Coordinated In-Situ Analysis of Meteoritic Nanodiamonds

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Introduction

Meteoritic nanodiamonds (NDs)

- carbon nanograins (2–5 nm) trapped in carbonaceous meteorites thought to be presolar
- carry stellar nucleosynthetic anomalies and encode processes predating the Solar System.

Challenge

Traditional bulk analyses mask ND subpopulation variation, preventing origin(s) identification.

Objective

Differentiate **presolar stardust** vs. **solar system** ND formation in carbonaceous chondrites and returned asteroid samples

Methods

Sulfur -embed Matrix, Microtome → **Sample Prep** → 70-100 nm thin section

In-situ aberration corrected STEM/TEM → **Imaging** → EDXS (composition) EELS (bonding)

NanoSIMS → **Isotopic Imaging** → C,N Isotopes

Technical Approach

Locate ND clusters embedded in organic matter in carbonaceous chondrites and returned asteroid samples

Measure C and N isotopes of clusters to check for multiple formation histories

References

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Initial STEM-EDXS-EELS Results

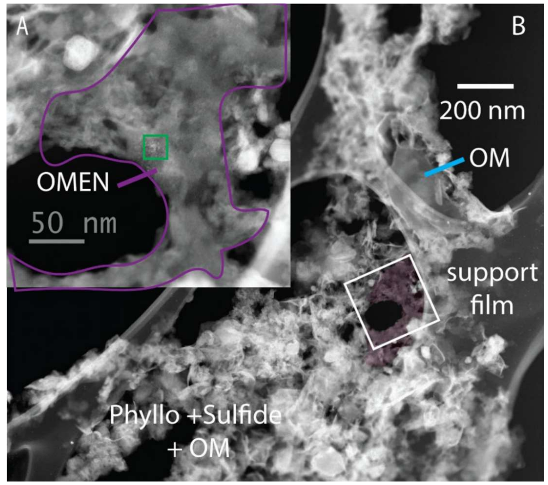


Figure 1 (left) STEM HAADF of microtomed Ryugu particle on lacey carbon grid.

(A) Organic matter (OM) with embedded nanodiamonds (OMEN) (magenta)

(B) Petrographic context OMEN in fine grained matrix (phyllosilicates/ sulfides/diamond-free OM). Elliptical void in OMEN suggests **NDs form as an <u>interstellar icy particle rind</u>.**

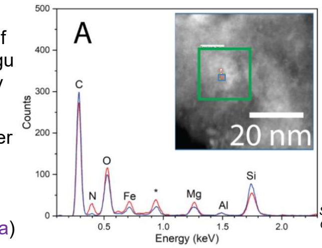
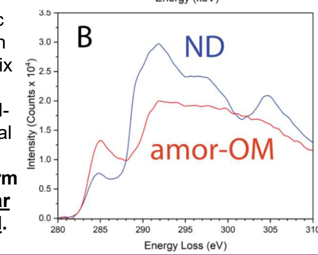


Figure 2
(A) Spectrum image ROI (inset) and Extracted EDXS spectra from Amorphous C is N-richer than ND (blue).

Cu peak = system artifact; Si/Al/Mg/Fe/O from heteroatoms in OM; residual from acid dissolution.



(B) Extracted EELS C K-edge From ND (sp^3) amor-OM (sp^2)

Potential Formation Mechanisms & Distinct Isotopic Fingerprints

Cold Formation Mechanisms

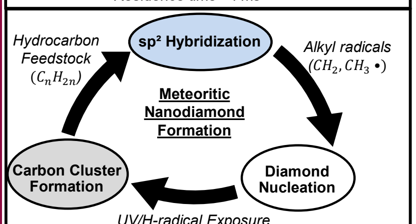
Radical Mediated Nucleation

Microplasma Alcohol Vapor Dissociation

$$(C_2H_5OH)_v \xrightarrow[k_1]{\text{plasma}} n(\text{C-based radicals})\cdot + OH + H_2$$

$$n\,(\text{C-based radicals})\bullet \xrightarrow[k_2]{\text{association}} H\text{-terminated } [C_nH_m]^*$$

Ethanol C-C Bonds are ideal
Atmospheric pressure microplasma
T ≈ 100 °C
Residence time ≈1 ms



UV Photolysis of Organic-Rich Ices

$G_0 > 30$

$$H_2O{:}CO{:}CH_4\,\text{ice} + h\nu(<200nm) \xrightarrow[k_1]{\text{UV}} [R]\,(CH_3, CH_2\bullet)$$

Organic ice mantles absorb FUV photons
(λ < 200 nm)
H_2O-rich ice + minor CH_4, CH_3OH, CO, NH_3
(1-5%)

Circumstellar Outflow (CTTS at 1 AU)
Early Solar System active accretion
Lyα Dominated (88%)

UV Flux	FUV Flux ($erg\ cm^{-2}\ s^{-1}$) (912-1700Å)	G_0
	~1.6 × 10^4	~10^7

Outer Nebula
cluster-mediated
CO–H_2 ice reactions

UV Flux	FUV Flux ($erg\ cm^{-2}\ s^{-1}$) (912-1700Å)	G_0
	0.05-5	~30-3000

Diffuse ISM & Cold Molecular Cloud
Photon-processed ice grains

UV Flux	FUV Flux ($erg\ cm^{-2}\ s^{-1}$) (912-1700Å)	G_0
	0.05-5	~30-3000

Inner Nebula
Hydrocarbon Catalysis on Fe-Ni grains under solar nebula conditions

UV Flux	FUV Flux ($erg\ cm^{-2}\ s^{-1}$) (912-1700Å)	G_0
	~1.6 × 10^4	~10^7

Isotopic Signature ⇌ Origin

$\delta^{13}C$		$\delta^{15}N$		Viable Environment
> Solar	~ Solar	> Solar	~ Solar	
✓			✓	C star outflow
	✓	✓		Diffuse ISM Cold Molecular Cloud
	✓	✓		Outer Nebula
	✓		✓	Inner Nebula

Hot Formation Mechanisms

HT/HP Processes

Vapor Condensation from Supernovae Ejecta

Precursor Flash Heating/Collisional Shock

$$C_{org} \xrightarrow[k_1]{\text{flash heating/shock}} C\,(v)$$

Carbon Vapor Supersaturation

$$C\,(v) \xrightarrow[k_2]{\text{supersaturation}} [C_n]^*$$

r-process enriched Carbon vapor
Extreme initial condition (IC)
(P > 10 GPa)
(T ≫ 1000 K)
Cooling ejecta under <u>low-pressure conditions (≤10^{-4} atm)</u>
<u>forms NDs to later enter presolar cloud</u>

Fischer-Tropsch Fe-Ni Catalysis

M = Fe-Ni catalytic site (metal grain surface)
Nebular conditions (~300-700K, 10^{-4} atm)

CO adsorption and activation

$$CO(g) + M \overset{k_1}{\rightarrow} M - C + M - O$$

H_2 activation

$$H_2(ads) + 2M \overset{k_H}{\rightarrow} 2M - H$$

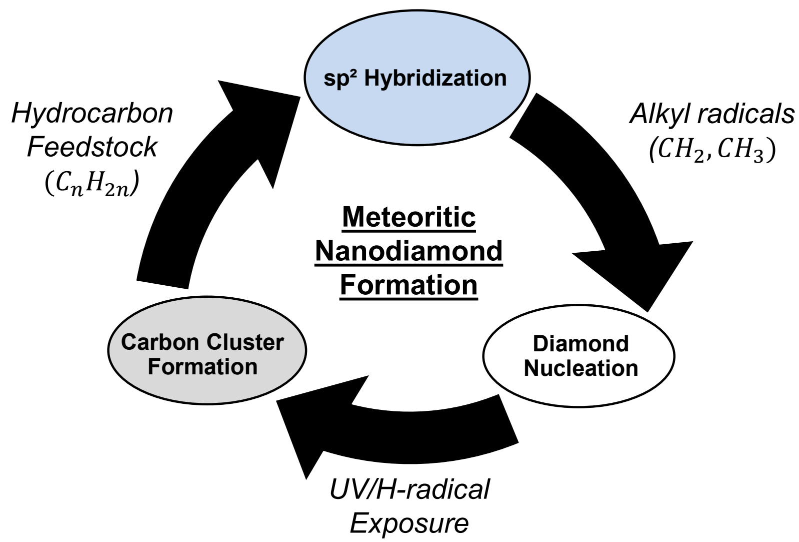
CH_2 initiation

$$M - C + 2M - H \overset{k_\alpha}{\rightarrow} M - CH_2 + M$$

Carbene insertion

$$M - CH_2 + CO(g) + M - H \overset{k_{ins}}{\rightarrow} M - C_2H_4 + M - O$$

Chain growth
repeat CH_2 initiation + Carbene insertion
build $M - C_nH_{2n}$


sp² Hybridization
Alkyl radicals
(CH_2, CH_3)
Meteoritic Nanodiamond Formation
Diamond Nucleation
UV/H-radical Exposure
Carbon Cluster Formation
Hydrocarbon Feedstock
(C_nH_{2n})