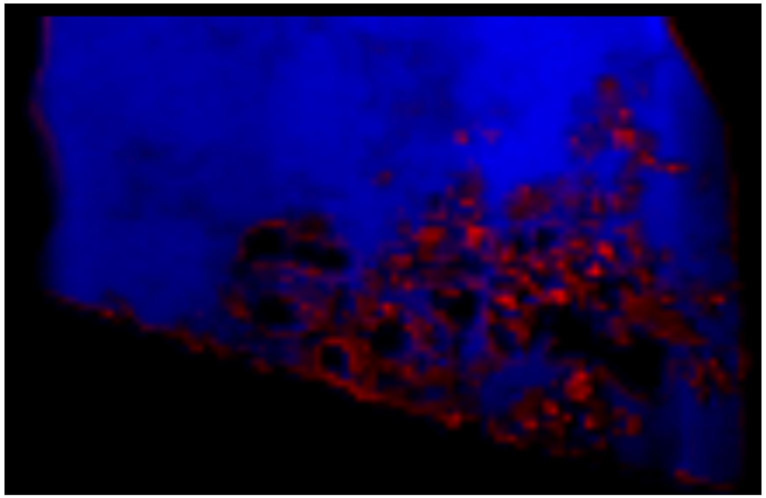


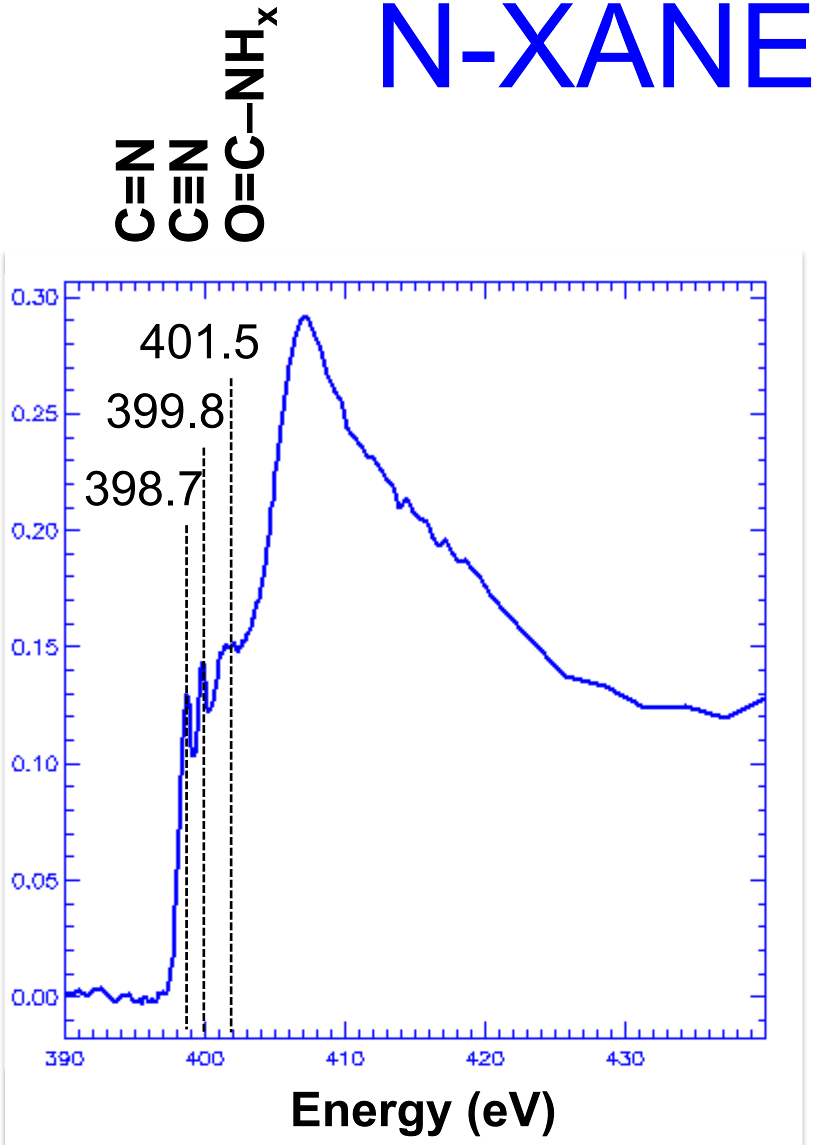




Engrand+2015 LPSC

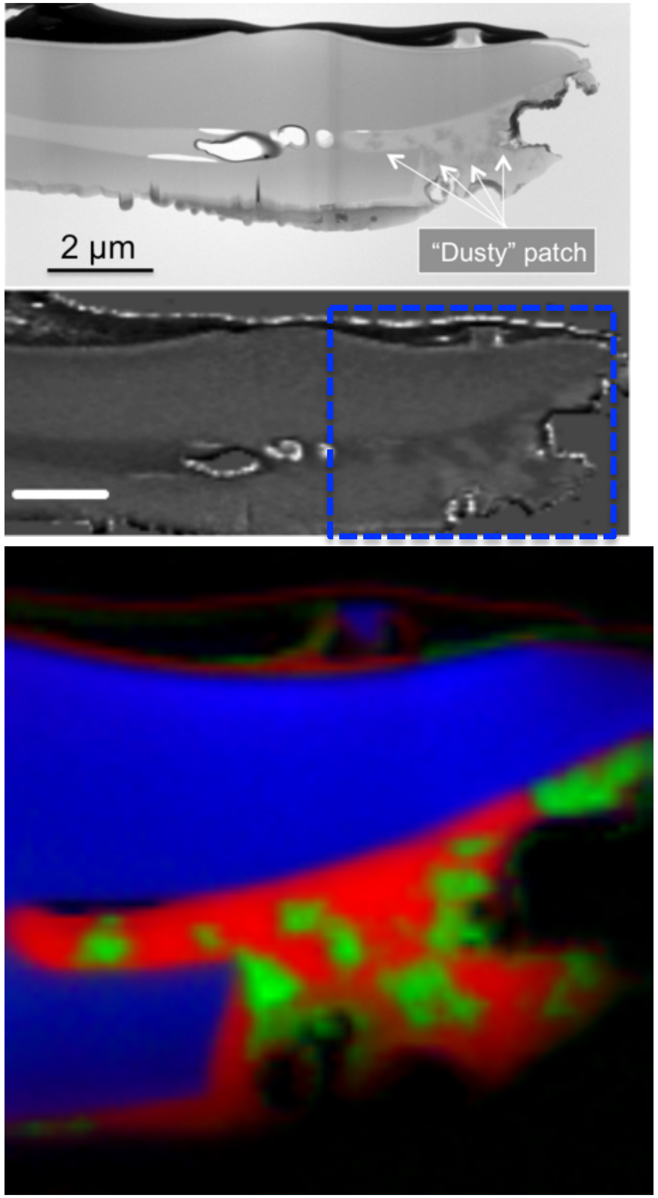
# DC-18
# N-XANES


2 µm

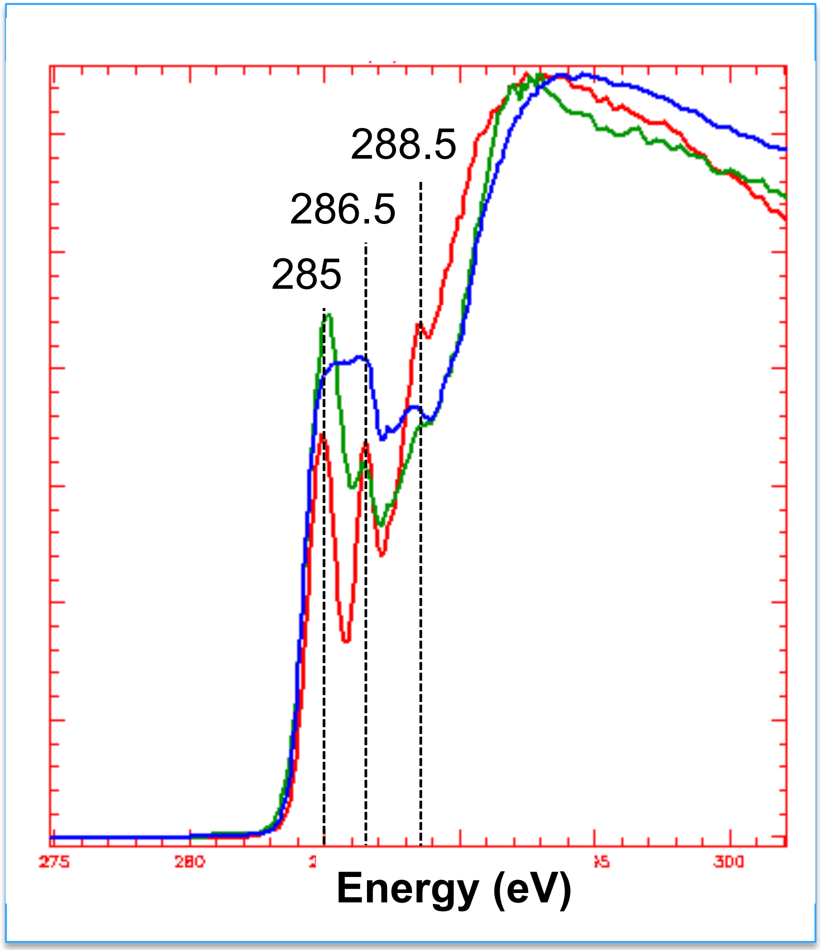



C=N
C≡N
O=C–NHx
401.5
399.8
398.7
0.30
0.25
0.20
0.15
0.10
0.05
0.00
390
400
410
420
430
Energy (eV)

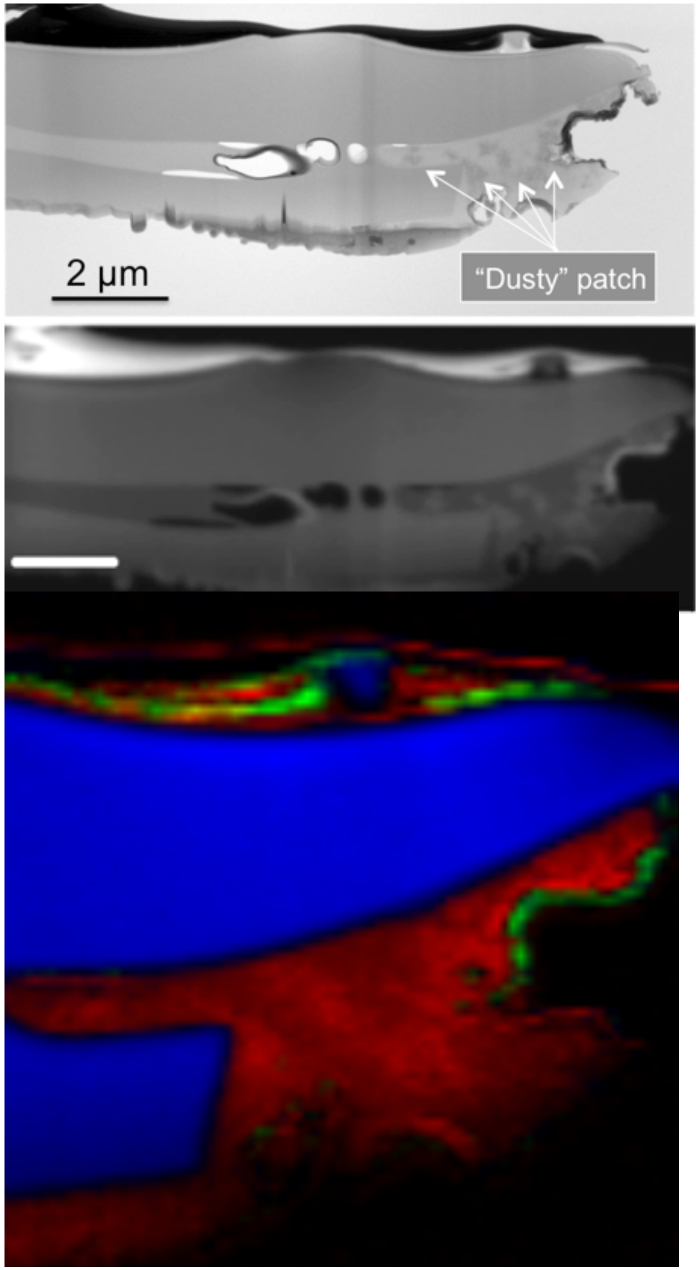
# DC65
# C-XANES



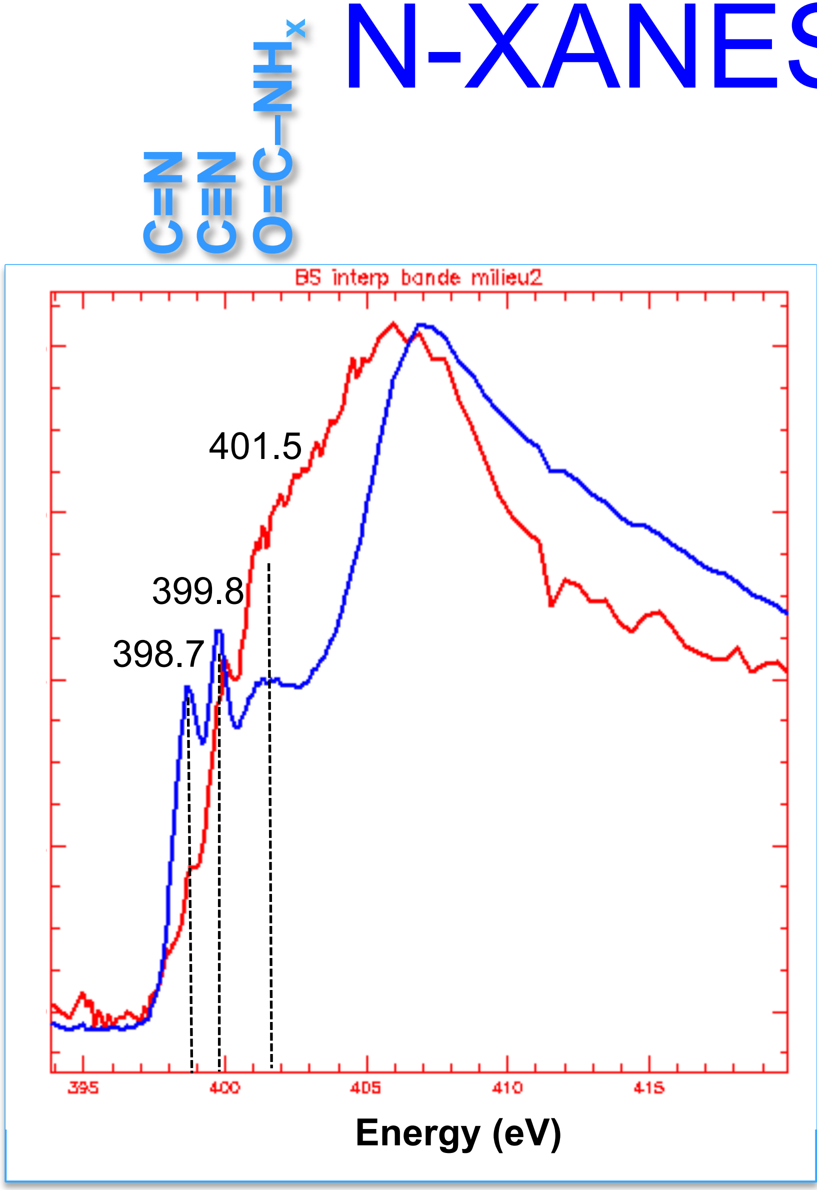

Engrand+2015 LPSC



# DC65
# N-XANES

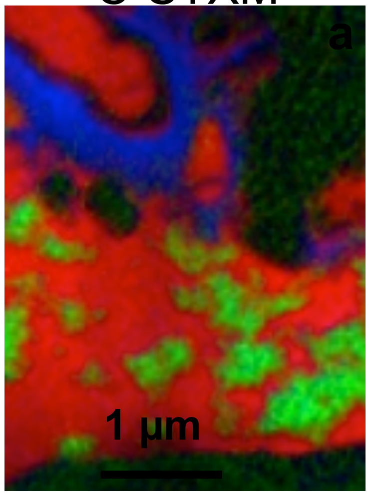



Engrand+2015 LPSC

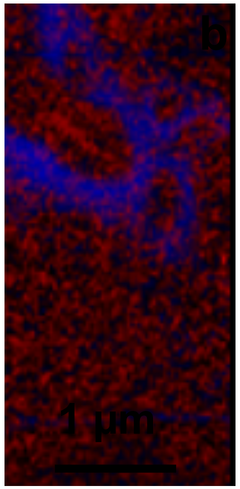


# UCAMM DC43 : a unique sample

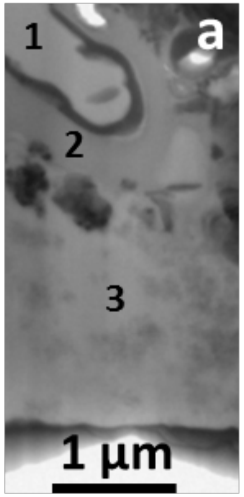
C-STXM

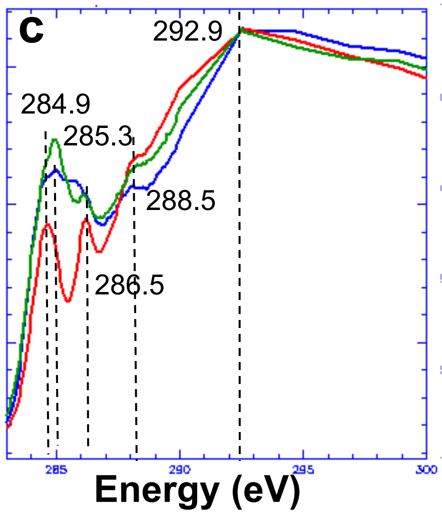


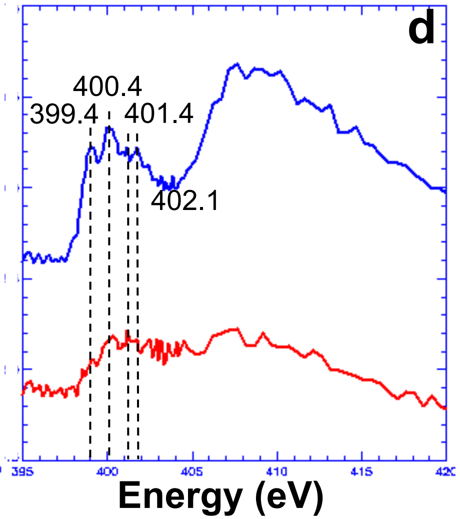

N-STXM




MET



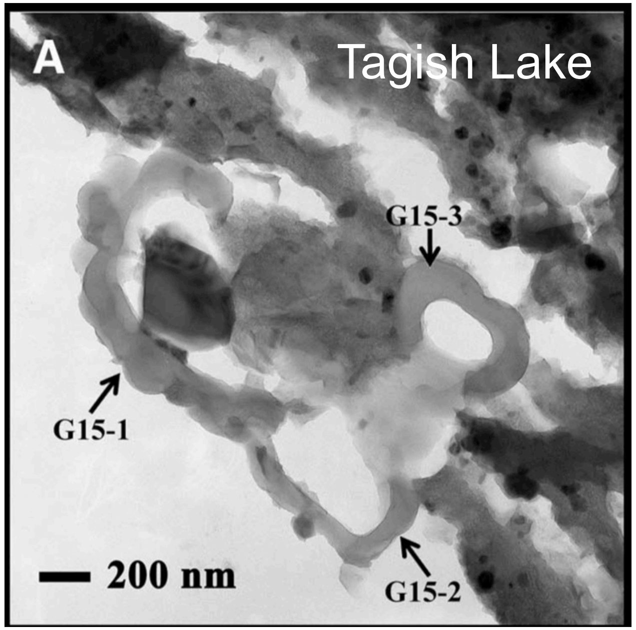



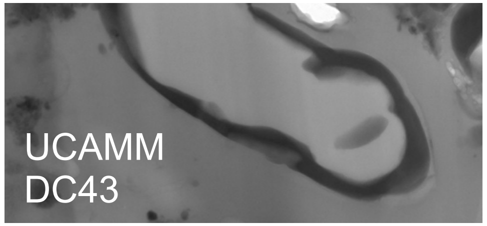

- 3 types of OM :
  - smooth : N-rich, mineral-poor (#2)
  - smooth: N-poor, mineral-poor (#1)
  - granular: N-poor, mineral-rich (#3)

(Charon+2017 LPSC)

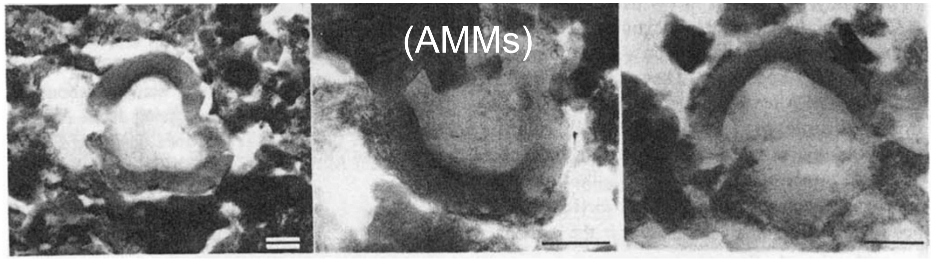
# Nanoglobules




(Nakamura-Messenger+2003)




(Charon+2017)




(Maurette+ LPSC1995)

- D and N isotopic anomalies
  - δD from 1800 to 8100‰ in Tagish Lake
  - $\delta^{15}$N from 200-1000‰ in Tagish Lake
- Present in many primitive materials
- Origin unclear : low T (outer regions or presolar cloud), processed ice coating?

# UCMM (Japan)

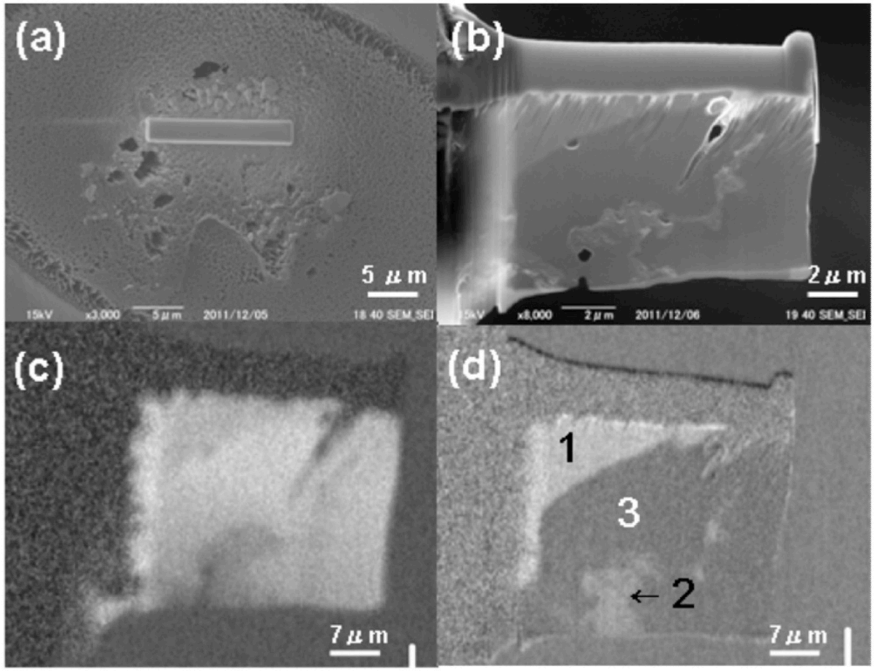
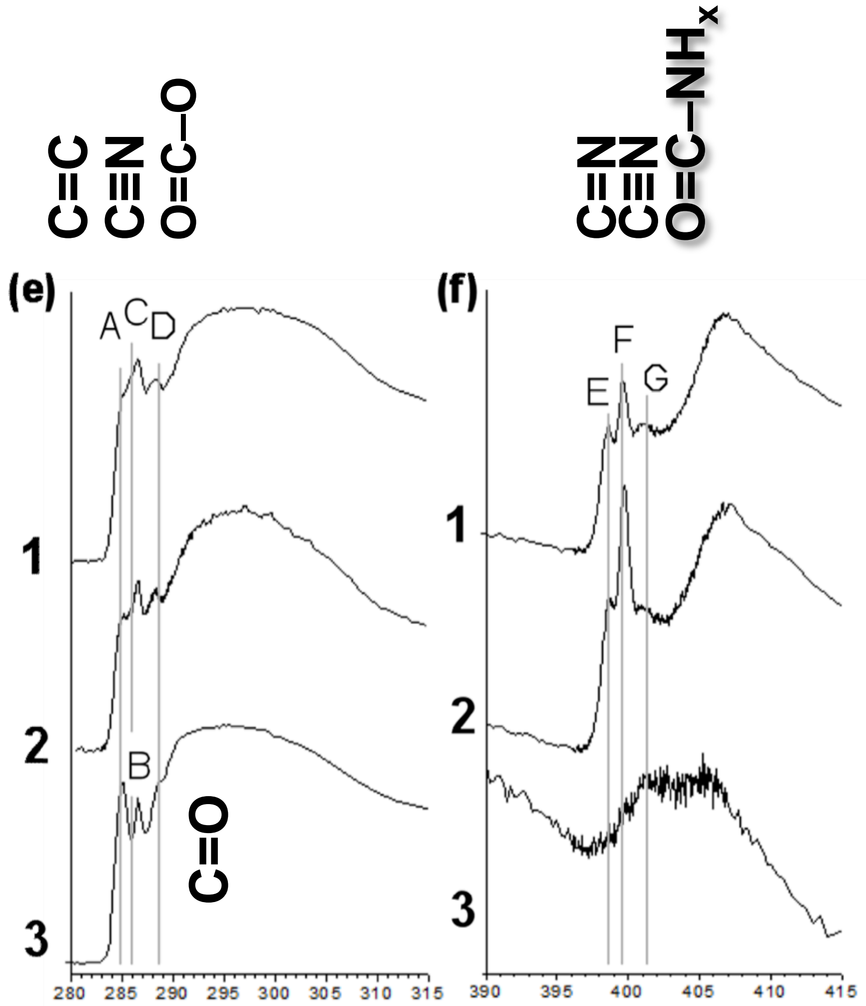
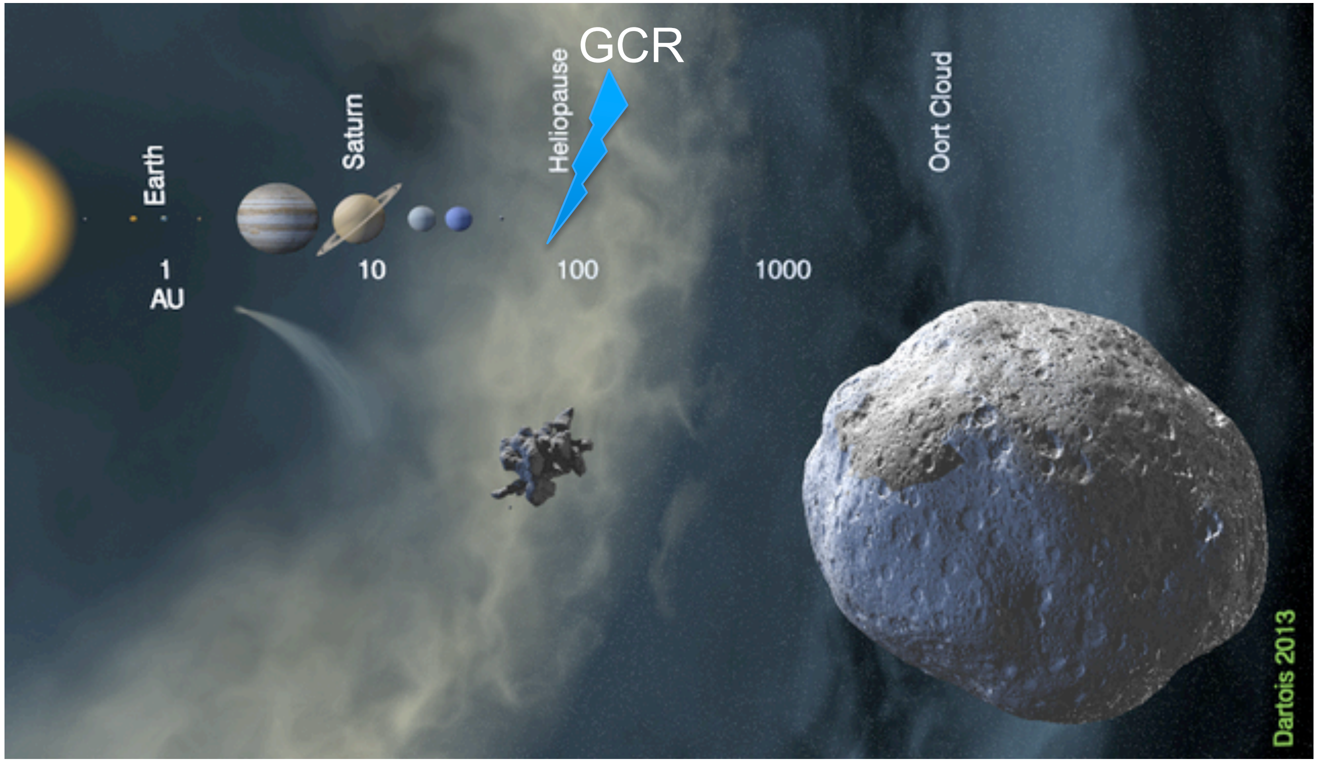



Fig. 2. (a) Tungsten strap of 1.3 µm thickness deposited on the surface of UCMM for FIB extraction, (b) An SEM image of the FIB section, (c) Carbon- and (d) Nitrogen- distribution maps obtained by STXM, and (e) Carbon- and (f) Nitrogen-XANES spectra of the regions 1, 2, and 3 indicated in (d). Peak assignments are based on [4] ; A (285.1 eV): C*=C, B (286.6 eV): C=C-C*=O, C (286.6 eV): C*≡N, D: NHx(C*=O)C (~288.3 eV) or OR(C*=O)C (~288.6 eV), E (398.8 eV): C=N*, F (399.7 eV): C≡N*, G (~401.5 eV): N*Hx(C=O)C.

Yabuta+2012



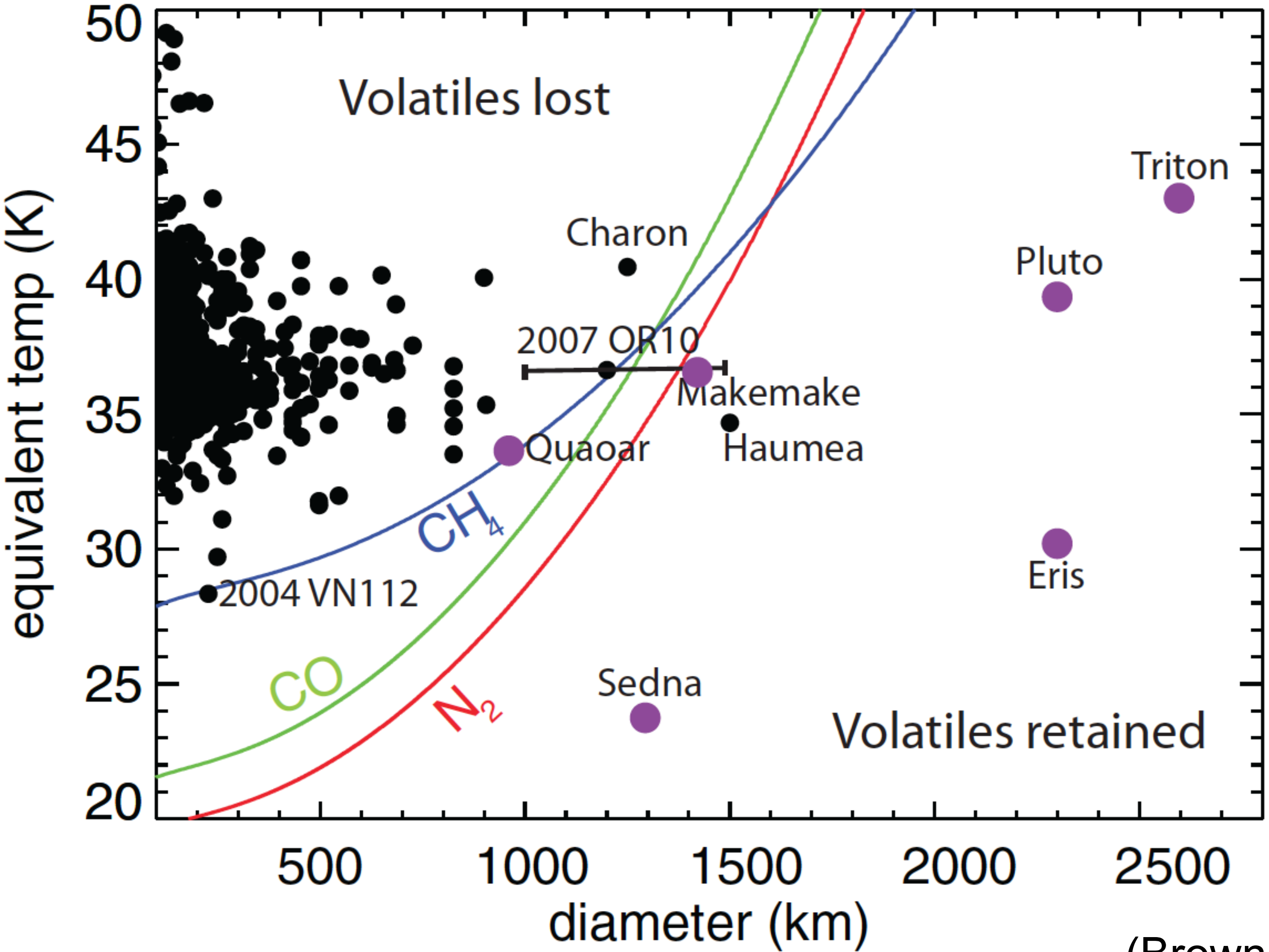
# Formation of N-rich OM by irradiation?




Dartois+2013

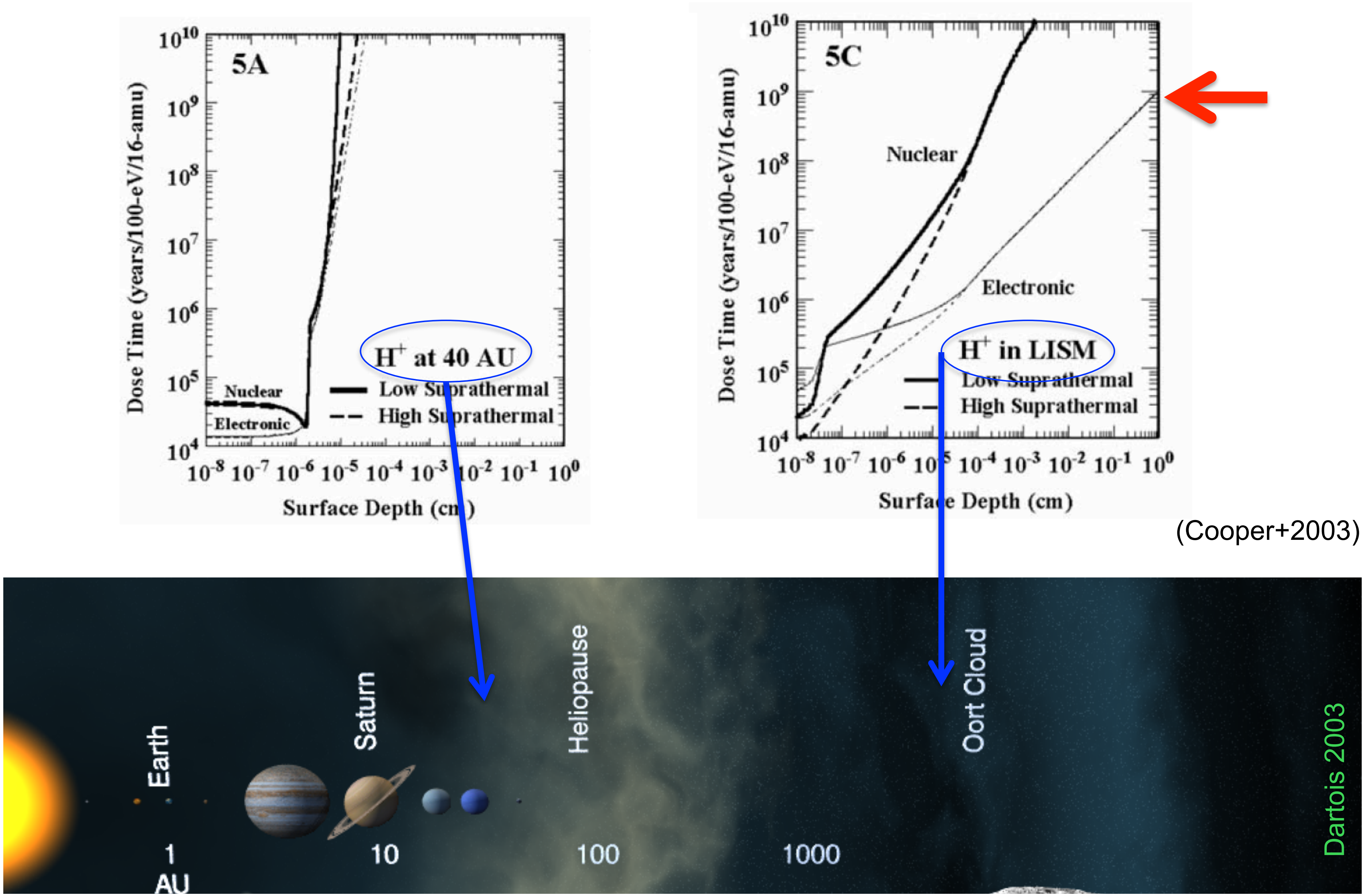
- UCAMMs : material from **beyond the nitrogen snow-line**
- **Formation of N-rich OM** by GCR irradiation at surface of a Kuiper belt or Oort cloud icy objet ?

# Ices stability



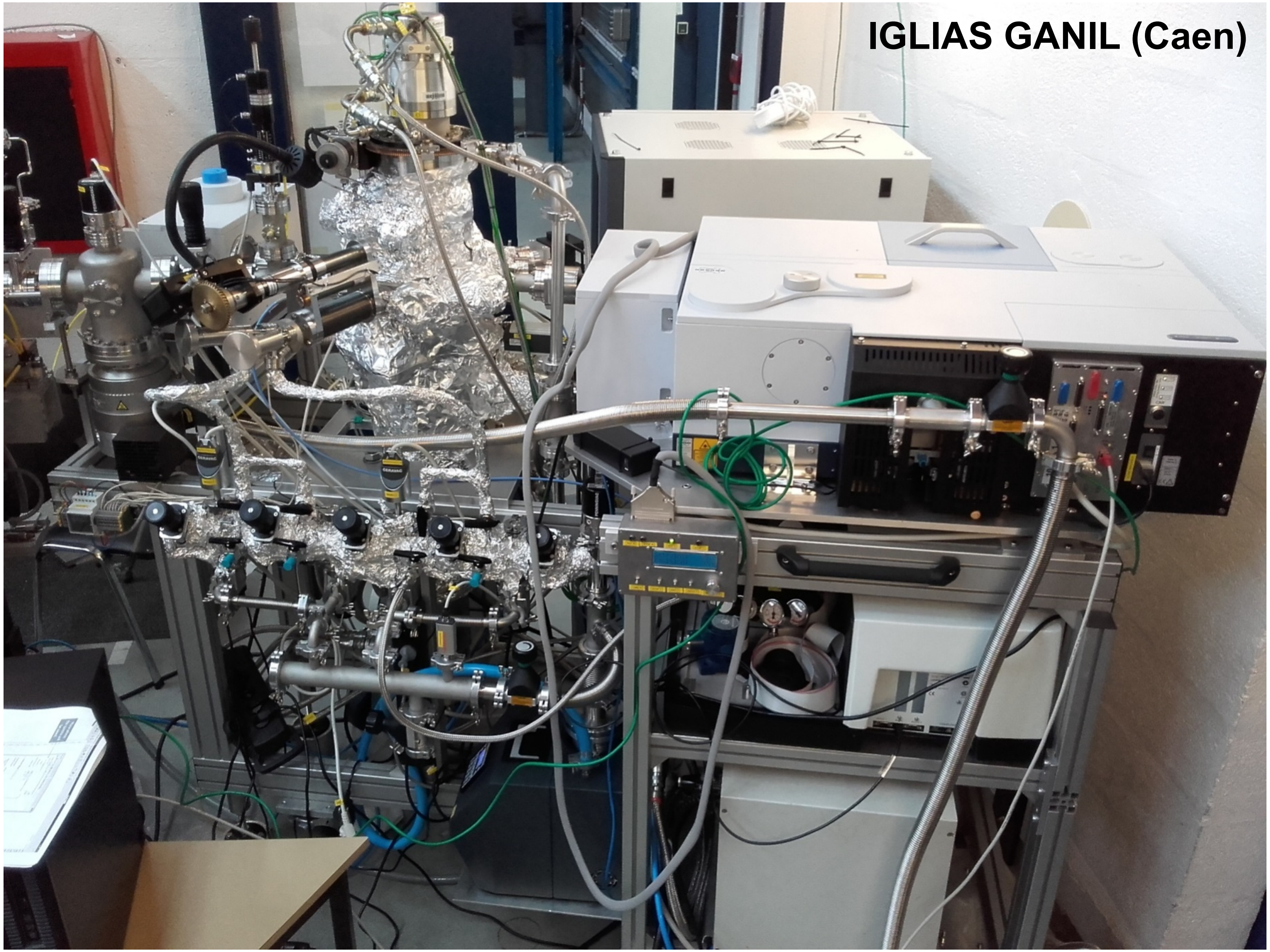

(Brown+2010)

# Radiative environments



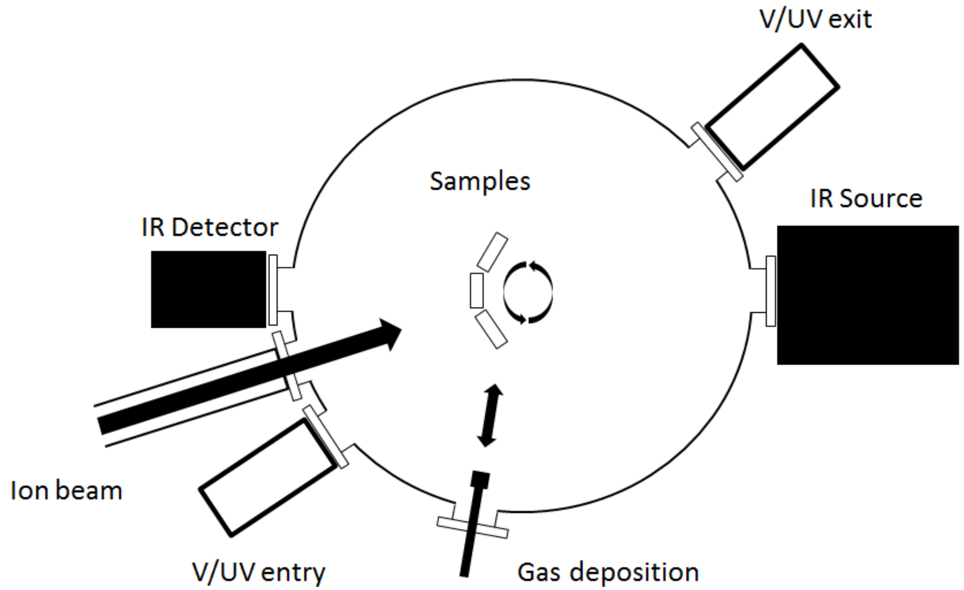

(Cooper+2003)

IGLIAS GANIL (Caen)



(Augé + 2016)

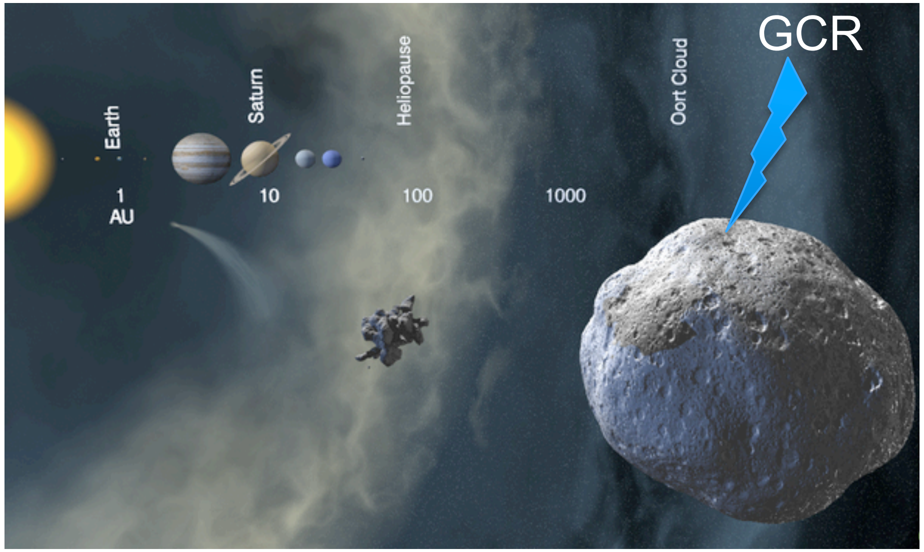
# Irradiation de GLaces d'Intérêt Astrophysique (IGLIAS) – GANIL Caen



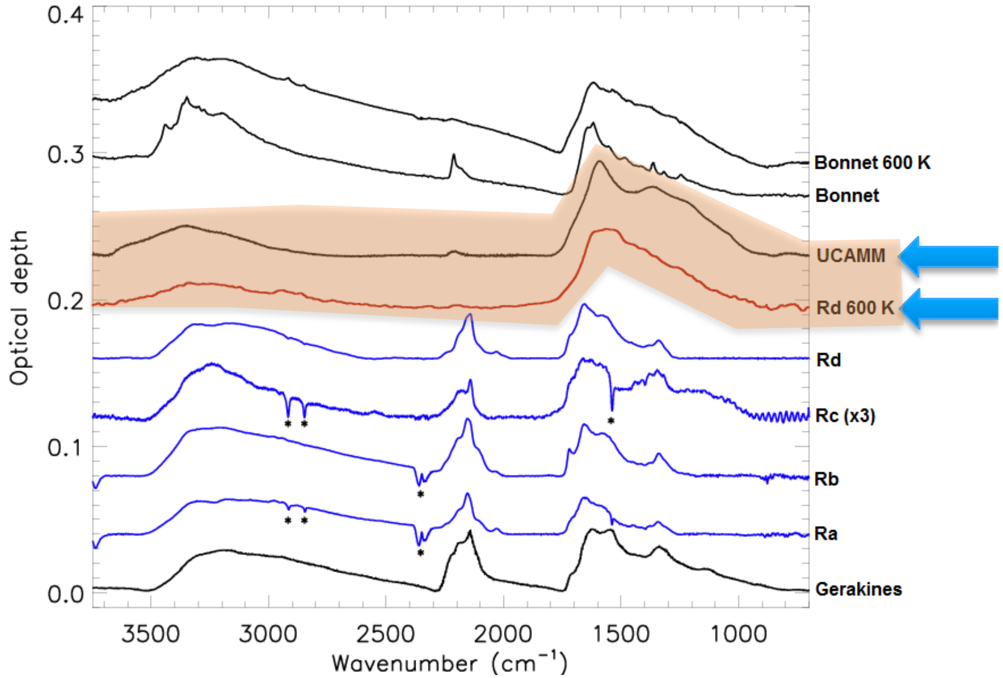

(Augé + 2016)

- P chamber : 1.5 $10^{-10}$ mbar @ 8 K
- Brucker Vertex 70v (6000-700 $cm^{-1}$)
- Perkin Elmer λ 650 (800-200 nm)
- 3 substrates (CsI, $SiO_2$, $MgF_2$ - 20*2 mm)

# Formation of N-rich OM by irradiation?



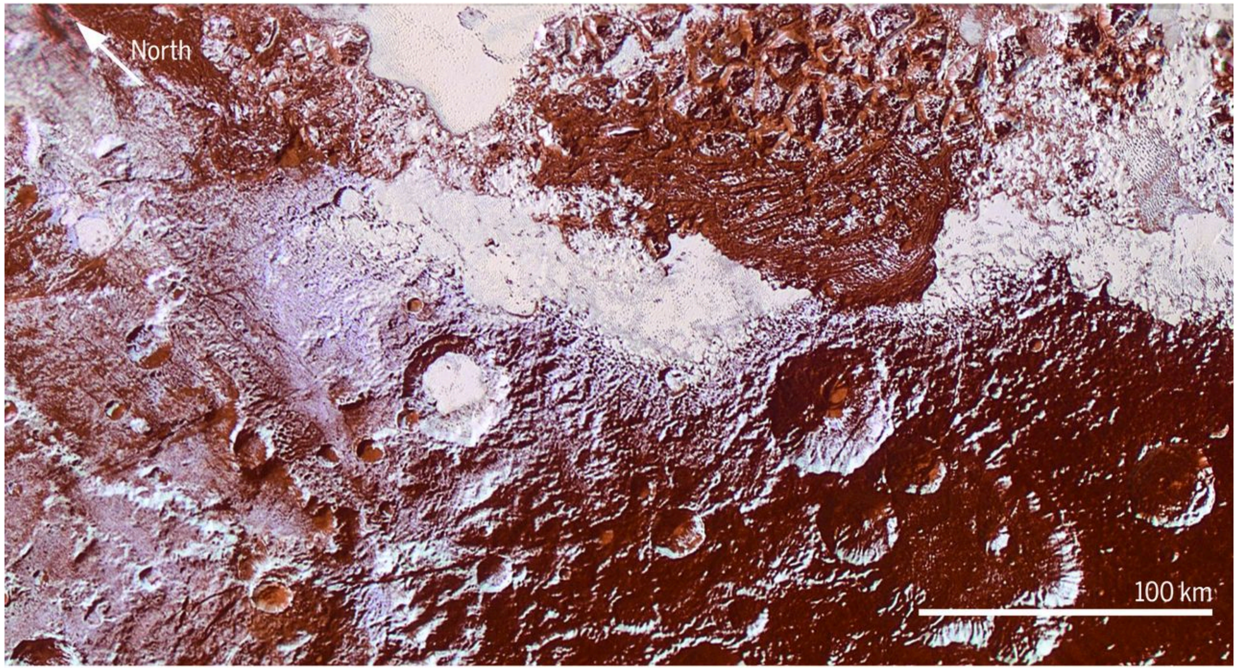

Dartois+2013

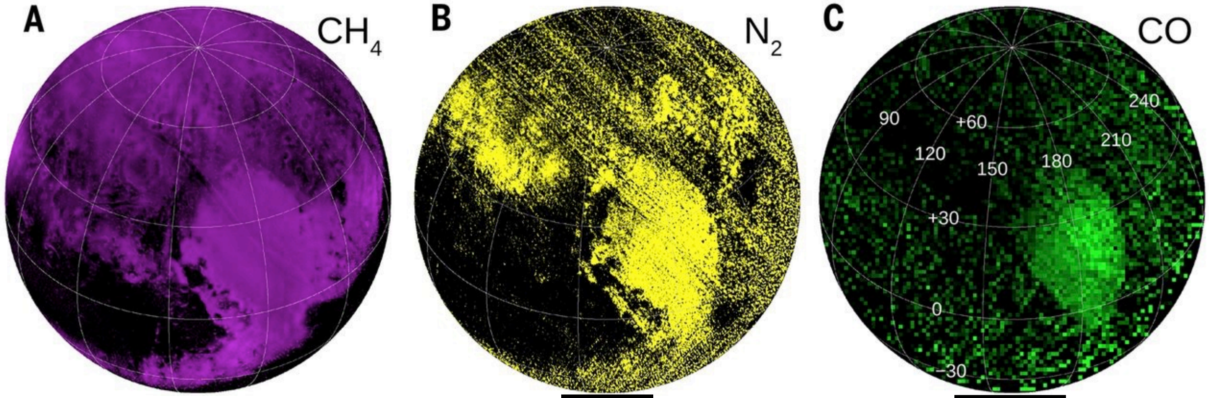



Augé+2016 A&A

- UCAMMs : material from **beyond the nitrogen snow-line**
- **Formation of N-rich OM** by GCR irradiation at surface of a Kuiper belt or Oort cloud icy objet ?

# New Horizons – Pluto's Surface diversity

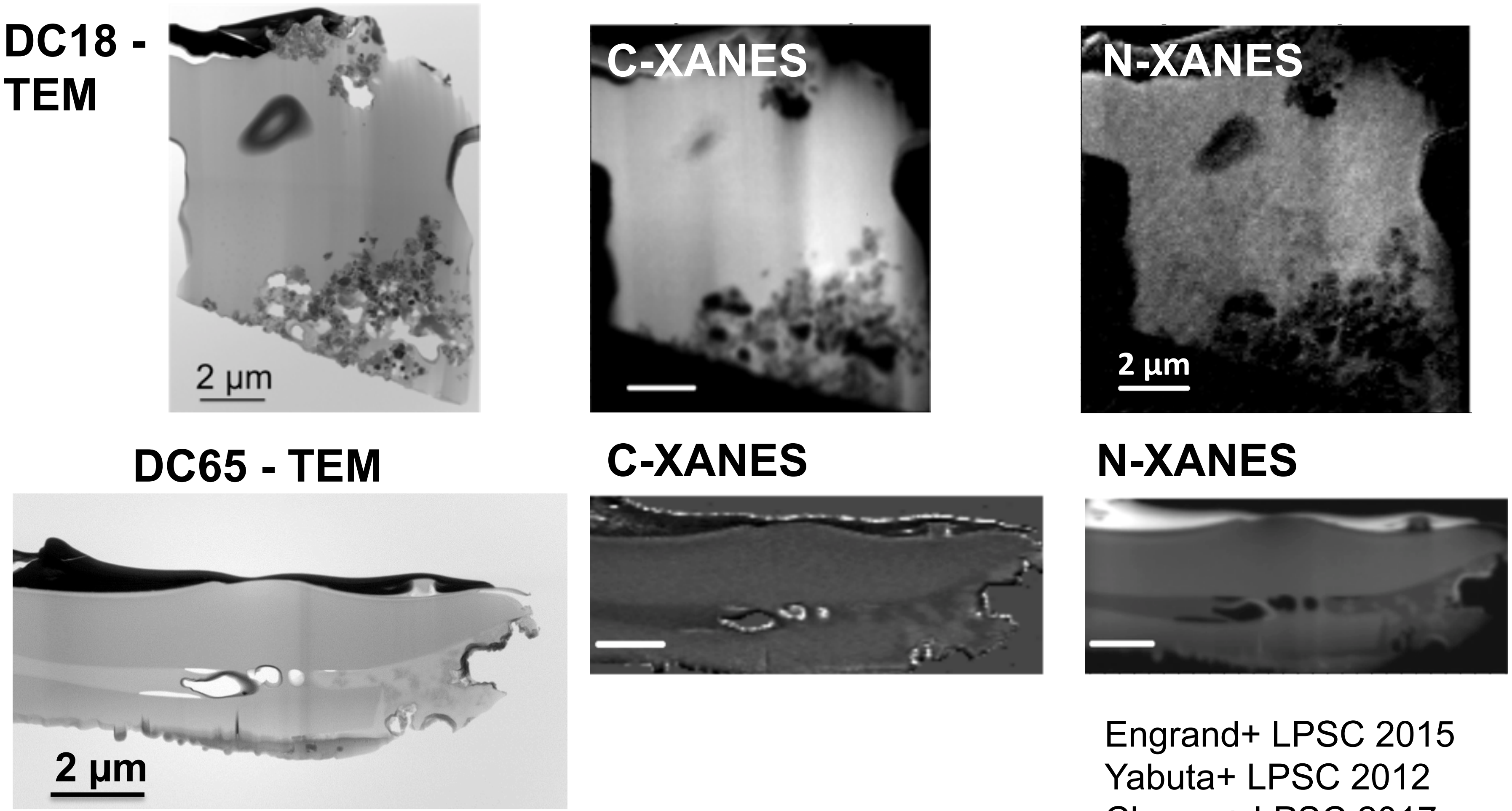



$CH_4$ $N_2$ CO

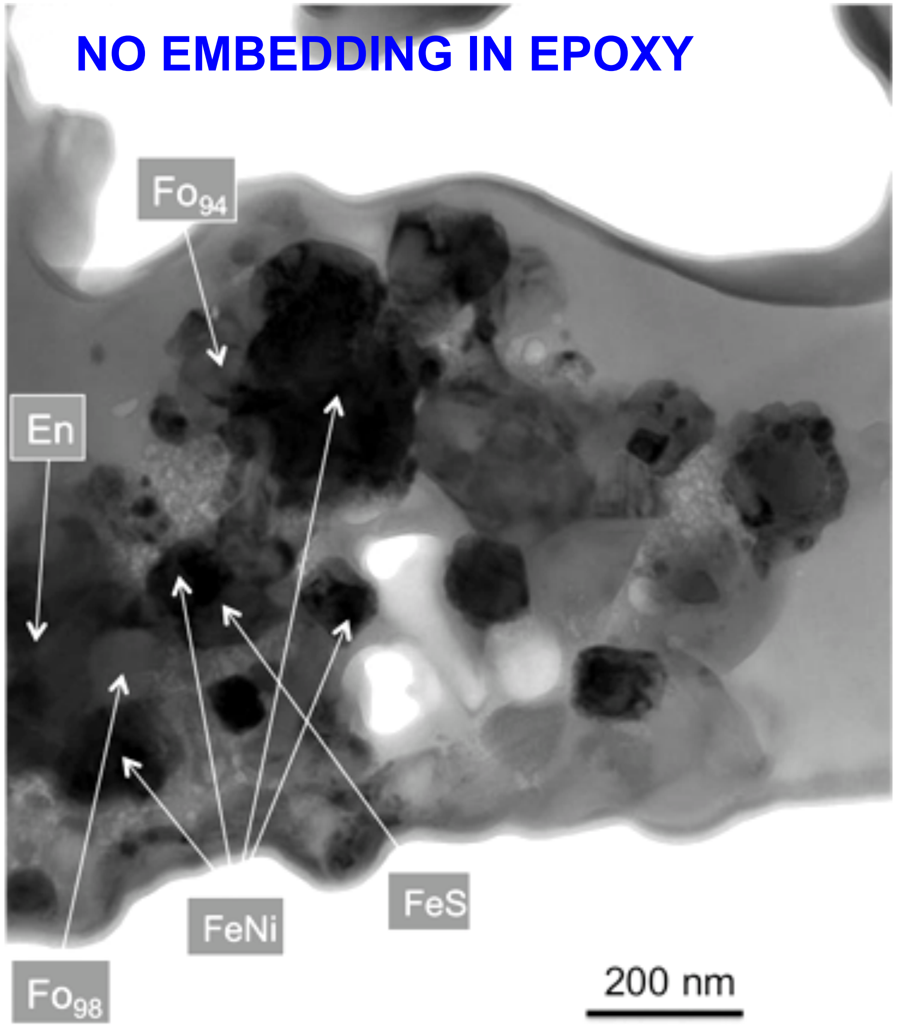
Grundy+2016

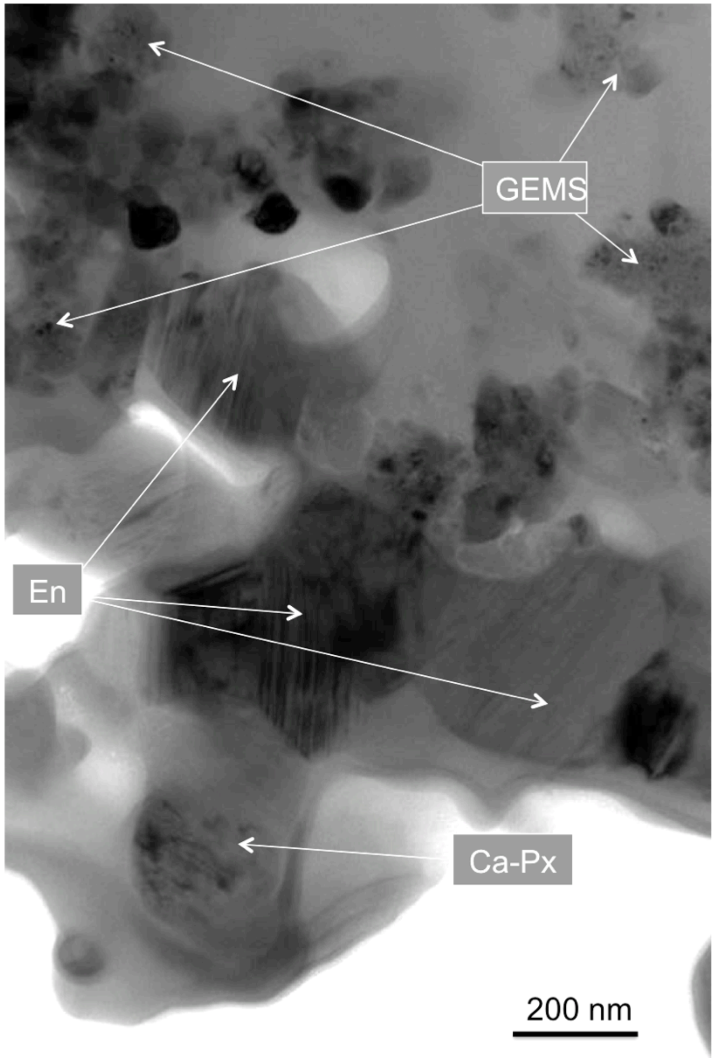
# N-rich and N-poor OM in UCAMMs
# Intimate mixing with minerals




Engrand+ LPSC 2015
Yabuta+ LPSC 2012
Charon+ LPSC 2017

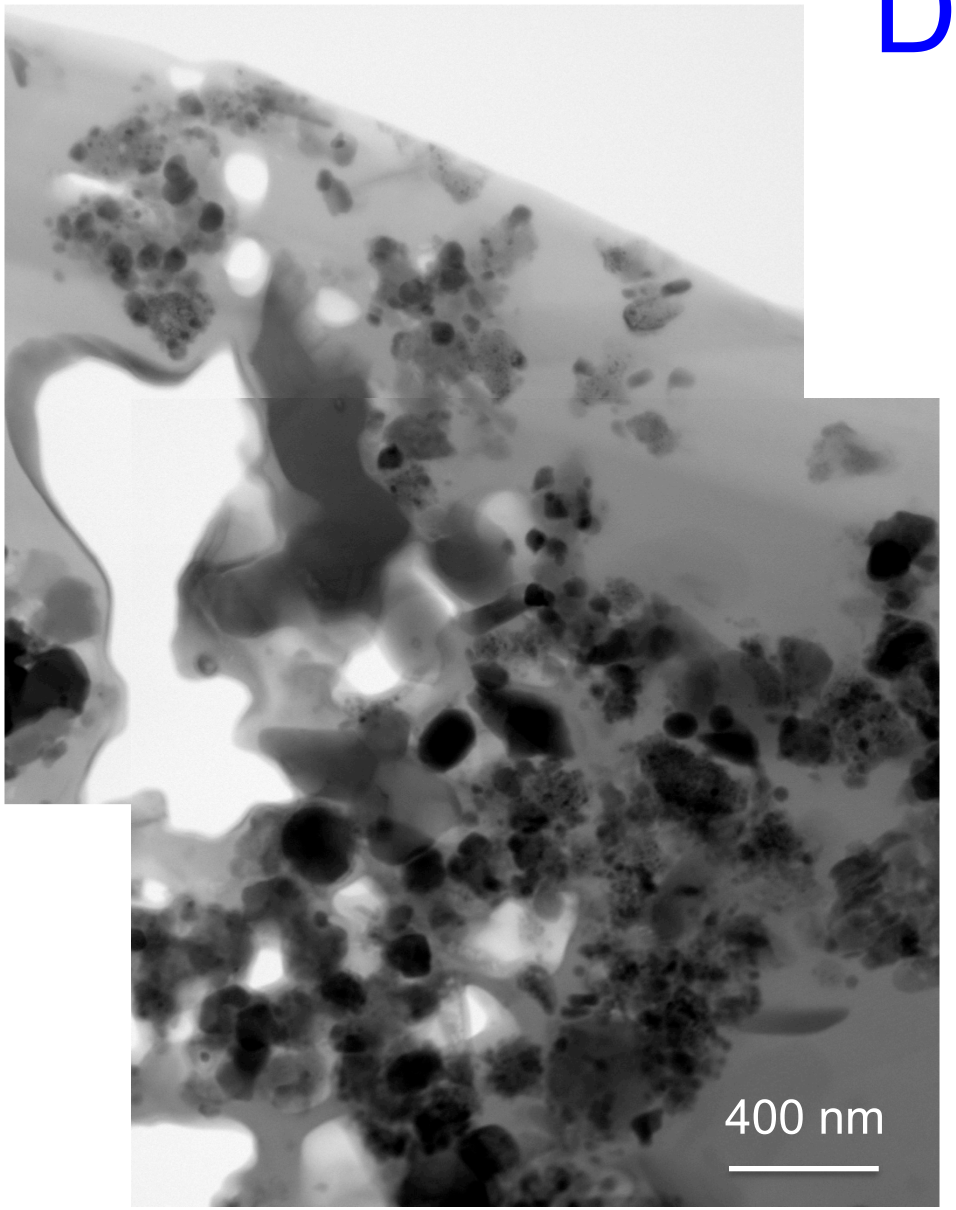
# UCAMMs : Mineral complexity

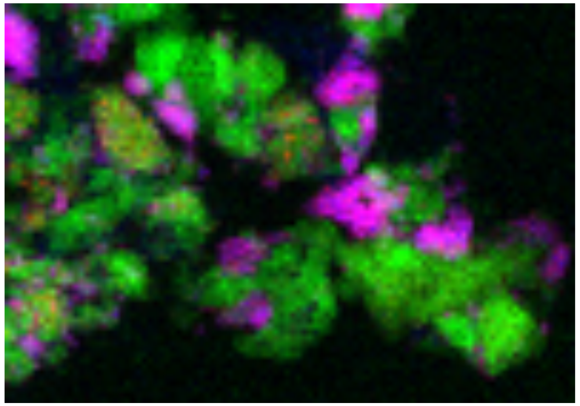


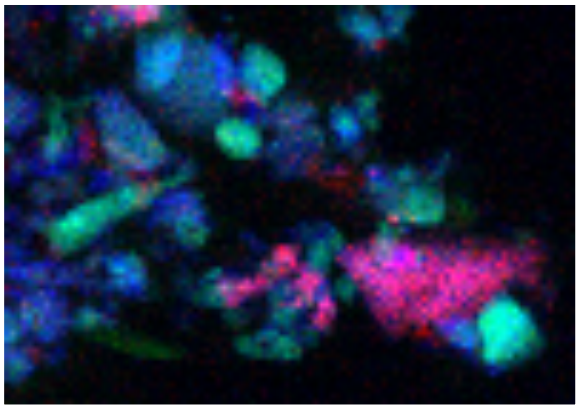




- Px/Ol ratio (in numbers ) ~ 1

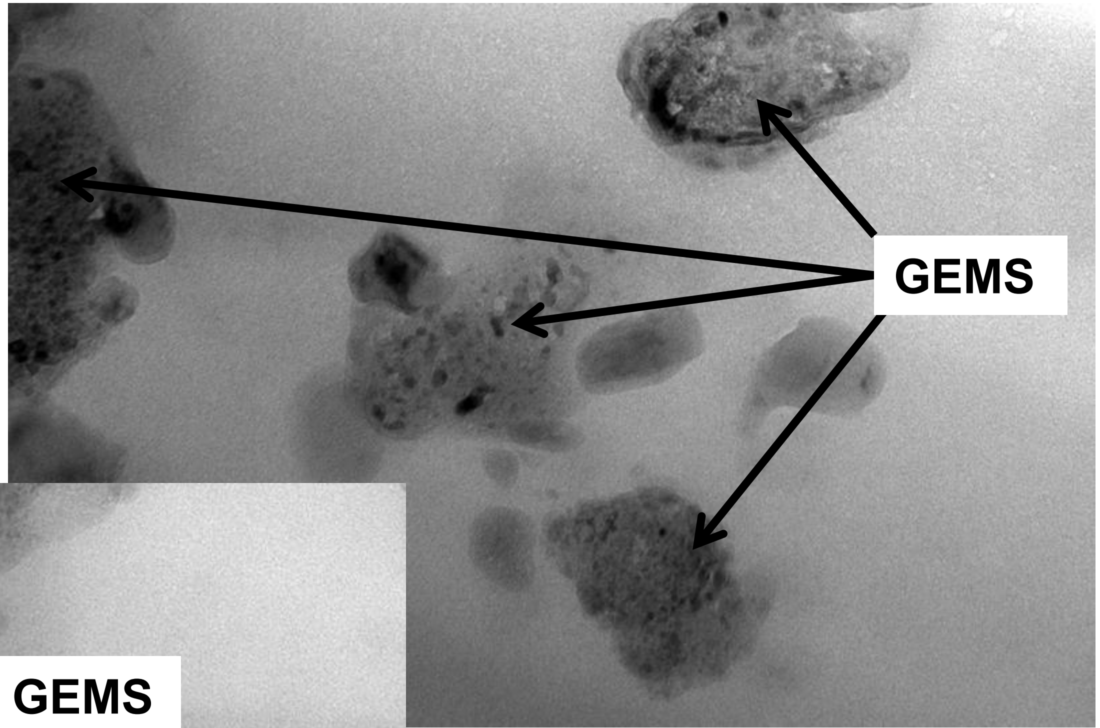
# DC18

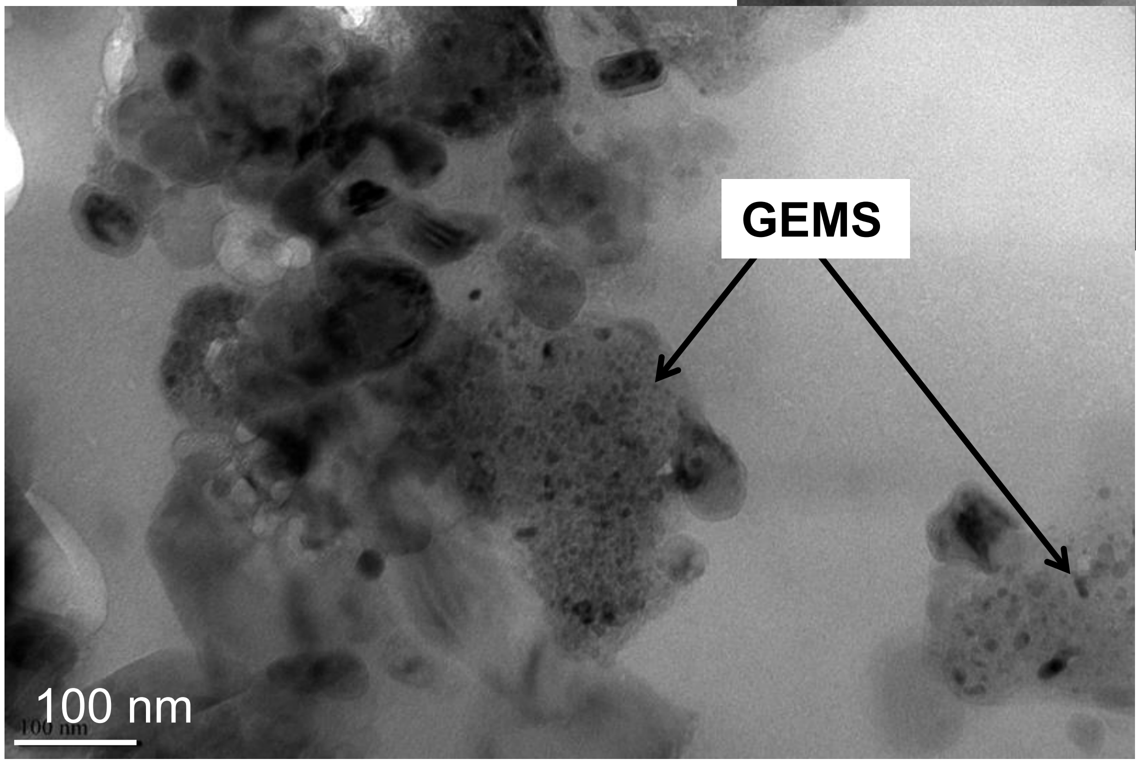


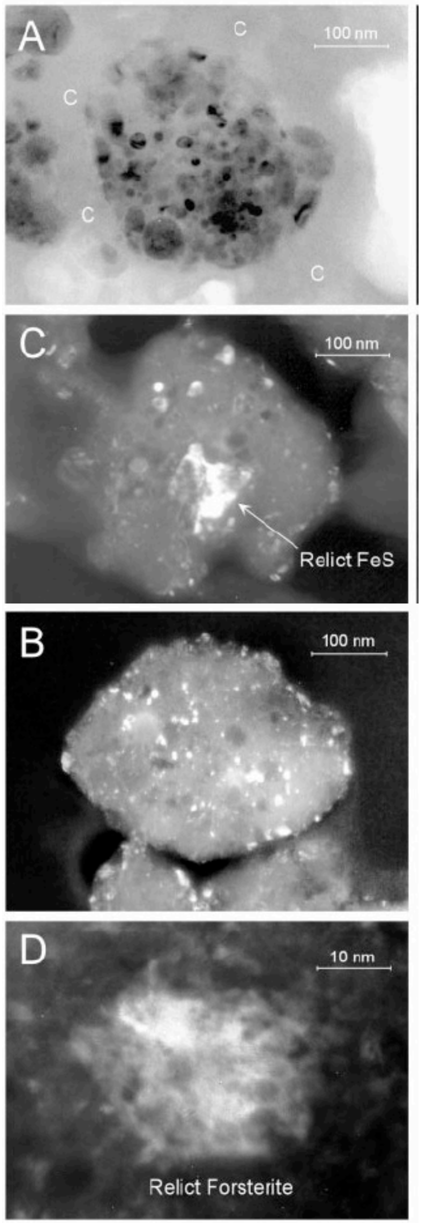
# Glassy phases : GEMS

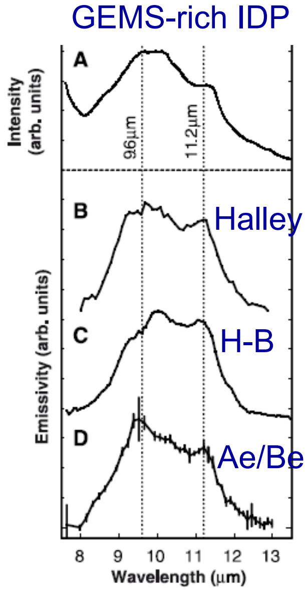


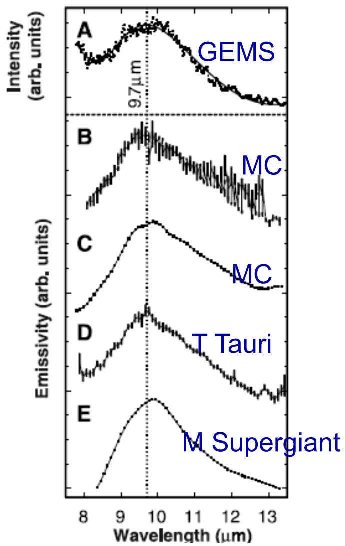



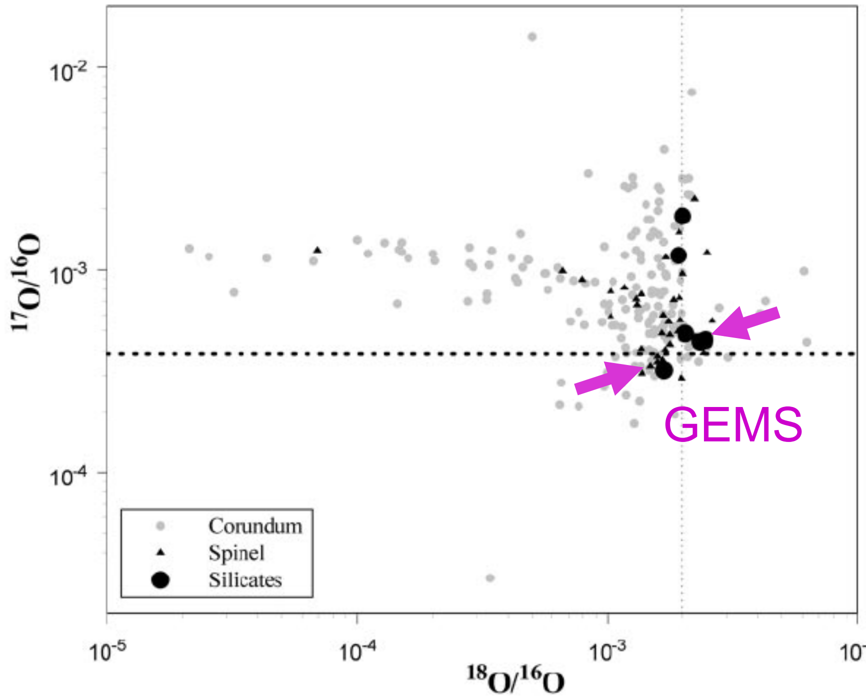

Engrand+2015 LPSC

# CP-IDPs contain abundant GEMS : an interstellar signature?



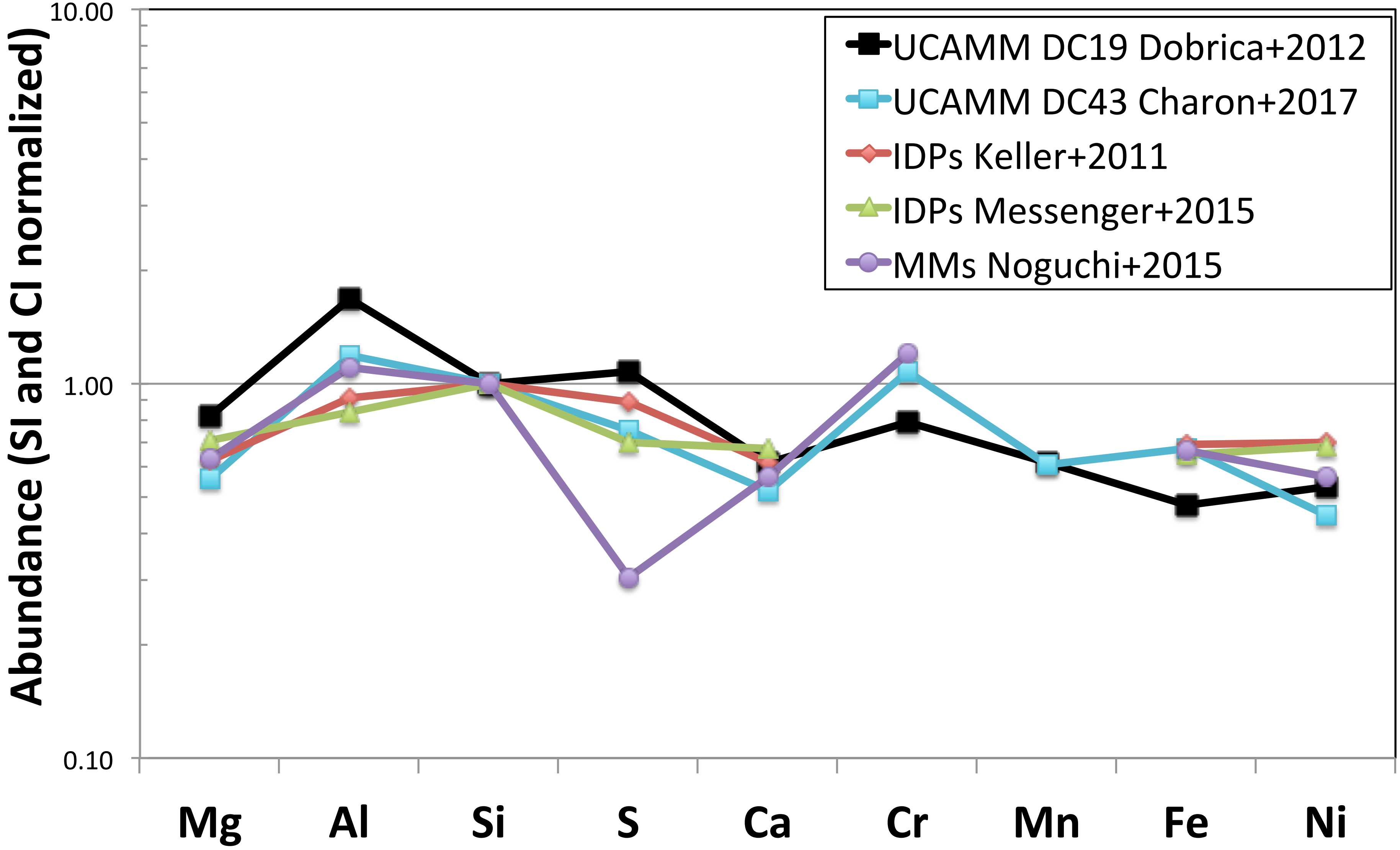




Messenger+2003

Bradley+1999

# GEMS composition in IDPs/(UC)AMMs



# Formation of GEMS?

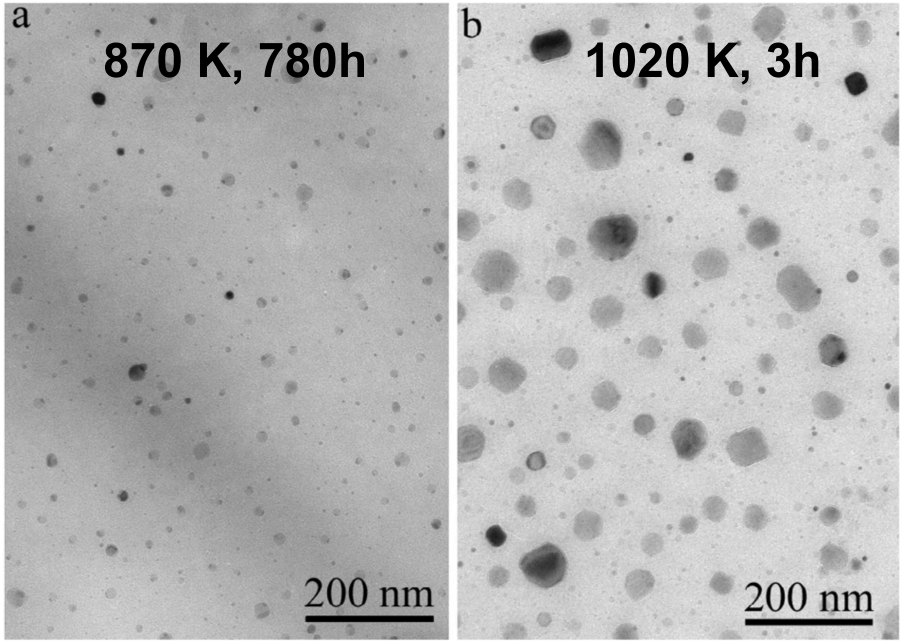



**Fig. 1.** TEM micrograph of annealed sample **a)** at 870 K for 780 h and **b)** at 1020 K for 3 h. Rounded metallic nano-particles enclosed in the amorphous silicate. They formed by a reduction reaction and further precipitation since metallic Fe is immiscible in silicates. The microstructure closely ressembles to those to GEMS found in IDPs.

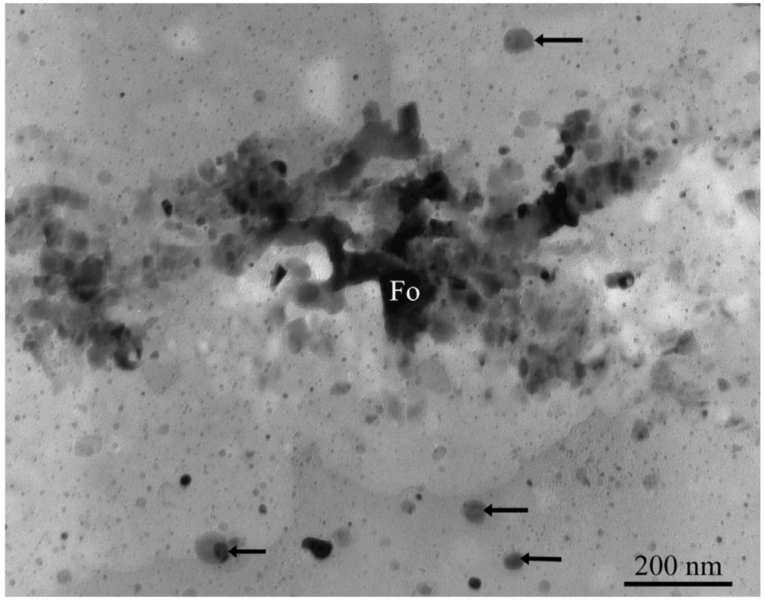
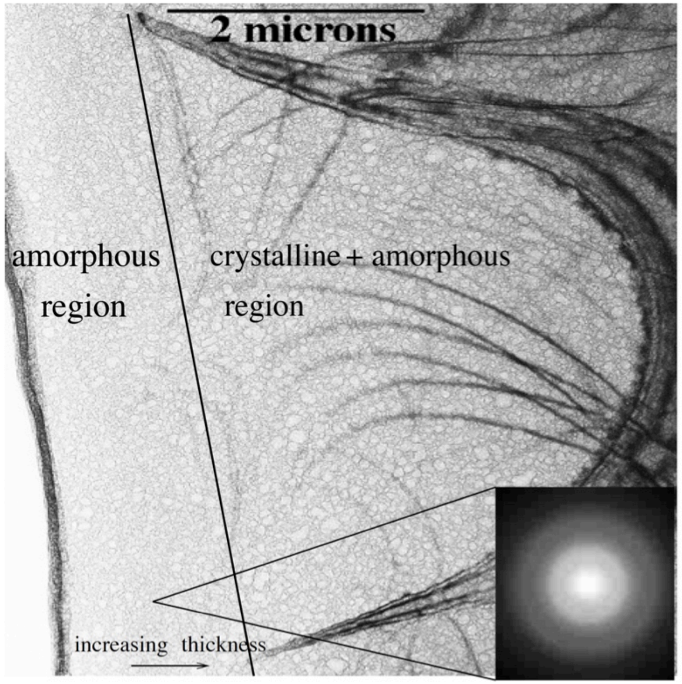



**Fig. 2.** TEM micrograph of sample annealed at 970 K (55 h) showing a forsterite crystal (Fo) embedded in a amorphous matrix. Note the dentritic structure at the edge of the grains. Some metal particles are also present in the amorphous phase (some of them are arrowed).

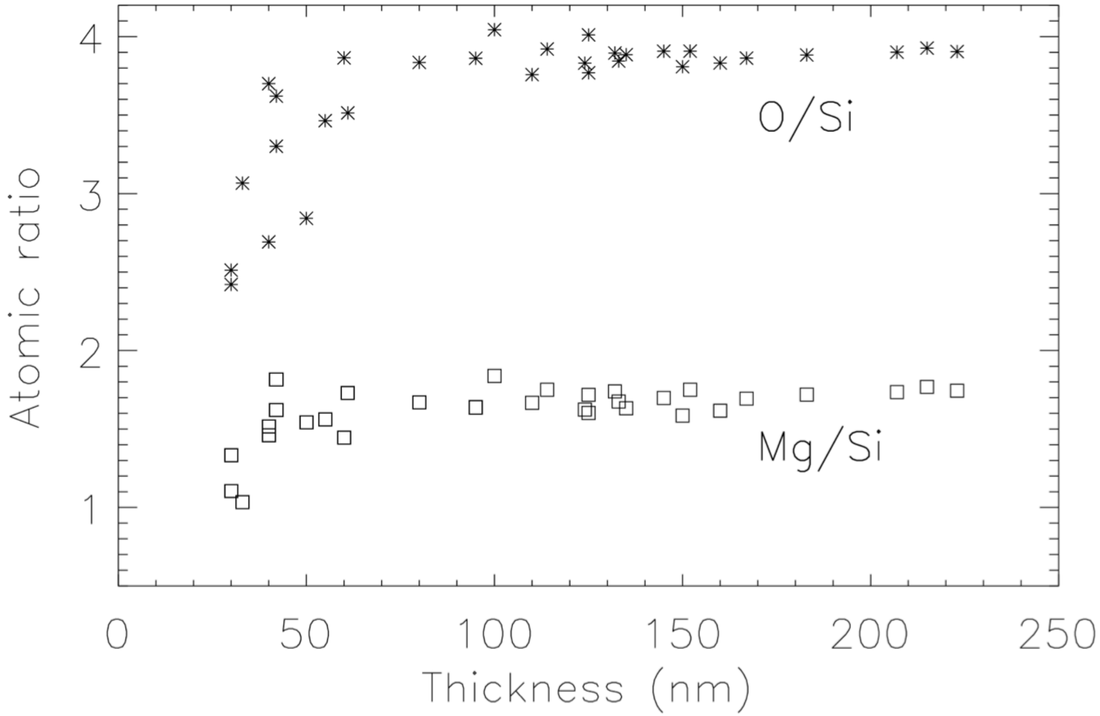
Davoisne+2006

- annealing (<1000K) of amorphous olivine under vaccum?

# Formation of GEMS?
# Low energy irradiation of olivine




$10^{18}$ 10 keV $He^{+}/cm^{2}$

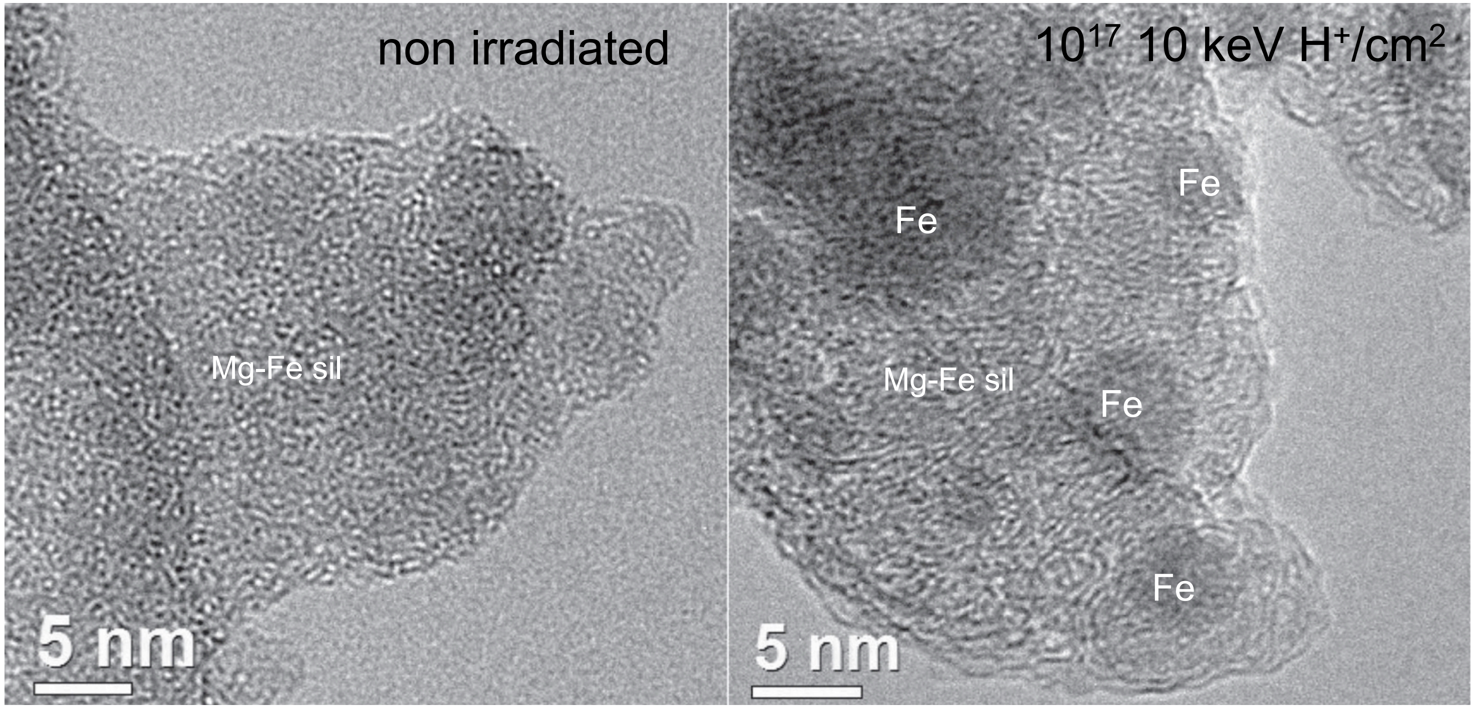



Demyk+2001
Davoisne+2008

- Disordered rim (40-90 nm)
- Change of composition (O, Mg)

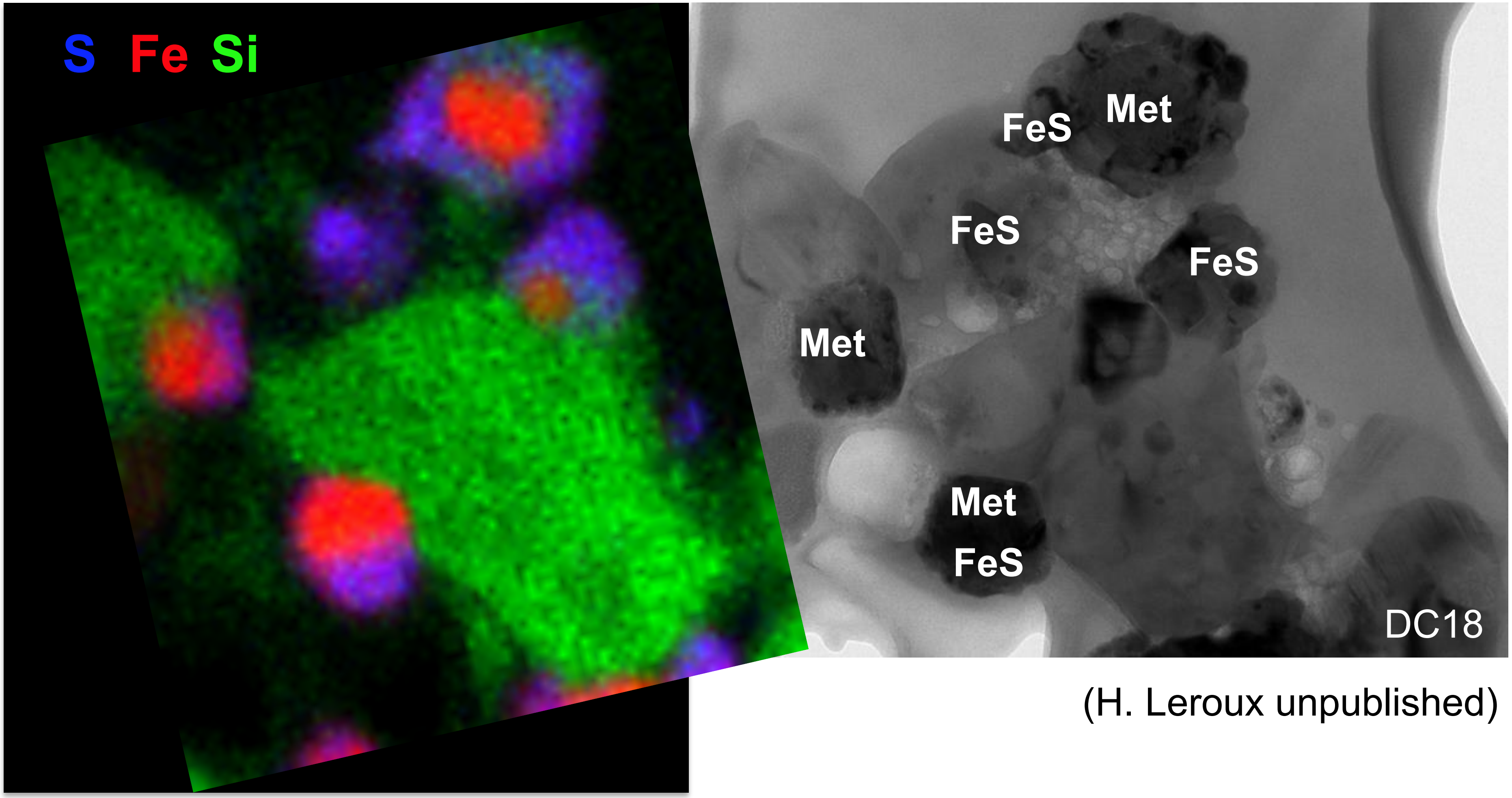
# Formation of GEMS?
# Irradiation of amorphous silicates?

- Amorphous nanometer-sized Mg-Fe and Mg silicate of olivine-type stoichiometry (LA of metal targets **(** Mg**-**Fe**-**Si**)** in He/$O_2$ or of Mg-Fe silicates in 4 mbar He atmosphere)




Jäger+2016

# Metal – Fe sulfides

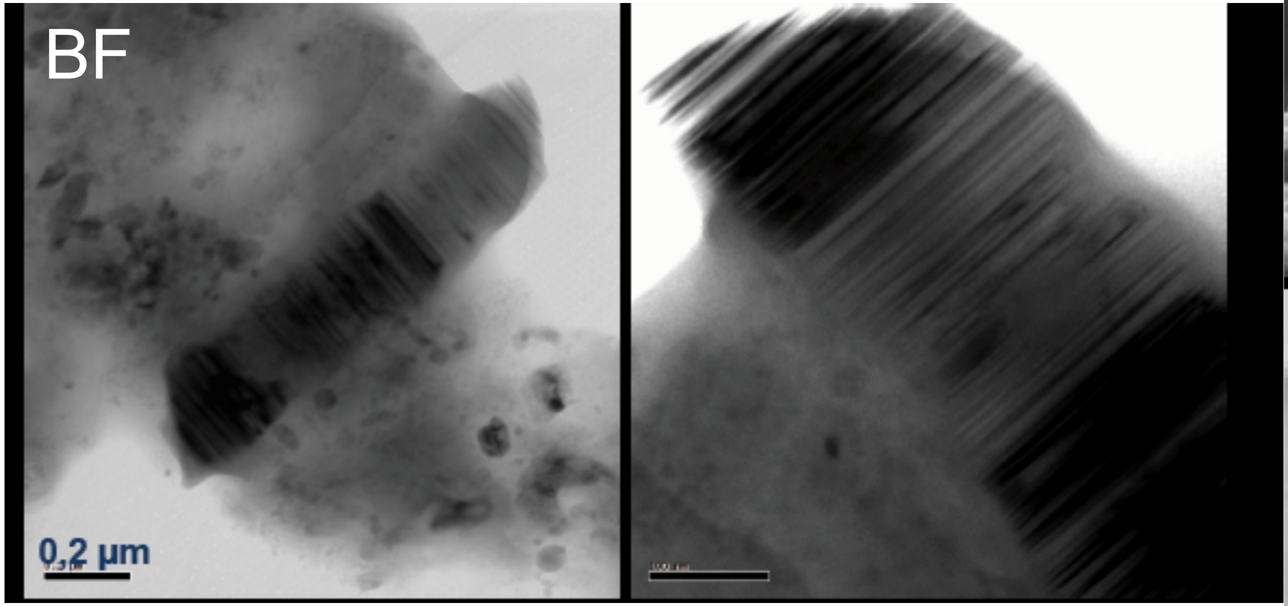



(H. Leroux unpublished)

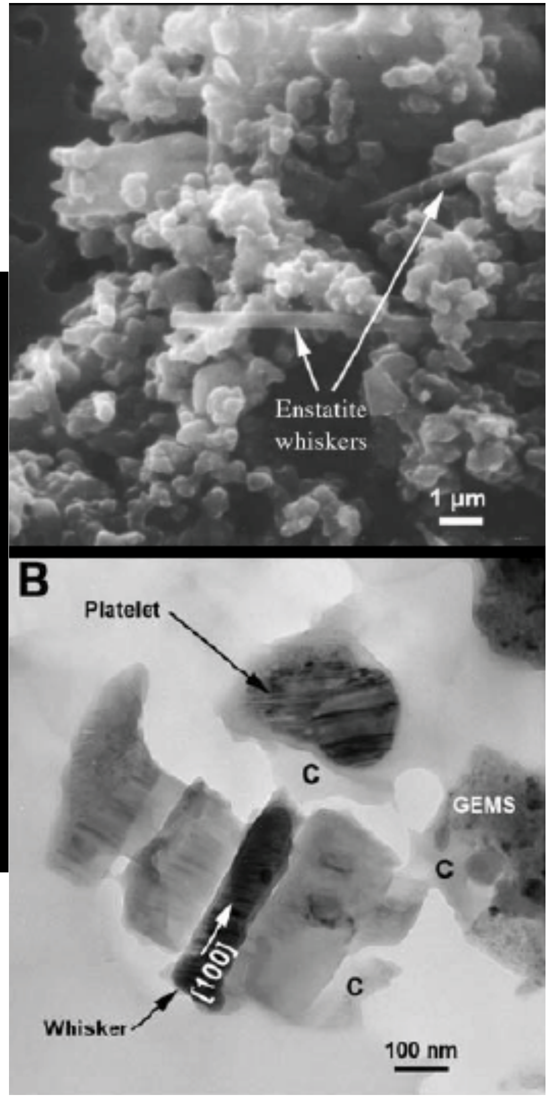
# Mineral condensates : enstatite whiskers

IDP

AMM

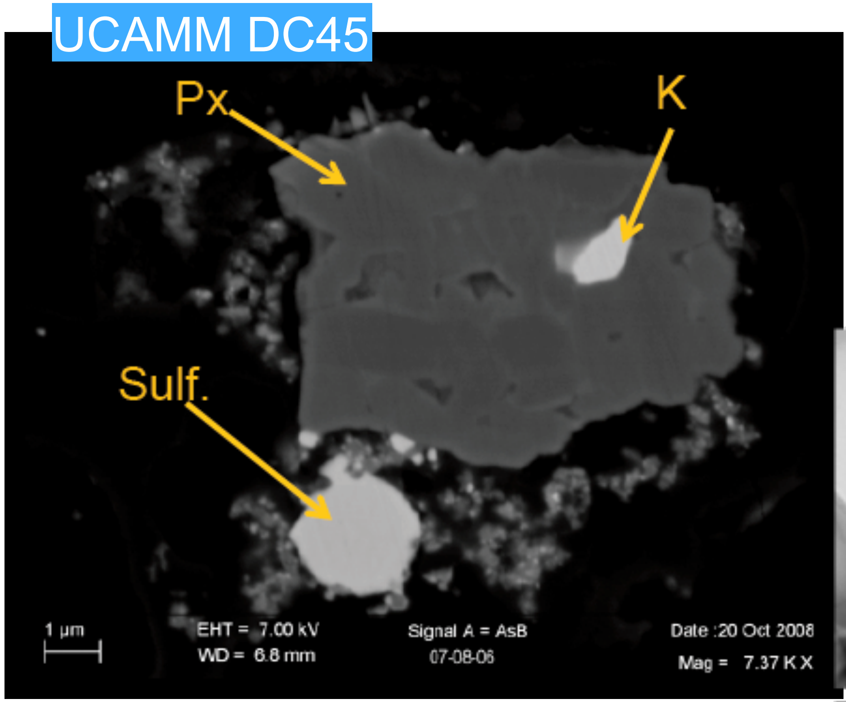



Dobrica+2009

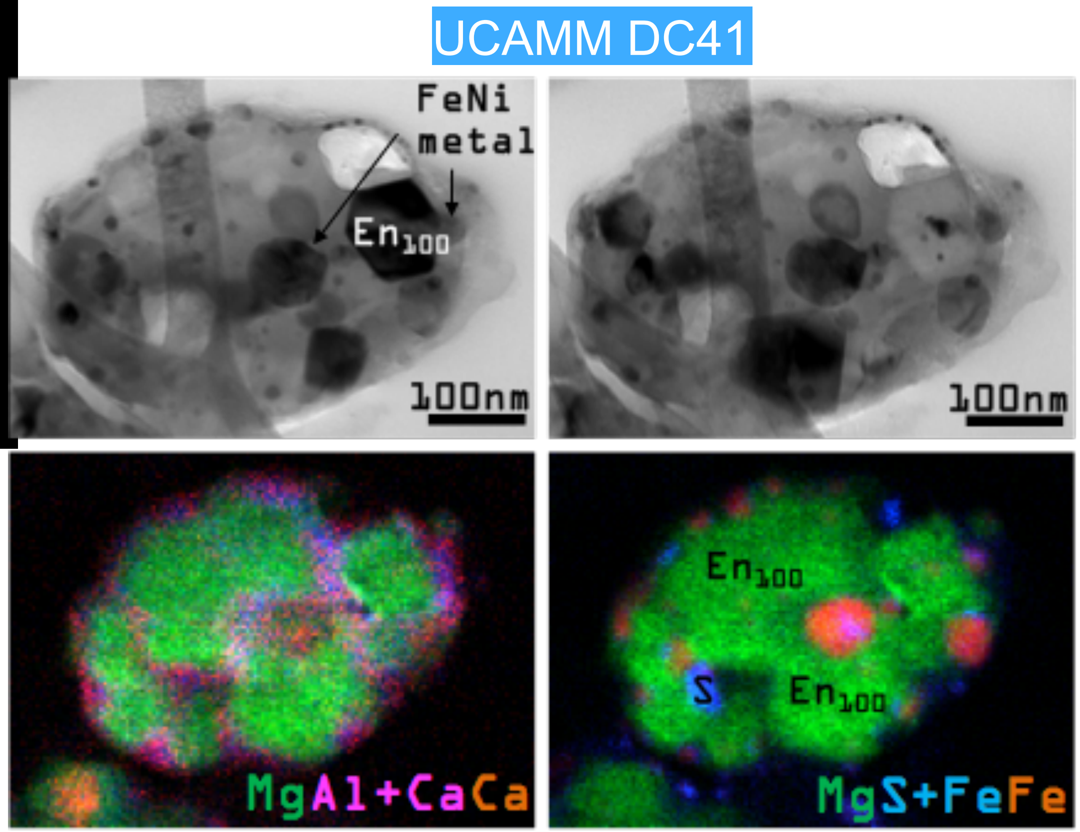



Bradley+1983

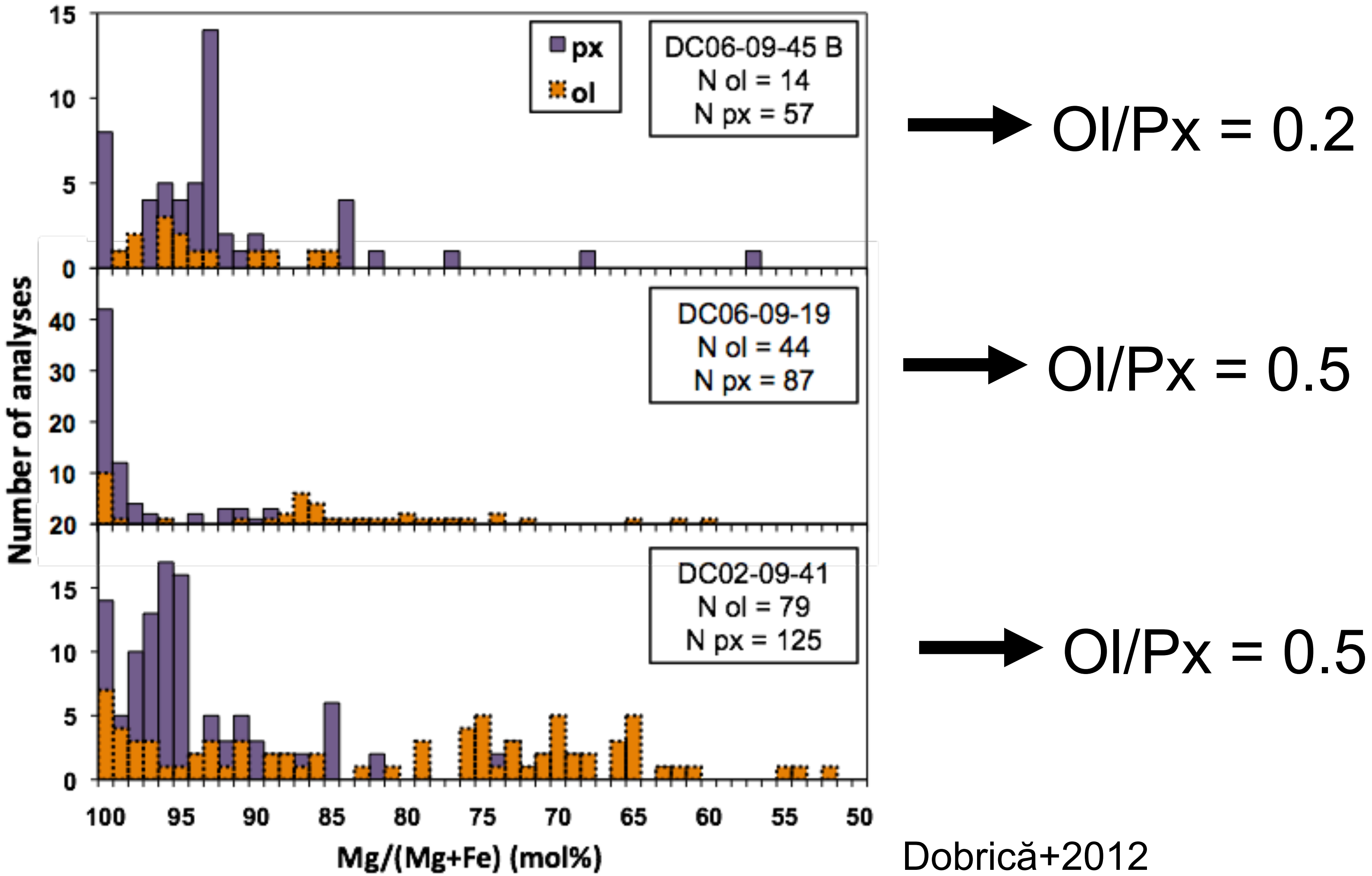
# Chondrules – « Nanochondrules »




Dobrica+2012 GCA



# UCAMM Olivines & Pyroxenes




Dobrică+2012

- Crystallinity > 25%

# Minerals:
# ISM vs protoplanetary disks

- Circumstellar environments:
  - Minerals crystalline, very small
- Diffuse ISM :
  - > 98% minerals amorphous
  - Silicates ~ 50% Ol - 50% Px
  - Size < 100 nm
- Disks :
  - 10-95% crystalline minerals
  - Sizes 0.1 – 2 µm
  - Silicates ~ 50% Ol – 50% Px
  - Mineralogical zonation

# A controversial mineralogical zoning in PPD

Herbig Ae/Ab

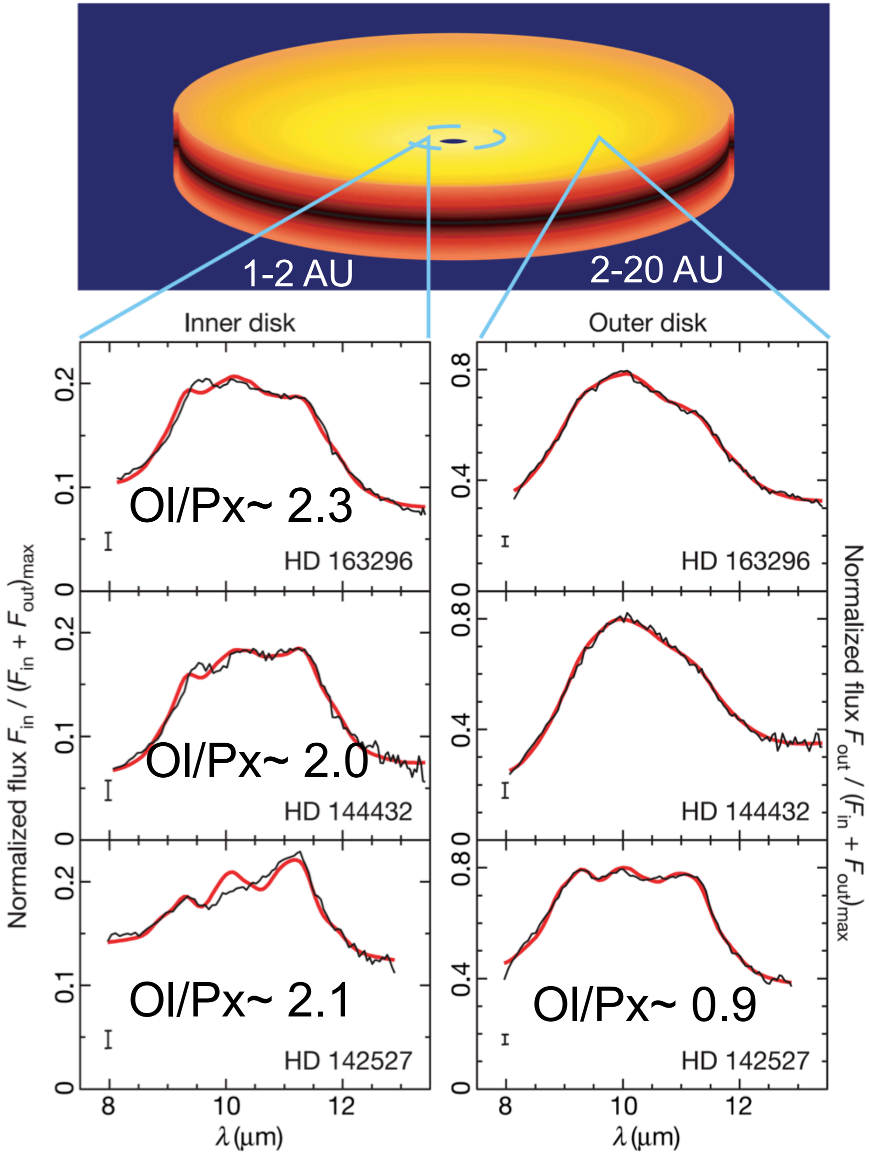


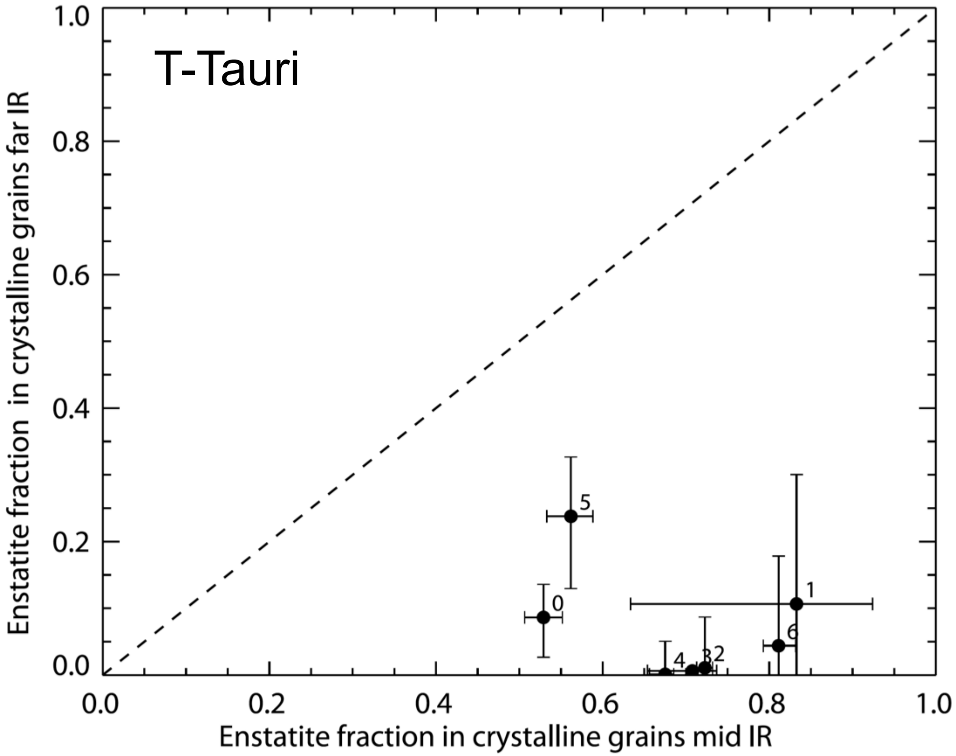

Table 1 **Dust properties in the inner and outer disk**

| | Crystallinity (%) | | Fraction of large grains (%) | | Crystalline olivine to pyroxene ratio | |
|---|---|---|---|---|---|---|
| | Inner disk | Outer disk | Inner disk | Outer disk | Inner disk | Outer disk |
| HD 163296 | $40^{+20}_{-20}$ | $15^{+10}_{-10}$ | $95^{+5}_{-10}$ | $65^{+20}_{-20}$ | $2.3^{+3.7}_{-0.5}$ | – |
| HD 144432 | $55^{+30}_{-20}$ | $10^{+10}_{-5}$ | $90^{+10}_{-10}$ | $35^{+20}_{-20}$ | $2.0^{+1.8}_{-0.6}$ | – |
| HD 142527 | $95^{+5}_{-15}$ | $40^{+20}_{-15}$ | $65^{+15}_{-10}$ | $80^{+10}_{-30}$ | $2.1^{+1.3}_{-0.7}$ | $0.9^{+0.2}_{-0.1}$ |

(Van Boekel+2004)

- Would agree with tendency observed in CP-IDPs, UCAMMs, Wild 2…
- But for T-Tauri...

# Mineralogical zoning in PPD



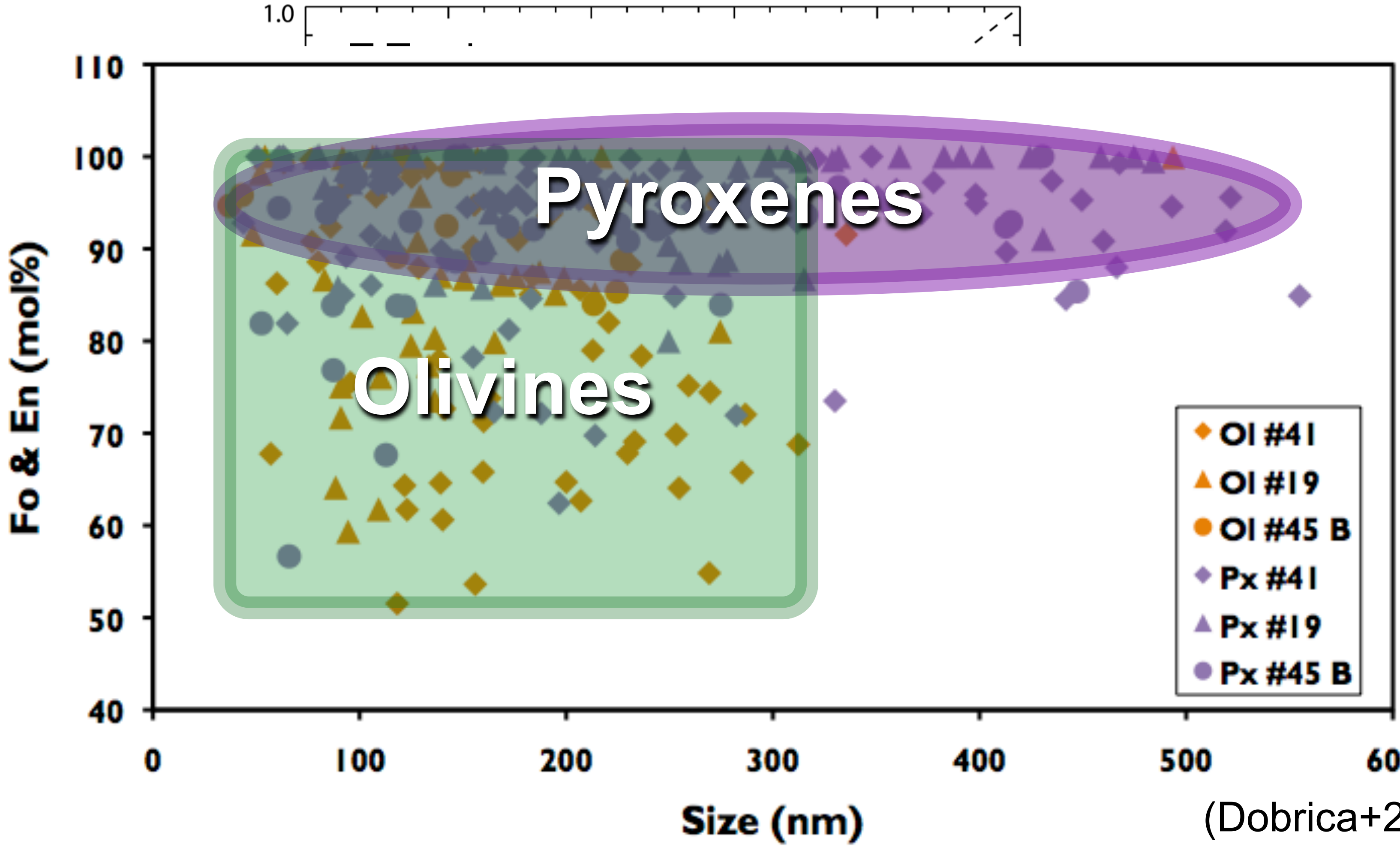

Crystalline En FIR (5-15 AU)

Crystalline En MIR (~ 1 AU)

(Bouwman+2008)

- Crystalline Ol/Px ~ 1.5 in inner regions (1 AU)
- Crystalline Ol/Px > 5 in outer regions (5-15 AU)
- Enstatite grains (~ 1 μm) larger than Fo grains (~ 0.1 μm)
- (Amorphous silicates ~ 6 μm)

# Mineralogical zoning in PPD




(Dobrica+2009)

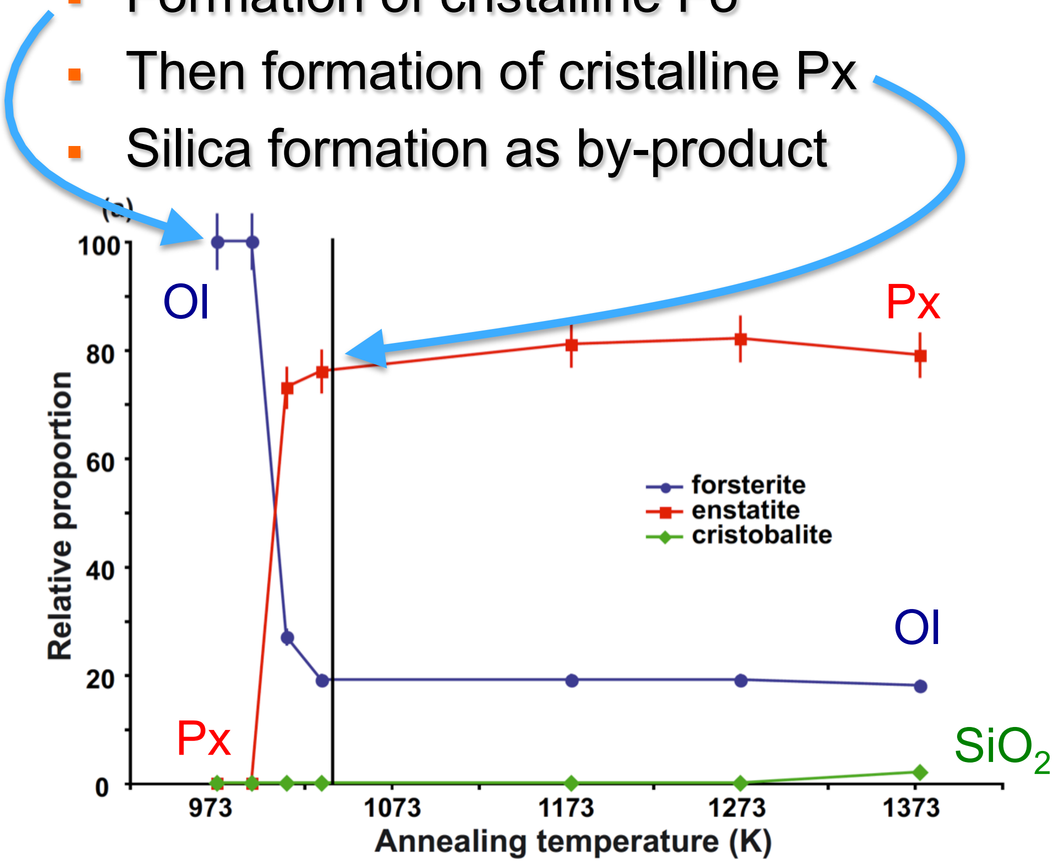
- Enstatite grains (~ 1 μm) larger than Fo grains (~ 0.1 μm)
- (Amorphous silicates ~ 6 μm)

# Outward transport

- All minerals/CAIs in cosmic dust particles (IDPs/MMs) and Stardust samples (comet 81P/Wild2) are miniature compared to their meteorite counterparts
- A consequence of radial transport ?

# Zonation of Ol and Px in PPDisk

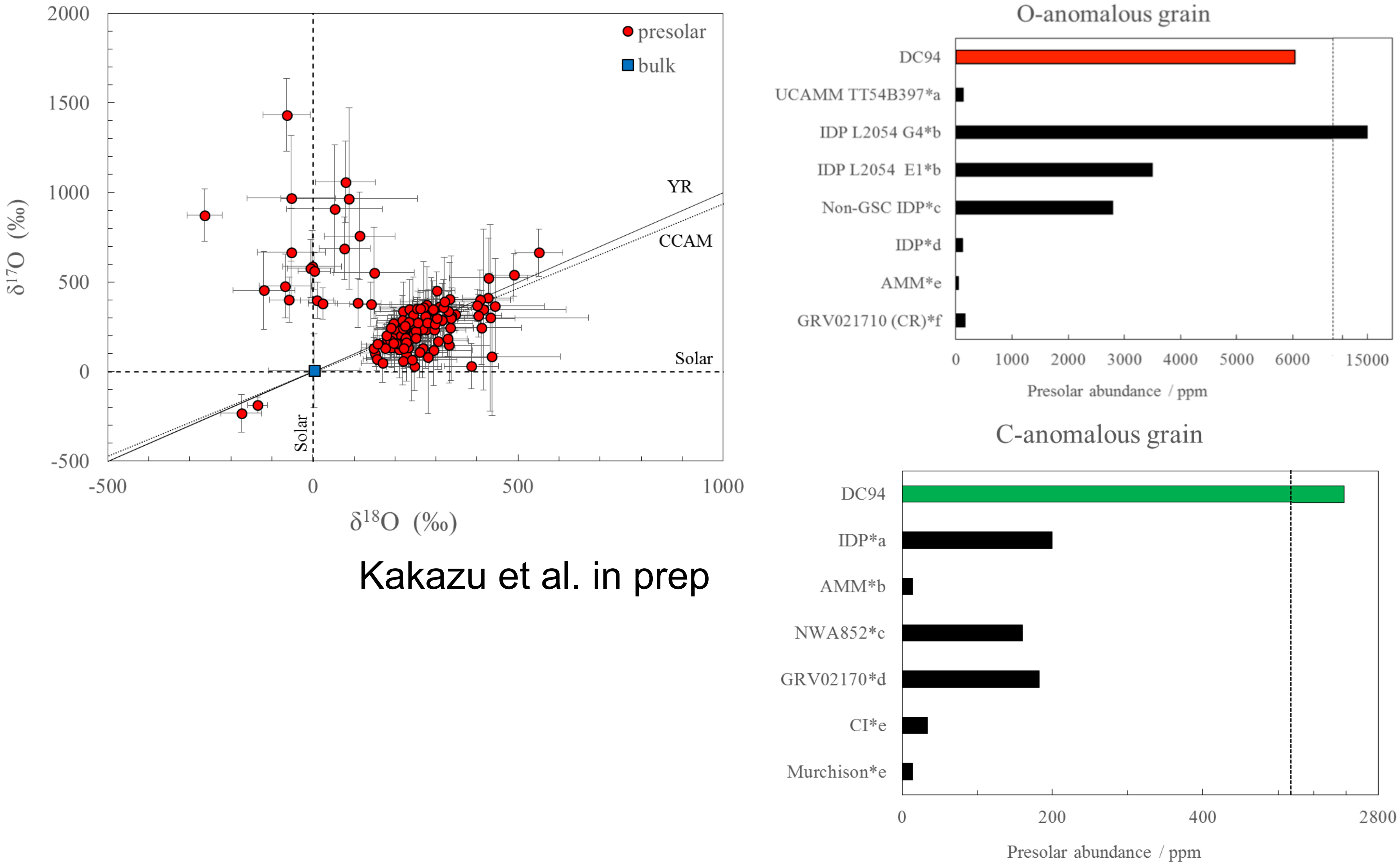
- Annealing of amorphous $MgSiO_3$ (Px) precursor ?
  - Formation of cristalline Fo
  - Then formation of cristalline Px
  - Silica formation as by-product




Roskoz+2011

  - Crystalline phases in CP-IDPs/Wild2/UCAMMs preserved inner S.S. mineralogy during transport?
  - But not meteorites?

# Presolar grains in UCAMMs

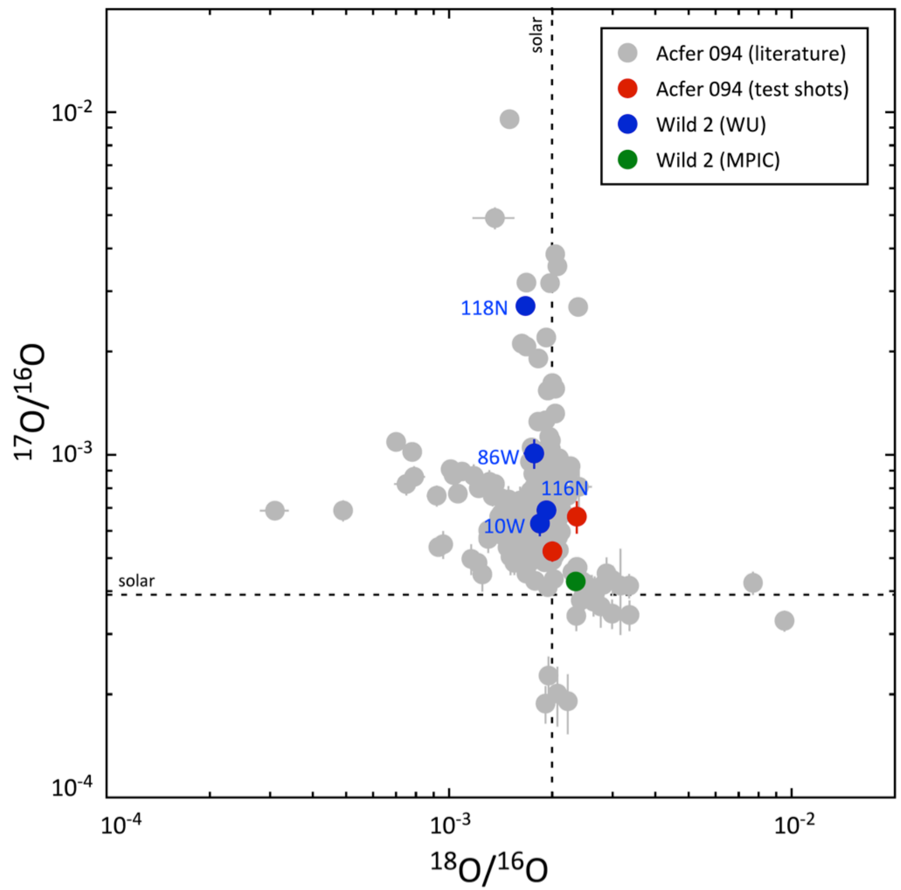



Kakazu et al. in prep

- Abundance of presolar grains ~ 0.5%

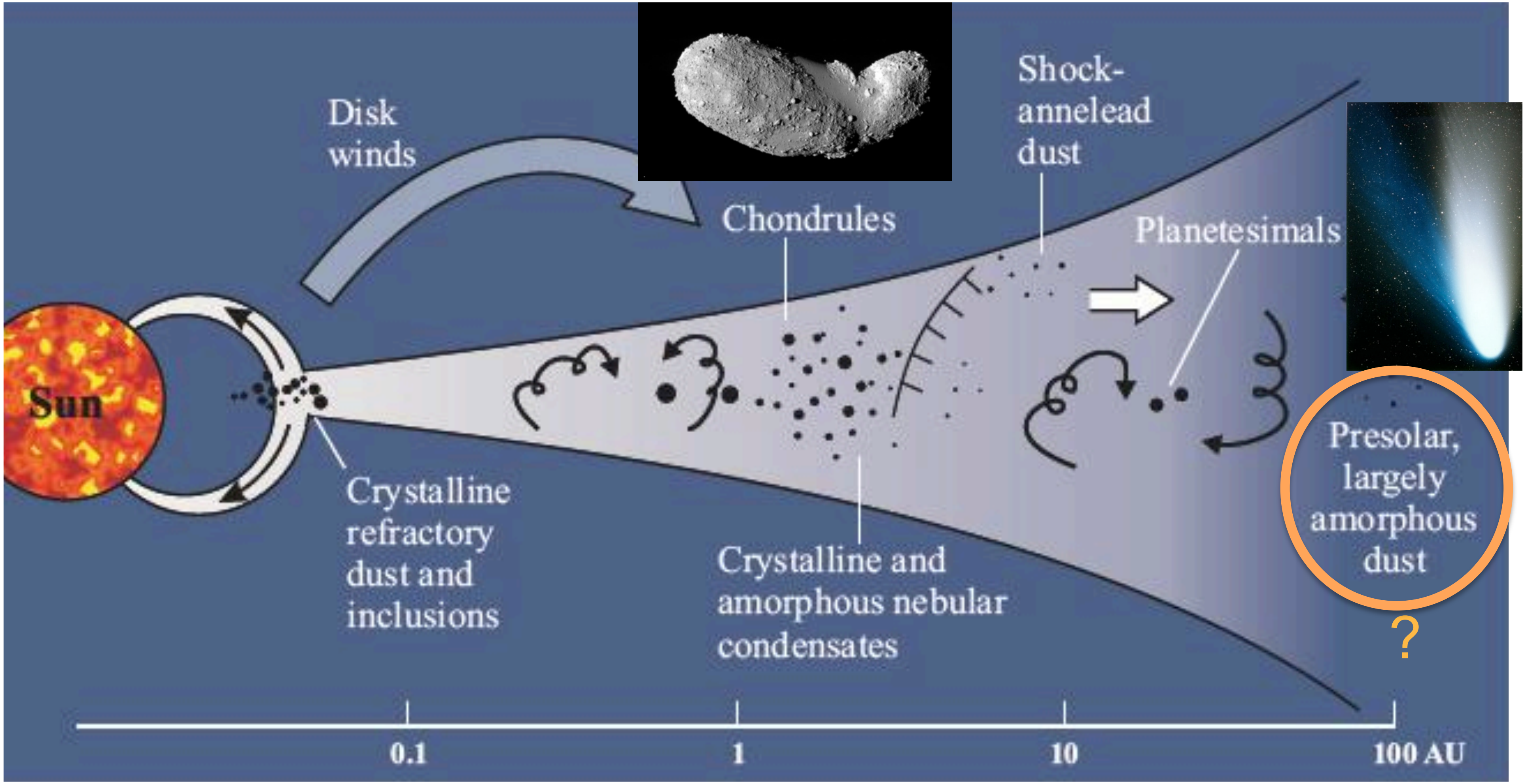
# Stardust Presolar grains

- Stardust mission (81P/Wild2)
- anomalous silicates or oxides
  - corrected abundance (destruction impact) = 600-830 ppm
- SiC : 45 ppm



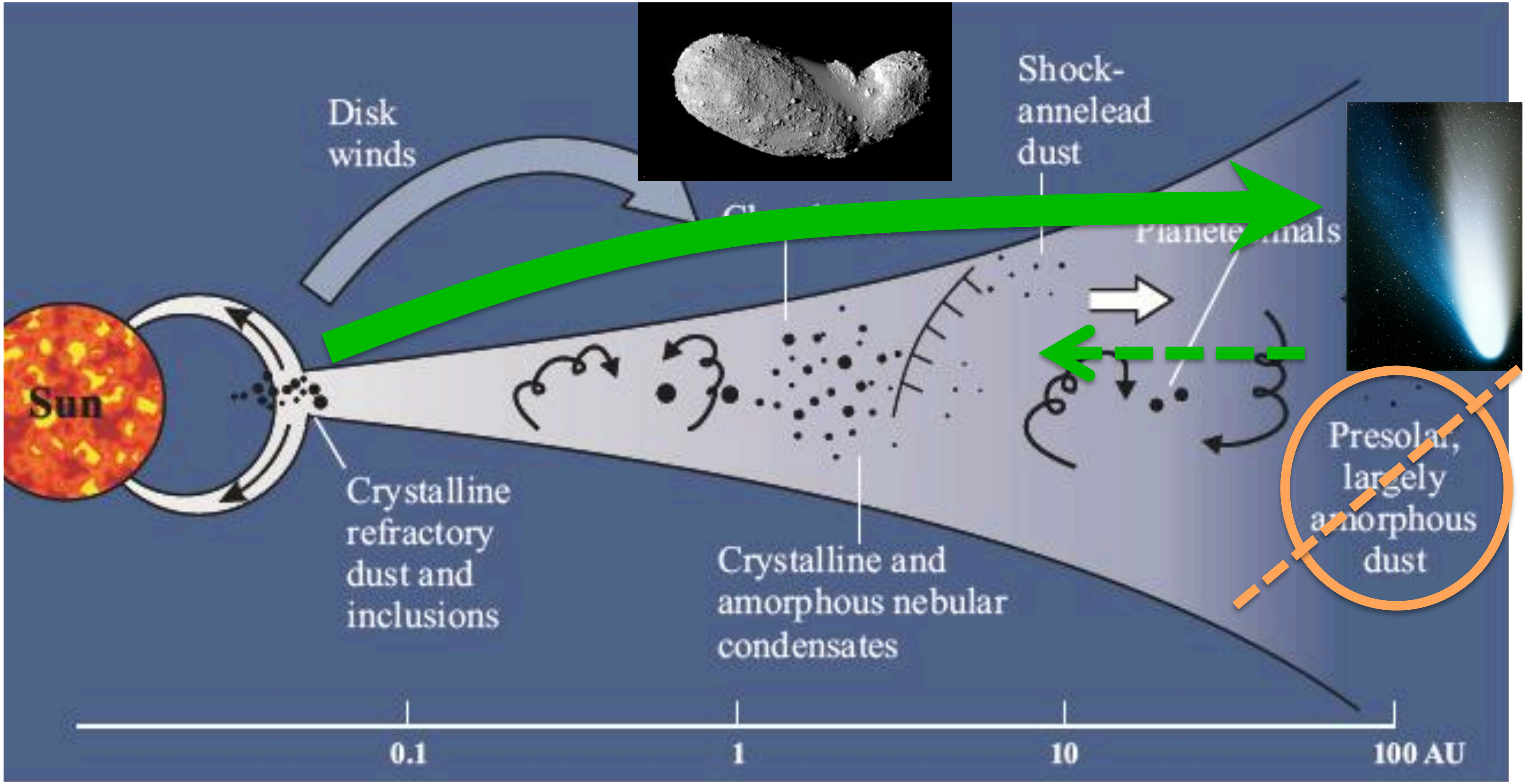

Floss+2013

# Structure of the protoplanetary disk ?




(Scott, 2007)

# Structure of the protoplanetary disk ?




(Scott, 2007)

# Summary (1/2)

- UCAMMs provide informations on the outer regions of the protoplanetary disk
- 2 C-rich phases (at least) in UCAMMs: N-rich and N-poor (see also Yabuta et al., 2012)
  - N-rich carbonaceous phase is smooth, no minerals
  - N-poor carbonaceous phase is associated with minerals (and GEMS)
- Different origins/formation mechanismes for N-rich and N-poor phases
  - Genetic link to meteorite IOM for N-poor phase? (but contains GEMS…)
  - Formation by irradiation of $CH_4$-$N_2$ ices for N-rich phase? (Dartois+2013; Augé+2016)

# Summary (2/2)

- Large D enrichments (low T chemistry) – no direct correlation with N isotopes
- « Large » abundance of presolar silicates (~0.5%) and C-rich anomalous grains
- Inner solar system material transported to the outer regions
  - Incomplete mixing from the inside out. OK with models (Shu et al. 1997, Bockelée-Morvan et al. 2002, Ciesla 2007, Vinković 2009…).
  - Mineral sizes usually smaller – size sorting effect?
  - Mineralogical gradient in the PPdisk ?

# Open Questions

- Wild2 – CP-IDPs – UCAMMs :
  - Differences…=> ?
- Formation of GEMS – ISM or not ISM?
- Zonation of the PPD : CP-IDPs& UCAMMs richer in px than meteorites… signature? altertion effect?
- Atmospheric entry models: UCAMMs (outer S.S.) do not know evidence for heating above ~300˚C?