



The Open University

## Laboratory Analyses of Marco Polo Samples

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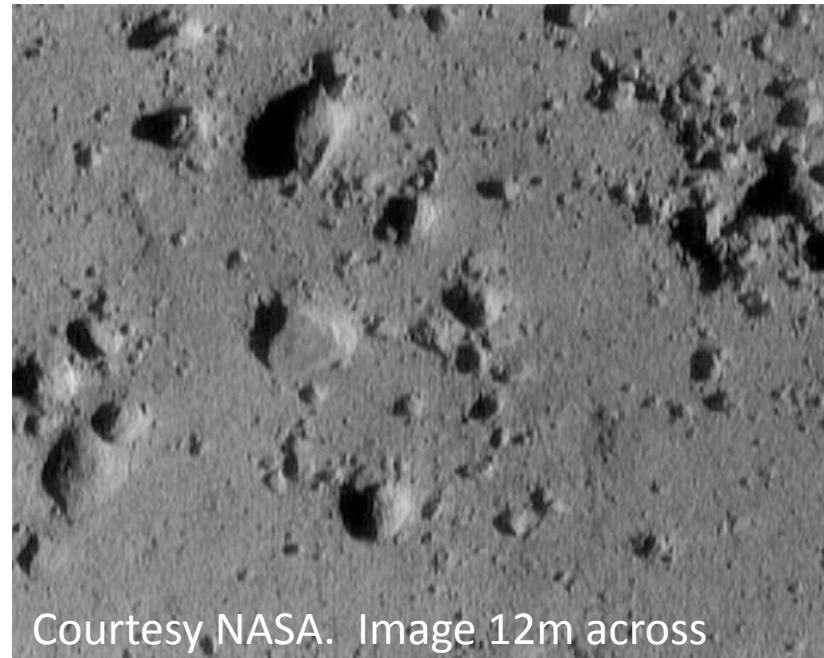
## Overview

- Principle Objective of Marco Polo is to return a sample of a primitive NEO to Earth
- Only laboratory analyses can provide the analytical precision, accuracy, sensitivity and sample selectivity required
- Great array of measurements and problems to be addressed
  - What? - types of analyses and studies required
  - How? - the instrumentation, approaches and sample requirements
  - Why? - the science addressed



## Expected Sample?

- Sample will be collected from the regolith of a primitive NEO
  - But we have never seen a close up image of a primitive asteroid...
- Eros – fine particle size
  - 10s microns, lots of boulders

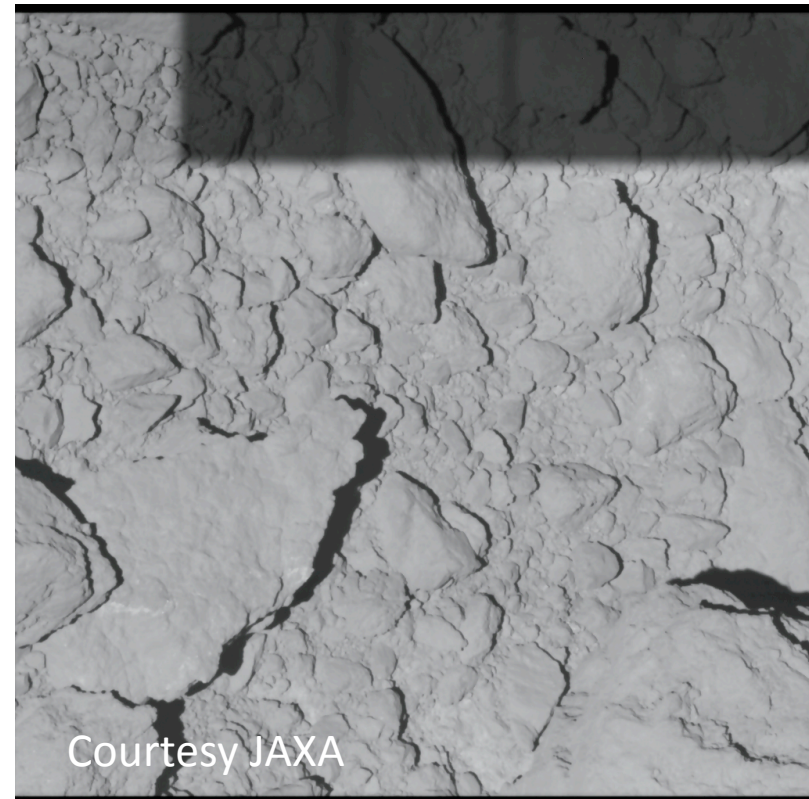


Courtesy NASA. Image 12m across



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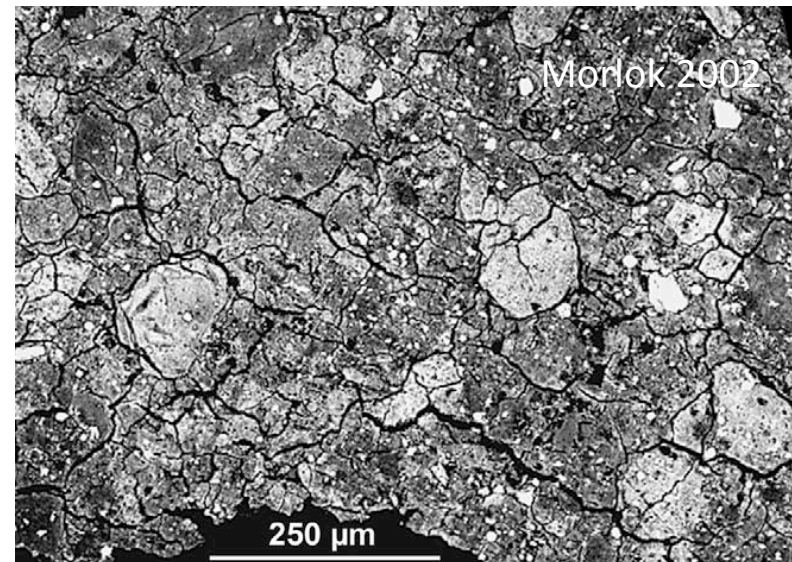
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  - mm to cm regolith plus blocks





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  - mm to cm regolith plus blocks
- Carbonaceous chondrites
  - Many regolith breccias
  - Sub-mm to cm particles

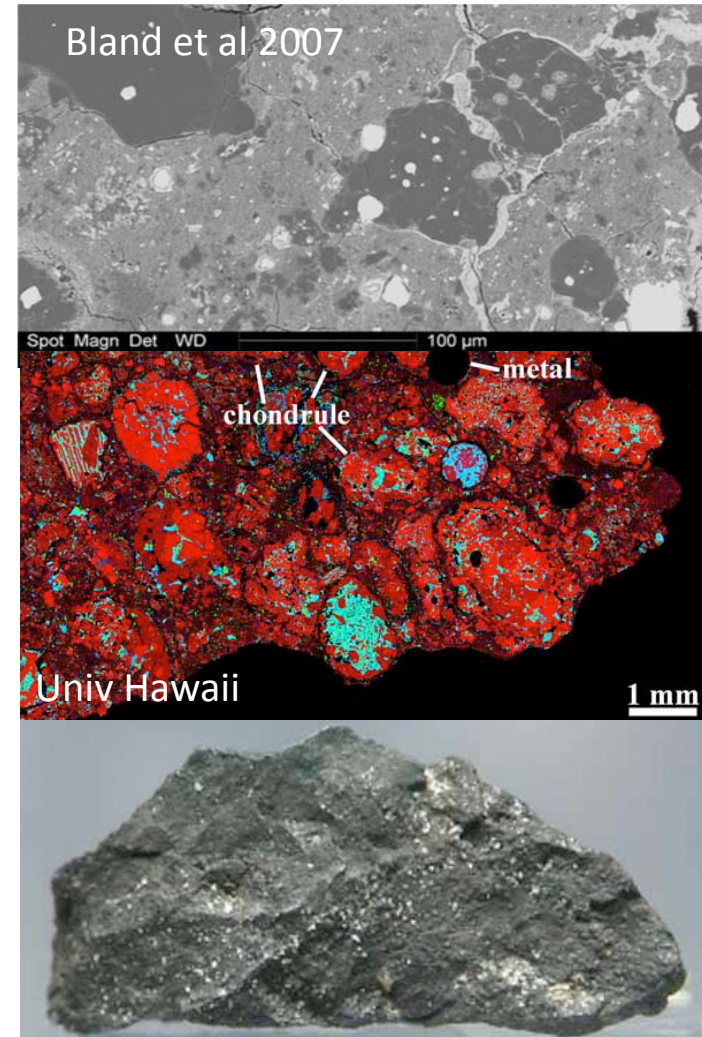
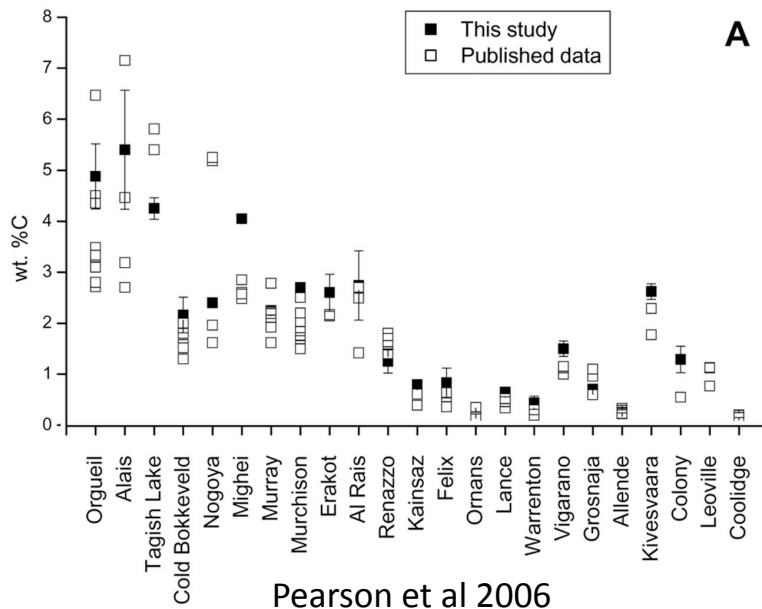




# Mineralogy of Expected Sample?

- Carbonaceous chondrites – very diverse mineralogy
  - 100nm condensate mineralogy
  - mm chondrules and CAIs
  - Fine phyllosilicate mineralogy

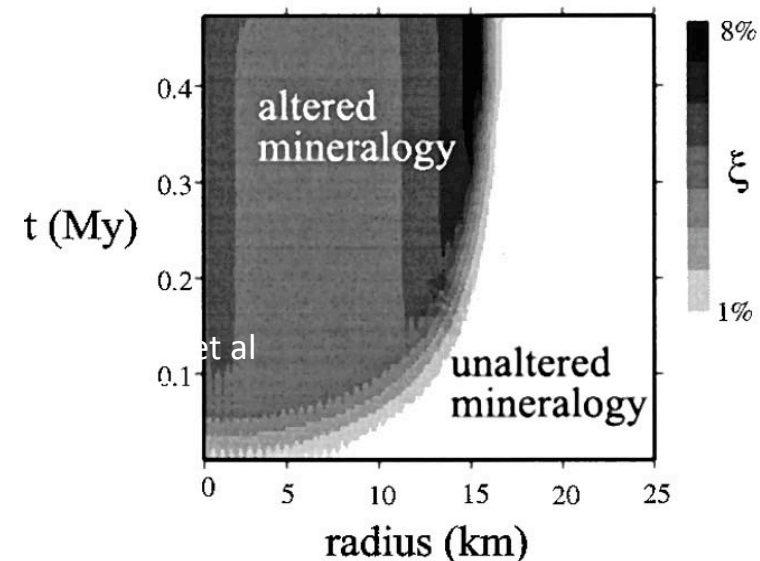
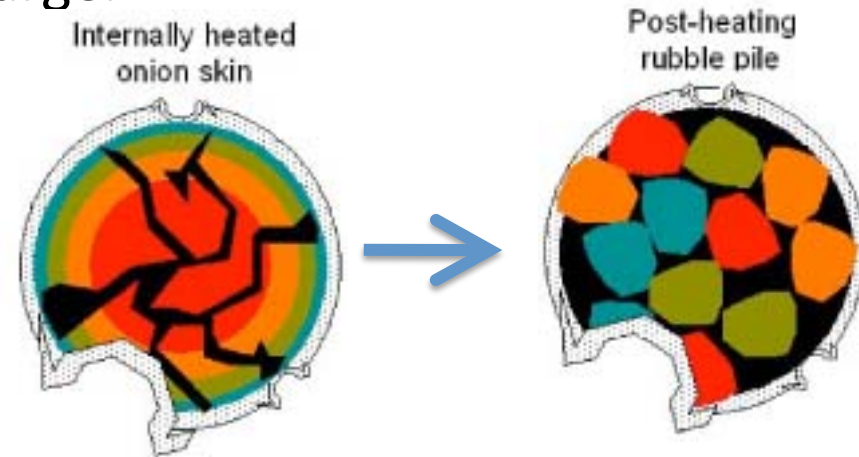
- Carbon content varies by factor 30





## Nature of Expected Sample?

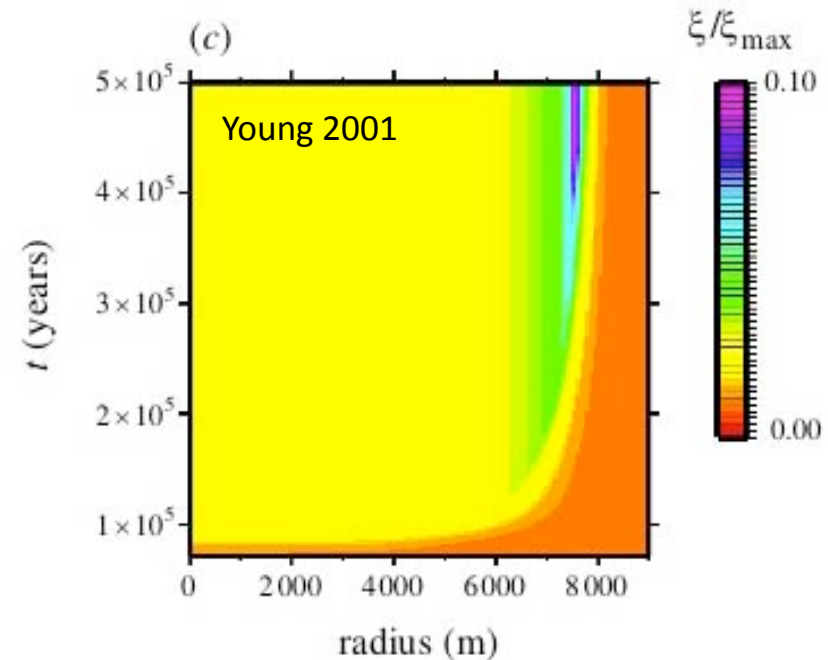
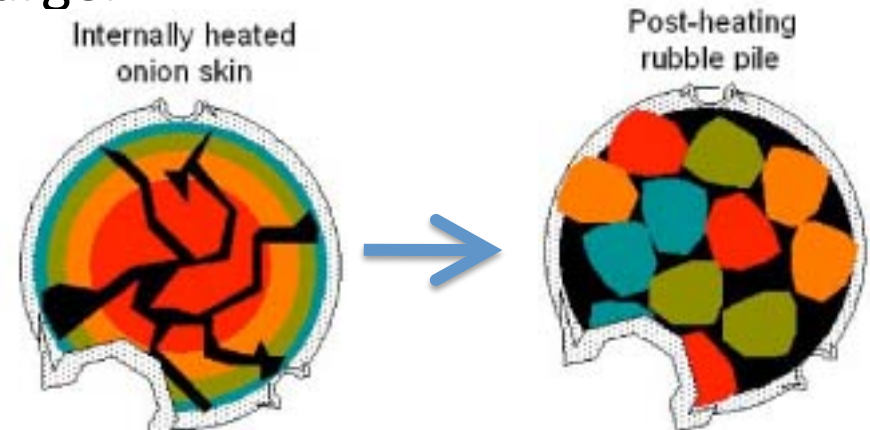
- Assume NEO is derived from larger main belt asteroid
  - Block fragment?
  - Rubble pile?
- Original lithic diversity?
  - Structured body – onion shell?
  - Peak temp/time decreases radially
  - Effects of fluid flow complex
- Unaltered material abundant
- MP sample – mix of lithologies?





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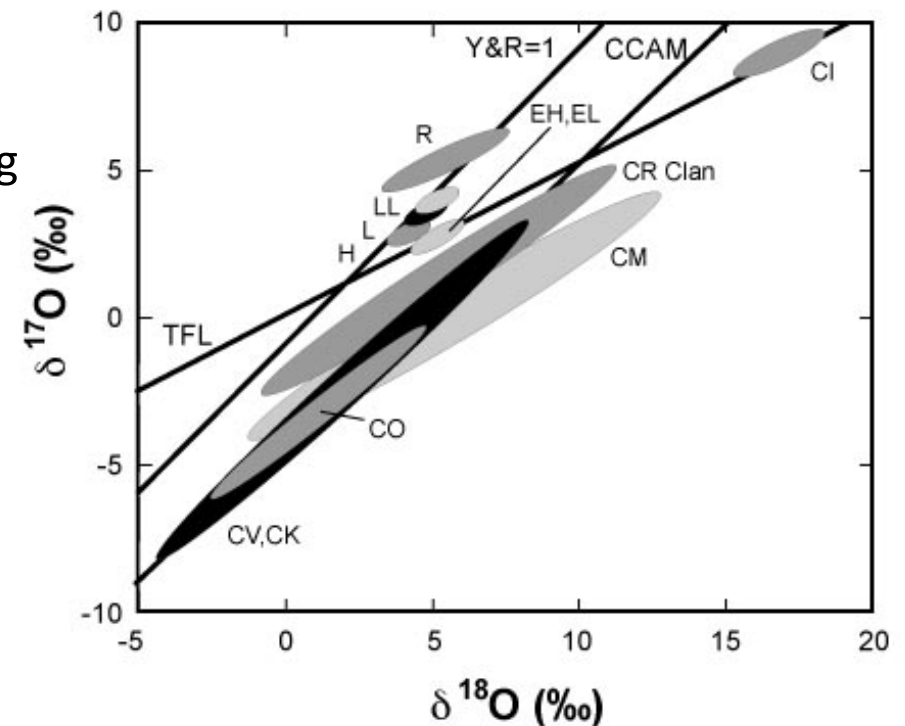
## Sample Analysis Outline

- MP sample – regolith with a mix of dust to pebbles and a number of different lithic components. What to do?
- Bulk properties
  - That relate to understanding overall properties of NEO
- Component properties
  - Asteroidal processes – post accretion history
  - Nebula, pre-solar processes – pre-accretion history
  - Organic compounds
  - Space weathering



## Bulk Properties I

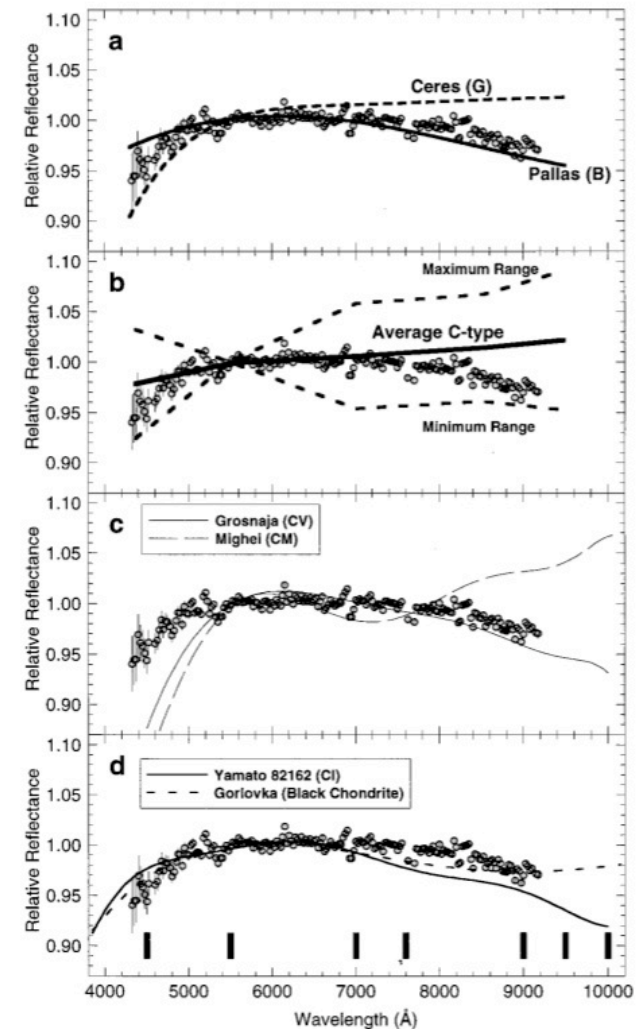
- Elemental Composition
  - ICPMS, INAA, noble gas MS, gas source MS
  - Each technique requires mg to 10s mg material
- Mineralogy
  - XRD, Mössbauer, ESR, NMR
  - Each technique requires mg to 10s mg material
- Isotopic Composition
  - e.g. Oxygen – requires mg quantities
- Provides comparison with bulk meteorites, Earth, Mars, etc





## Bulk Properties II

- Density & Porosity
  - Pycnometer – requires large sample (currently)
- Spectral Properties
  - UV to near-IR (300nm to 2.5  $\mu\text{m}$ ) and mid-IR (up to 50  $\mu\text{m}$ ?)
  - Requires  $\approx 20$  mg of material
- Magnetic susceptibility
- Non-destructive, contamination-free?
  - Could use large representative sample
- Understanding overall structure and properties of asteroid
- Cross-characterisation between sample, MP spectrometer, telescopes.



Binzel et al 1996



# Identification of Lithologies

- To provide initial characterisation of samples

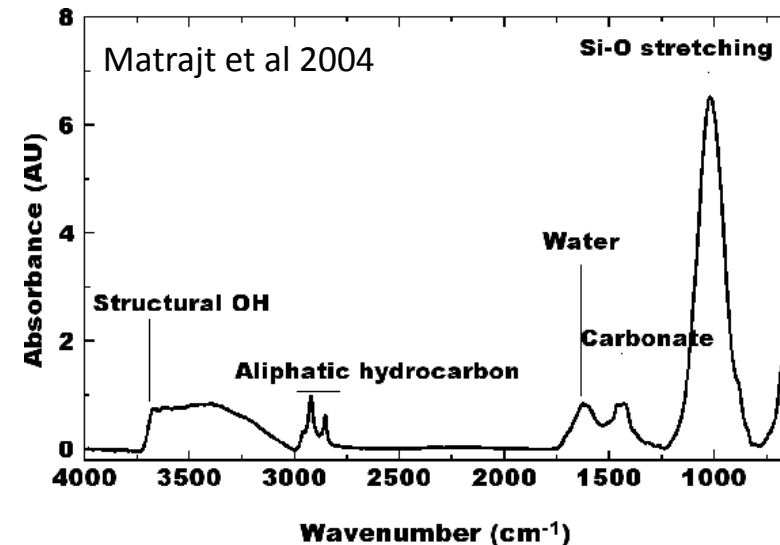
- Optimise sample selection for detailed studies, e.g.:

- Organic rich samples
- Aqueously altered sample
- Pristine nebula rich samples

- No sample preparation

- Non-destructive techniques

- Non-contaminating techniques

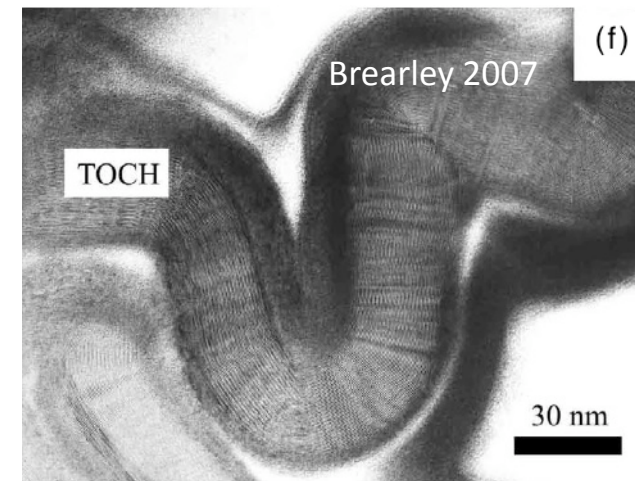
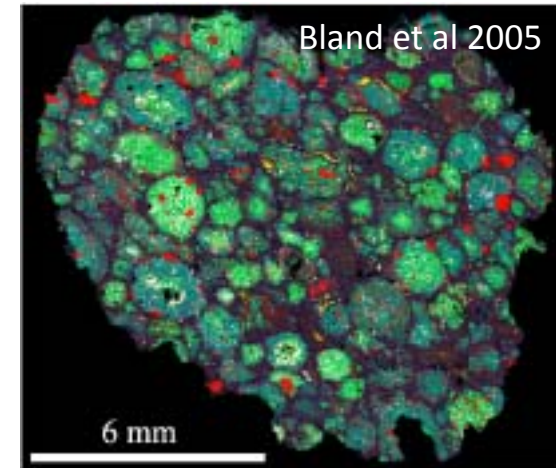


- Optical microscopy, spectroscopy, magnetic susceptibility, etc
  - Requires some initial feedback from destructive techniques
- Part of sample curation facility activities



# Lithology Characterisation

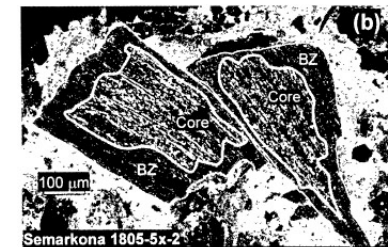
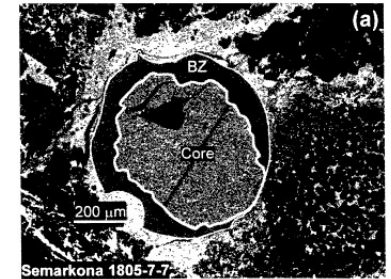
- Bulk composition, mineralogy, spectral and physical properties
  - Same approach as for bulk sample
- Mineralogy & petrography of sample – from nm to mm scale
  - Textures – optical and electron microscopy (SEM, TEM)
  - Mineralogy - optical and electron microscopy (SEM, TEM),  $\mu$ -XRD, FTIR/Raman spectrometry
  - Mineral chemistry – ASEM, EMPA, XANES, SIMS, LA-ICPMS
  - All in situ techniques – requiring preparation of polished sections
    - Some destructive – e.g. LA-ICPMS, SIMS
  - Preparation of sub-samples from sections
    - E.g. FIB wafers for synchrotron, TEM



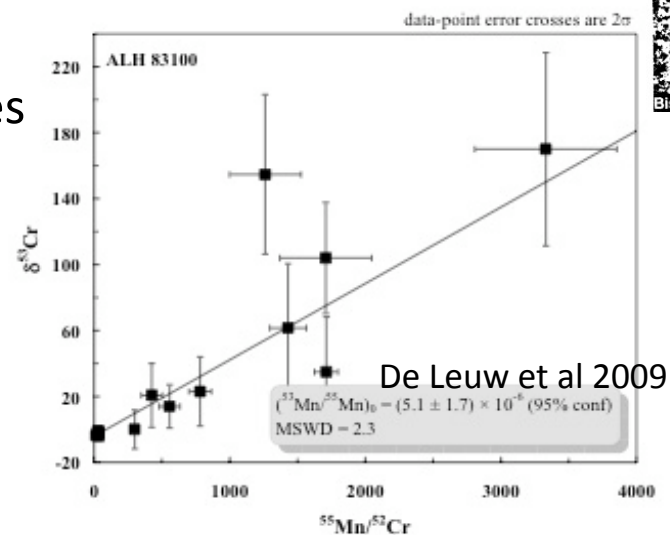


## Asteroidal Processes

- Much information derived from component characterisation
  - Multiple fragments - range of alteration effects
- Absolute & relative ages require specific phases
  - Known histories (usually simple)
  - Specific compositions - e.g.  $^{53}\text{Mn}$ -Cr dating – range of Mn contents with low Cr contents
- Mostly performed by SIMS
  - If ICPMS/TIMS – large samples



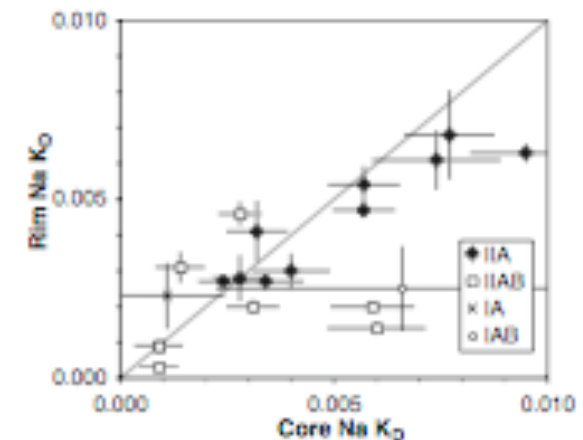
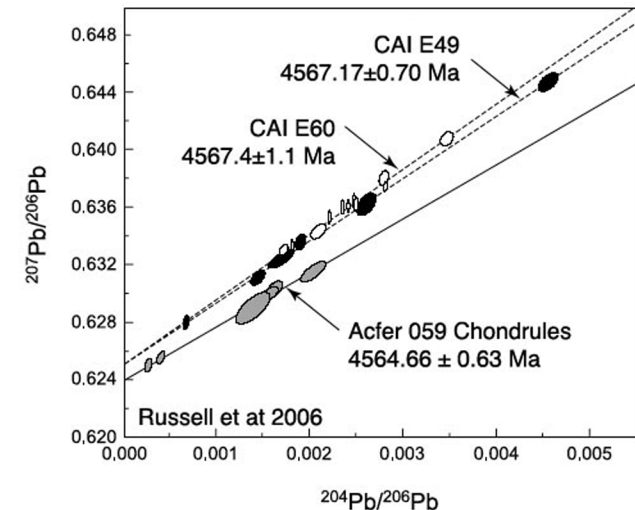
Grossman et al 2000





## Solar Nebula Processes

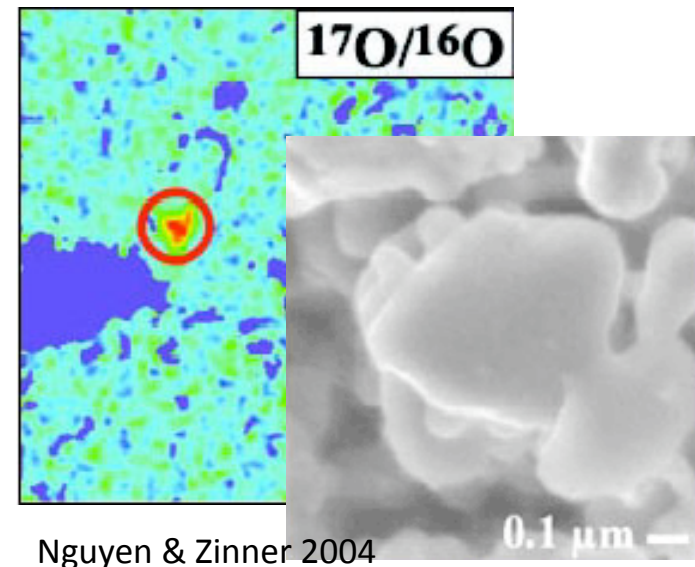
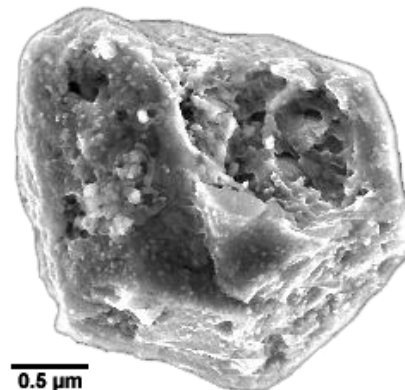
- Much information derived from component characterisation
  - Concentrate on those components least affected by asteroidal effects
- Detailed study of sub-components – chondrules, CAIs, AoAs, mineral frags, etc
  - Trace element distributions, isotopic variations – especially oxygen and short lived radionuclides
- Age dating - specific components & well understood histories
  - Which processes are we attempting to date
- Principle techniques – SEM, TEM, EMPA, SIMS, ICPMS, noble gas MS – mix of in situ and separated samples (10s mgs – of specific components)





## Pre-Solar Grains

- In situ analyses identification – SIMS
  - Followed by both in situ and extraction for characterisation – Raman, XANES, TEM, Auger
  - From polished sections prepared from characterisation
- Statistics benefit from preparation of grain concentrates
  - Acid dissolution
  - Requires large samples – from organic demineralisation
  - Gentle separation – grain mantles

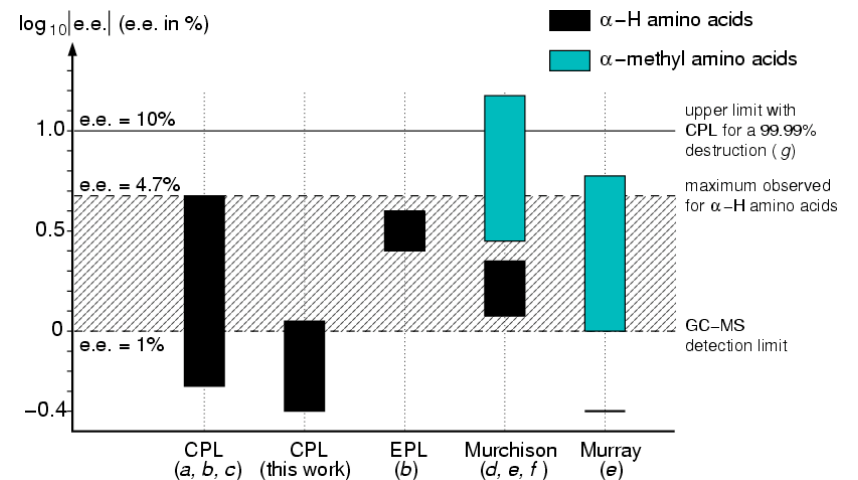
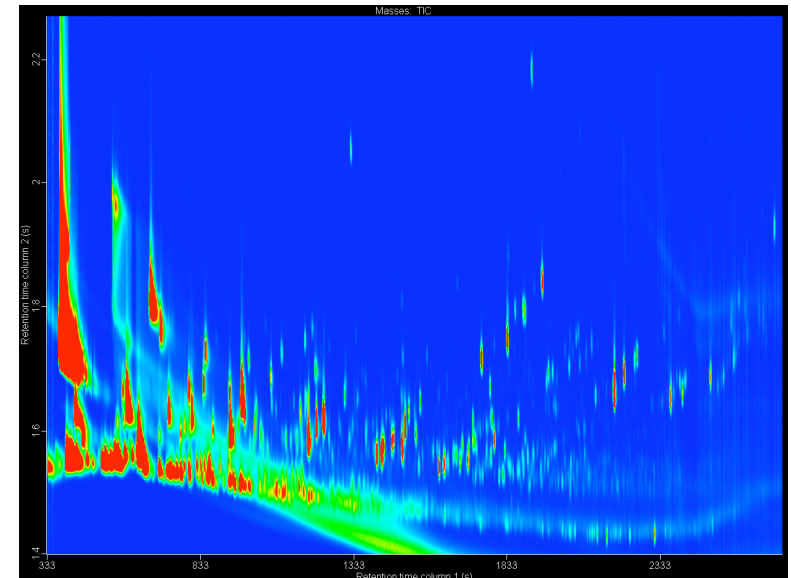






# Organic Compounds

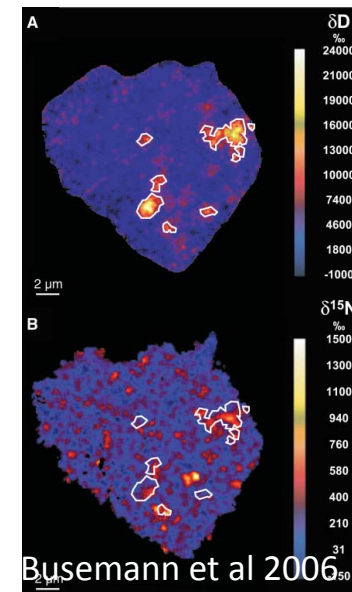
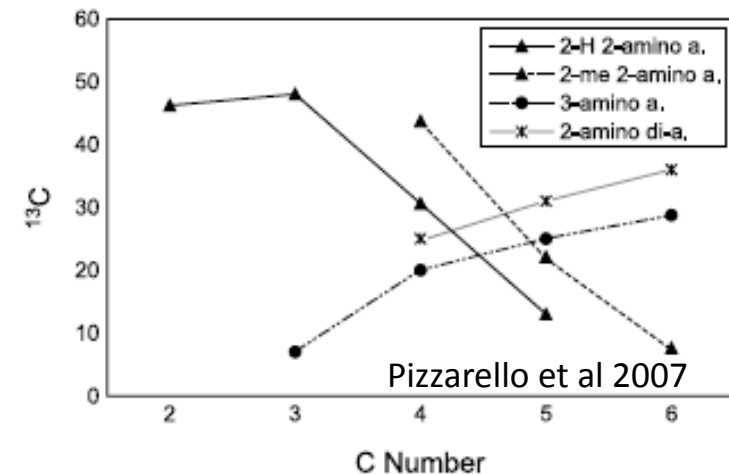
- Intimately related to asteroidal and nebula studies
  - Relationship to rocky matrix and info derived from matrix
- Inventory of free organic compounds
  - Extraction by various polar and non-polar solvents, pyrolysis
  - GC/GC-MS, LC/LC-MS – 10s mg
  - Amino acid chirality – 10s mg
  - Nucleobases low abundance – 10s to 100mg sample





## Organics – Isotopic Ratios

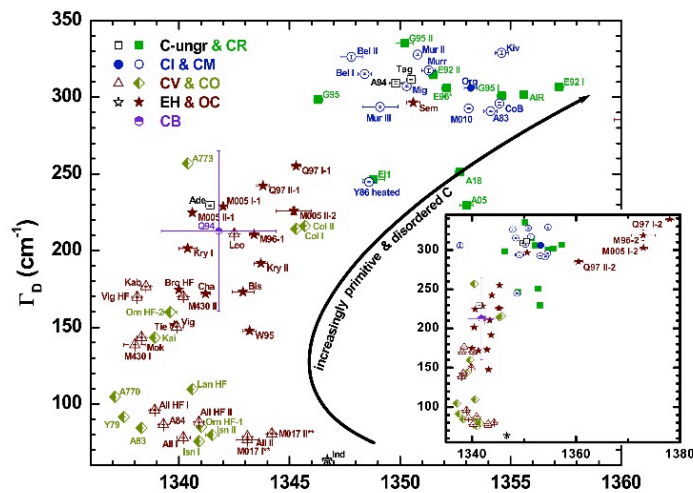
- Introduce a combustion/reduction reactor before MS
  - Isotope ratio MS - D/H,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$  of individual compounds
- Verification of extra-terrestrial origin
- Important in understanding formation processes
  - Distinctive fractionation patterns
  - Signatures of different environments – e.g. ISM
  - Identifies links between compound classes and mineralogy
- Requires 5 – 10g of C-rich carbonaceous chondrite
  - Separate sample for nucleobases and other organics



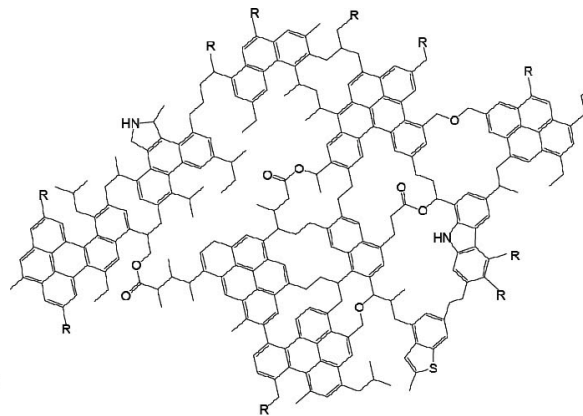


## Organics – Insoluble & *In Situ*

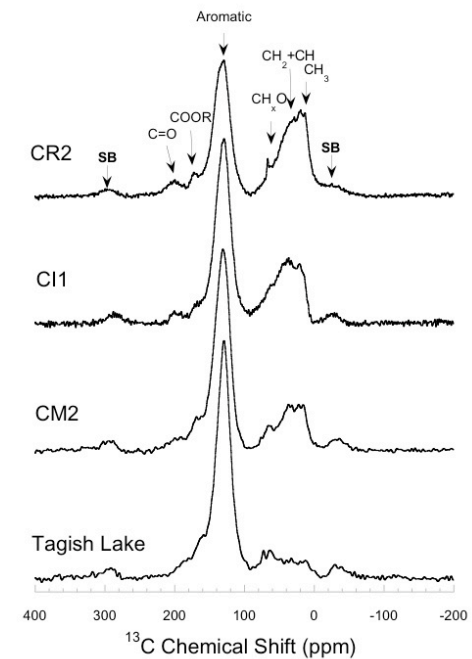
- Organic Macromolecule – very difficult to study
  - Complex, inter-linked structure of PAHs, heterocycles and aliphatics
- Mineral matrix readily removed (very destructively)
- Structure – NMR, Raman, FTIR, XANES, Pyr-GCMS
- Composition – GS-MS, NMR
- NMR requires grams of C-rich meteorite



Busemann et al 2007  $\omega_D$  (cm<sup>-1</sup>)



Laurent Remsaut



Cody & Alexander 2005



# Organics Requirements Summary

- What can be achieved if sample is like CM2 – i.e. few wt% C
- With a few grams of good quality sample, multiple analyses of:
  - All in situ techniques
  - All compound abundance techniques
  - Not structural info on macromolecule
  - Not detailed isotopic measurements

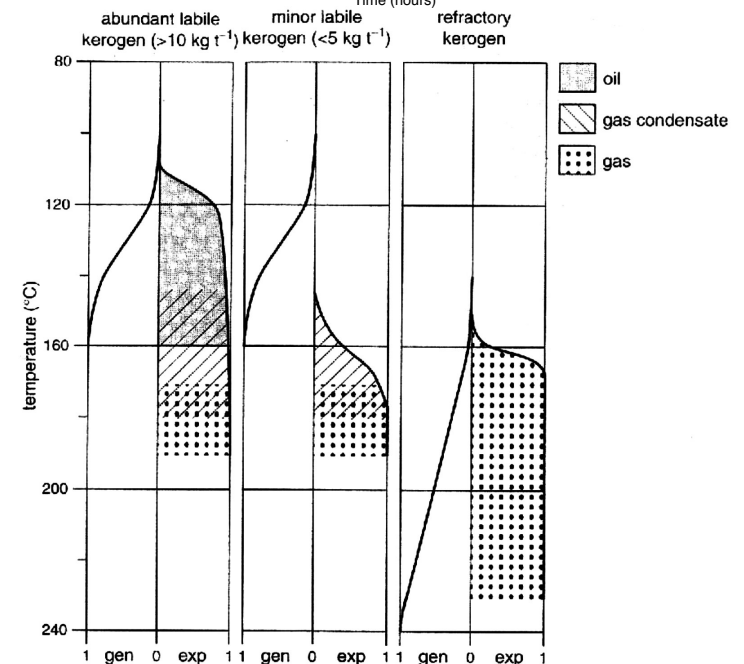
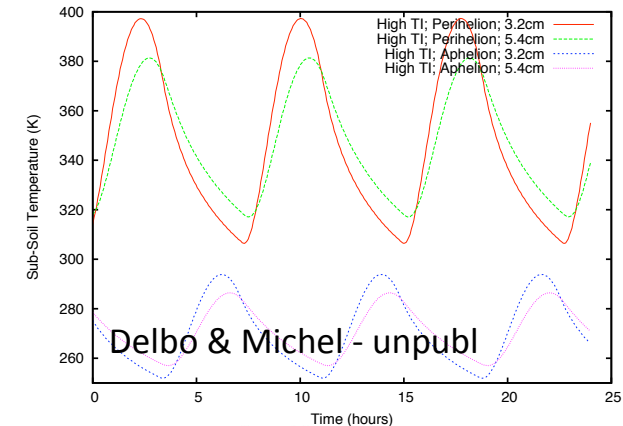
| Technique                  | * | Scientific Objectives achievable for returned mass (g) |   |    |    |     |
|----------------------------|---|--|---|----|----|-----|
|                            |   | 1  | 5 | 10 | 50 | 100 |
| <i>Fluorescence</i>        | N |  |   |    |    |     |
| <i>PAS</i>                 | P |  |   |    |    |     |
| <i>XANES</i>               | P |  |   |    |    |     |
| <i>L2MS</i>                | Y |  |   |    |    |     |
| <i>IR-VIS spectroscopy</i> | P |  |   |    |    |     |
| <i>TOF-SIMS</i>            | Y |  |   |    |    |     |
| <i>nSIMS</i>               | Y |  |   |    |    |     |
| <i>Step combustion-MS</i>  | Y |  |   |    |    |     |
| <i>μRaman</i>              | N |  |   |    |    |     |
| <i>TEM</i>                 | P |  |   |    |    |     |
| <i>LC-GC-MS</i>            | P |  |   |    |    |     |

| Technique   | * | Scientific Objectives achievable for returned mass (g) |   |    |    |     |
|---|---|--|---|----|----|-----|
|   |   | 1  | 5 | 10 | 50 | 100 |
| <i>Free solvent extractable Organics Abundance</i>        | P |  |   |    |    |     |
| <i>Free water extractable Organics Abundance</i>          | P |  |   |    |    |     |
| <i>Macromolecule component abundance</i>                  | P |  |   |    |    |     |
| <i>Whole-rock Hydro and Hydrous-Pyrolysis - abundance</i> | Y |  |   |    |    |     |
| <i>Nucleobase Abundance</i>                               | P |  |   |    |    |     |
| <i>NMR</i>  | P |  |   |    |    |     |
| <i>Whole-rock Hydro and Hydrous-Pyrolysis - isotopes</i>  | Y |  |   |    |    |     |
| <i>Nucleobase Isotopes</i>                                | P |  |   |    |    |     |
| <i>Free solvent extractable Organics Isotopic</i>         | P |  |   |    |    |     |
| <i>Free water extractable Organics Isotopic</i>           | P |  |   |    |    |     |
| <i>Macromolecule component isotopes</i>                   | P |  |   |    |    |     |



## ...Space Weathering

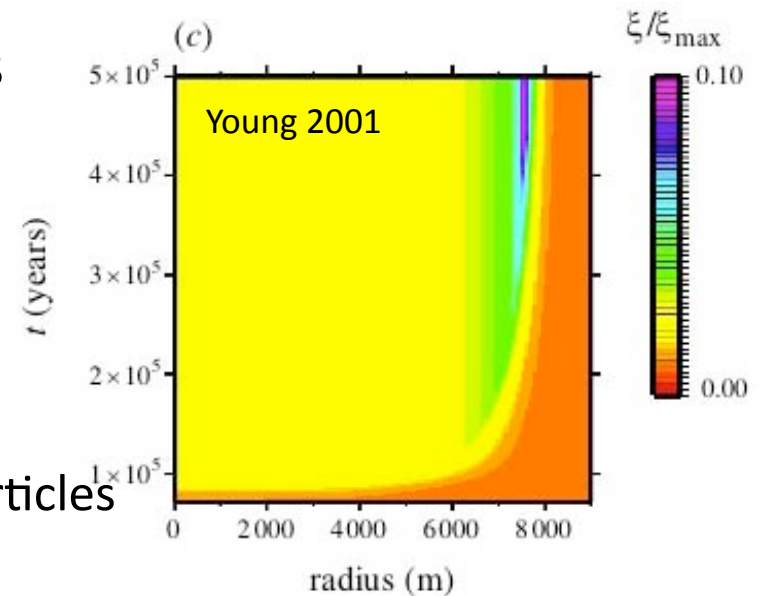
- Galactic/Solar cosmic ray, solar wind, uv irradiation, heating/impacts, etc
- Affects all aspects of sample - organics most susceptible
- Solar Wind and UV – only micron(s) depth penetration
- Many organic analyses low spatial resolution
  - Physically separate irradiated material from interior before analyses
- Heat modification of organics – depth (time) main defense
  - Few cms can have a marked effect





## Organic Analyses Requirement

- Integrate mineralogy etc with organics
  - Organic analyses from gram(s) of specific, characterised rock types
  - Range of rock types
- Physical separation of irradiated/non-irradiated material
  - Low surface:volume ratio of irradiated particles
- Protection from peak temperatures
  - Some sampling to shallow depth



### Dust rich sample

Mixed lithologies?  
High surface:vol

### Solid rock sample

Single lithology  
Carb Chondrite?

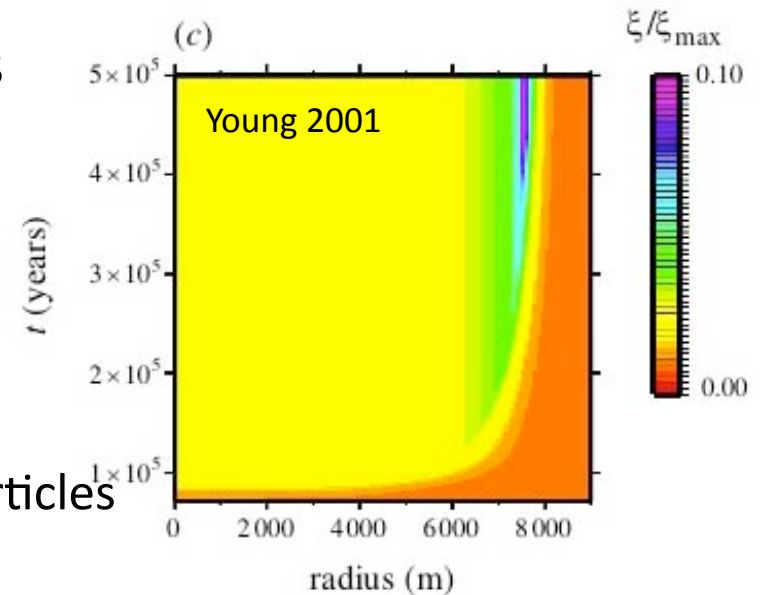
### Pebbles (cm sized)

Each single lithology?  
Range of lithologies  
Low surface:vol



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## Sample Requirements

- Bulk properties, composition and mineralogy – few 10s mgs
- Properties of components – 10s to 100s mg per component
  - Plus sufficient material for polished section(s) – gram amounts
- For each lithology in a regolith of different alteration:
- Organics – 100s mg for abundances & overall characterisation
- Organics – 5g plus for isotopic studies – for origin, formation