

## Particle Transport and Thermal Processing during FU Orionis Events in the Solar Nebula Particle Transport and Thermal Processing during FU Orionis Events in the Solar Nebula

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Solar-type young stars undergo ~100-year-long FU Orionis outbursts roughly every ~0.01 Myr during their early evolution. Such outbursts are thought to be caused by rapid mass accretion by the protostar during phases when the disk is marginally gravitationally unstable (MGU). We study here the trajectories of particles embedded in the solar nebula during a MGU phase of disk evolution.

These trajectories have profound cosmochemical consequences, ranging from large-scale outward transport of refractory grains, such as the calcium, aluminum-rich inclusions (CAIs) found in Comet Wild 2 by the Stardust Mission, to an explanation for a CAI found in Allende whose variations in oxygen isotopes imply repeated passages both inward and outward in the disk, to time scales (~10 yr) for sublimation of CAIs similar to those inferred for a Leoville CAI, as well as for the transport and mixing of ices throughout the nebula.

キーワード: CAIs, solar nebula, FU Orionis, thermal processing, WL rims, transport  
Keywords: CAIs, solar nebula, FU Orionis, thermal processing, WL rims, transport

## Nature, origins and thermal processing of carbonaceous material in chondritic meteorites Nature, origins and thermal processing of carbonaceous material in chondritic meteorites

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We have been studying the distribution of carbonaceous material in situ in carbonaceous chondrites using energy filtered transmission electron microscopy. Extensive studies of carbonaceous materials in carbonaceous chondrites have provided a wealth of information about the types of compounds that are present as well as their isotopic composition. We now know that a significant proportion of the organic material in these meteorites is present as an insoluble organic material that has some similarities to terrestrial kerogen. However, significant questions still remain as to the exact location of this material within chondritic meteorites are still unanswered. For example, although the organic material is known to be concentrated in the fine-grained matrix of chondritic meteorites, the associations of this material with the mineralogic constituents of matrix have, until recently been unknown. Using energy filtered TEM, we have studied the distribution of carbonaceous material in CM and CR carbonaceous chondrites.

## CALCIUM-ALUMINIUM INCLUSION IN THE KABA METEORITE AND ITS APPLICATION TO ASTROMINERALOGY

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CAI of the Kaba meteorite has a complex texture and consists of spinel, anorthite and augite (fassaite), where spinel grains (up to 10 micron in size) are surrounded by anorthite and augite grains. CAIs are observed and maximum 1.8-2.0 mm in size. The composition of anorthite is An<sub>95.6</sub>Ab<sub>4.4</sub>Or<sub>0</sub>. Augite has a composition of En<sub>45.5-55.1</sub>Wo<sub>44.0-53.9</sub>Fs<sub>0.6-0.9</sub>.

The age of Kaba as determined from Mn-Cr dating is thought to be between 4,562 and 4,563 Ma (Hua et al. 2005). It is instructive to attempt to place the formation and properties of Kaba in the context of protoplanetary disk evolution as observed around other stars. Any such comparison relies on the zero points of the astronomical and cosmochemical timescales, i.e. the time of the protostellar collapse and the time of the CAI formation. While these zero points are likely to be slightly shifted, detailed comparisons of protoplanetary disk evolution and events in the proto-solar nebula suggest that they could not differ by more than 1 Myr, if the proto-solar nebula was a typical disk (Pascucci & Tachibana 2010). Consistent with the above description we assume that CAIs have formed at the time of or very shortly after the protostellar collapse.

In contrast, the younger disks in Cha I and Taurus frequently display disks with flaring geometry (disk opening angle increasing with radius, see e.g., Szűcs et al. 2010, Ciesla and Dullemond 2010). These disks also commonly display sharp and prominent crystalline silicate peaks, revealing the presence of sub-micron-sized forsterite and enstatite grains (e.g. Apai et al. 2005) with a few disks showing amorphous silicate emission features. The observed evolution of the small, initially amorphous dust grains into larger, crystalline grains is poorly understood, but it is often thought that grain-grain collisions and destructive planetesimal collisions will replenish and gradually replace the dust population. In this context, Kaba grains could provide an insight into the dust population of a disk halfway between a young protoplanetary disk and a debris disk: if so, a substantial amount of the building blocks of Kaba may have been recycled material from previous generation of small bodies. Furthermore, a systematic Micro-Raman spectral study (as future work) of an interaction between the organic compounds and CAIs in Kaba meteorite can provide us better understanding of the evolution of organic matter in the early Solar System.

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Pascucci I. and Tachibana Sh. 2010: The Clearing of Protoplanetary Disks and of the Protosolar Nebula. In Protoplanetary Dust: Astrophysical and Cosmochemical Perspectives, Eds.: Apai D. and Lauretta D.S., Cambridge University Press, p. 263-298

Sz?cs L., Apai D., Pascucci I. and Dullemond C.P. 2010: Stellar-mass-dependent Disk Structure in Coeval Planet-forming Disks. The Astrophysical Journal 720: 1668-1673.

キーワード: meteorite, Early Solar System, CAI, astromineralogy

Keywords: meteorite, Early Solar System, CAI, astromineralogy

## 近地球型C型小惑星からのサンプルリターン Sample return from near-Earth C-type asteroid

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Several sample return missions from primitive undifferentiated asteroids, such as Hayabusa-2, Osiris-REx, and MarcoPolo-R, have been planned to obtain samples without any terrestrial contamination but with geological information. The target asteroids for the future missions are near-Earth C-type or related asteroids, from which rocks potentially keeping the interactions between minerals, ice and organic matter in the protosolar disk intact are expected to be sampled. In this talk, primary scientific goals of sample return missions from near-Earth primitive asteroids will be discussed.

キーワード: サンプルリターン, 近地球型C型小惑星  
Keywords: sample return, near-Earth C-type asteroid

## 赤外線天文衛星「あかり」を用いた小惑星 21 Lutetia の 3- $\mu$ m 帯の分光観測 Spectroscopic observations of asteroid 21 Lutetia over the 3-micrometer region by AKARI satellite

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アルベドが高く (0.15-0.25) 全体的に右上がりなスペクトルをもつ小惑星は、M 型小惑星と呼ばれる。M 型小惑星は鉄やニッケルのような金属で構成されており、分化天体のコアが分裂した破片であると考えられている。地上望遠鏡による分光観測によって、2つの M 型小惑星 (55 Pandora と 92 Undina) のスペクトルの 3- $\mu$  m 帯に吸収が存在することが分かった。このことは含水鉱物の存在を意味する。含水鉱物が存在することは、M 型小惑星が分化天体の分裂したコアであるという解釈と反する。しかし小惑星が加熱されたあとに、水が高温鉱物を変成するくらい十分長く存在していたとすると、理論上は含水鉱物が分化天体上に存在することができる可能性がある。このように含水鉱物が存在すれば、M 型小惑星の形成と熱史に制約を与えることができる。さらに 3- $\mu$  m のスペクトルの形状や吸収帯の深さから、M 型小惑星由来の隕石や M 型小惑星を構成する鉱物を推定することができる。

代表的な M 型小惑星として 21 Lutetia が挙げられる。21 Lutetia は 3- $\mu$  m 帯に吸収有りという先行研究がある一方で、吸収無しという観測結果も報告されている。但し先行研究では、3- $\mu$  m 帯を取得できておらず、その周辺の反射率の傾きでのみ吸収の有無を判断していた。そのため 21 Lutetia の 3  $\mu$  m 帯のスペクトルを観測する必要があるが、2.6-2.8  $\mu$  m の光は地球大気の透過率がほぼ 0% であり、この波長域を地上から観測することはできない。そこで地球大気の影響を受けない宇宙空間においてあかり衛星を用いて 21 Lutetia の観測を行なった。

あかり衛星は 2006 年 2 月 21 日 (UT) に打ち上げられた日本初の赤外線天文衛星である。波長解像度 0.097  $\mu$  m/pix で波長域 2.5-5.0  $\mu$  m のグリズム分光観測を行なった。21 Lutetia は 2008 年 9 月 2 日 (UT) に観測した。解析は IRC Spectroscopy Toolkit for Phase 3 data (version 20090211) と the new spectral responsivity (version 20091113) を用いた。

2つの観測結果 (ID 1520157 と ID 1520158) とその平均スペクトルは 2.6-3.6  $\mu$  m で平坦であった。

地上望遠鏡で観測が難しい 2.6-2.8  $\mu$  m において、あかり衛星による観測では他の波長域と変わらない精度でスペクトルを取得できた。本研究と先行研究の観測結果を以下で比較する。ID 1520157 は [1] の Fig. 1. の 2007 年と 2008 年のスペクトルは 2.85-3.5  $\mu$  m において 10% 以下の範囲で一致している。2.85-2.9  $\mu$  m における反射率の減少と約 3.3  $\mu$  m 以上の緩やかな傾斜が両者に現れている。ID 1520158 は [1] の Fig. 1. の 2003 年のスペクトルと 2.85-3.5  $\mu$  m において 5% 以下の範囲で一致している。約 3.2  $\mu$  m と 3.3  $\mu$  m に存在する浅い吸収と約 3.5  $\mu$  m に存在する凸状の形状も同様の傾向を示している。[2] と比較すると、2.85-3.5  $\mu$  m の範囲において、ID 1520157 とは 5% 以内、ID 1520158 とは 10% 程度で一致する。

3- $\mu$  m 帯の吸収の有無の判断方法は、以下の通りである。2.55-2.60  $\mu$  m における観測誤差を含む反射率の最小値が、2.7-2.8  $\mu$  m における観測誤差を含む反射率の最大値より大きければ、吸収があると判断する。その結果、21 Lutetia 吸収は存在しないか、存在してもとも浅いということが分かった。今後は 21 Lutetia 以外の M 型小惑星のスペクトルの 3  $\mu$  m を観測することにより、M 型小惑星の中で含水鉱物が存在する小惑星がないかを探す。もしあれば、鉱物や隕石のスペクトルと fitting を行なう。

[1] Rivkin A. S. et al. (2011) *Icarus*, 216, 62-68. [2] Vernazza P. et al. (2011) *Icarus*, 216, 650-659.

キーワード: 赤外線天文衛星「あかり」、小惑星, 21 ルテティア, 含水鉱物, 熱史

Keywords: AKARI, asteroid, 21 Lutetia, hydrated mineral, thermal history

## 星間塵表面での水分子とその重水素置換体生成 Formation of H<sub>2</sub>O and its isotopologues on interstellar grains

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Solid H<sub>2</sub>O is the most abundant component in icy grain mantles in molecular clouds. Since the observed abundance of solid H<sub>2</sub>O in molecular clouds cannot be explained only by gas-phase synthesis, it has been considered that solid H<sub>2</sub>O is produced on the surface of interstellar grains. Tielens and Hagen (1982) proposed that solid H<sub>2</sub>O is produced by hydrogenation of O, O<sub>2</sub>, or O<sub>3</sub>. Since then, the formation of H<sub>2</sub>O through those reactions has been experimentally demonstrated to occur by several research groups (e.g. Miyauchi et al. 2008; Ioppolo et al. 2008).

In addition to these hydrogenation processes, reactions of hydroxyl radicals (OH) with H<sub>2</sub> have been accepted as an important route to H<sub>2</sub>O formation in dense molecular clouds where the UV field is very weak. Under those conditions, it is unlikely that the reaction thermally occurs due to the significant barrier of about 2000 K; the reaction should proceed through quantum tunneling if it really occurs in dense clouds. However, it has not been experimentally demonstrated so far.

In this presentation, we will show experimental results on the formation of H<sub>2</sub>O and its isotopologues (HDO and D<sub>2</sub>O) by the reaction of OH/OD with H<sub>2</sub>/HD/D<sub>2</sub> at 10 K, and discuss its astrophysical implications.

キーワード: 水, 重水素濃縮, 分子雲, 表面反応, トンネル反応, 同位体効果

Keywords: water, deuterium enrichment, molecular cloud, surface reaction, tunneling reaction, isotope effect



## D-H exchange kinetics between organic solids and water: Implications for D/H content in chondritic organic matter

## D-H exchange kinetics between organic solids and water: Implications for D/H content in chondritic organic matter

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The high deuterium enrichment in insoluble organic matter (IOM) in chondrites has largely been attributed to small molecule chemistry prior to IOM, in the results of ion-molecule interactions at low temperature ( $<200$  K) interstellar medium (ISM) [1]. A possible synthesis scenario of IOM formation has been proposed using highly deuterated interstellar formaldehyde [2]. However, even among the highest D enriched IOM has significantly lower (by a factor of  $\sim 2$ ) D content compared with ISM molecules [3]. While water in the solar system is much depleted in D [4]. Thus, D-H exchange between D enriched IOM precursor and D depleted water could have occurred during and/or after the formation of IOM. Here we report D-H exchange kinetics obtained using laboratory synthesized organic polymers, in order to evaluate the D-H exchange between D enriched organic polymers and D depleted water.

Our recent study revealed that insoluble organic matter (IOM) in primitive chondritic meteorites is predominantly derived from the polymerization of interstellar formaldehyde with incorporation of ammonia, evidenced by molecular spectroscopic characters [2,5]. In addition, montmorillonite (clay mineral) was shown to enhance the yield of the formaldehyde polymer. We used laboratory synthesized D enriched formaldehyde polymer (D-FormPoly) as a starting material of D-H exchange experiments. The polymers were incubated in H<sub>2</sub>O at 150°C, 200°C and 250°C for 1 hour up to 504 hours (21 days) in sealed glass tubes. Fourier transform infrared (FTIR) spectra of D-FormPoly were collected after the incubations. We use a peak area ratio of an aliphatic C-H stretching band at 2985-2835 cm<sup>-1</sup> and an aliphatic C-D stretching band at 2250-2055 cm<sup>-1</sup> as an indicator of D-H exchange.

The D-H exchange rates were faster in the higher incubation temperatures. Several kinetic rate laws were considered for these D-H exchange profiles, e.g., *n*-order reaction and diffusion. Three-dimensional diffusion was found to be the best fit among the rate laws tested. The apparent reaction rate constants were obtained by the fitting curves with a combination of three-dimensional diffusion equations [6]. Then the apparent activation energy and the frequency factor are obtained by the apparent rate constants and the temperature with the Arrhenius equation.

Using obtained kinetic expressions, D-H exchange profiles can be estimated for a certain time and temperature, based on the assumption that the kinetic rate law is invariance. Compared with aliphatic C-H loss profiles which is obtained by Murchison IOM [7], D-H exchange occurs faster than aliphatic loss in lower temperature range ( $<200^\circ\text{C}$ ). This result suggests that D in highly D enriched IOM precursor could exchange with H in D depleted water without significant molecular structure change in low temperature aqueous alteration process.

The diffusion controlled D-H exchange is consistent with the fact that organic nano-globules have higher D/H values compared with fluffy IOM [8]. Because the D-H exchange rate depends on the grain size, therefore final D/H values depends on the grain size.

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**References:** [1] Robert F. and Epstein S. (1982) GCA, 46, 81-95. [2] Cody G. D. et al. (2011) PNAS, 108, 19171-19176. [3] Alexander C. M. O' D. et al. (2010) GCA, 74, 4417-4437. [4] Hartogh P. et al. (2011) Nature, 478, 218-220. [5] Kebukawa Y. et al. (2010) Meteoritics & Planet. Sci., 45, A103. [6] Crank J. (1970) In Mathematics of Diffusion. [7] Kebukawa Y. et al. (2010) Meteoritics & Planet. Sci., 45, 99-113. [8] Nakamura-Messenger K. et al. (2006) Science, 314, 1439-1442.

キーワード: Insoluble organic matter, Chondrite, Isotopic compositions, Kinetics, FTIR

Keywords: Insoluble organic matter, Chondrite, Isotopic compositions, Kinetics, FTIR



## 超炭素質南極微隕石から見つかった窒素に富む有機物 Finding of Nitrogen-rich Organic Material in Antarctic Ultracarbonaceous Micrometeorite

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### Introduction:

Ultracarbonaceous micrometeorites (UCMMs), first discovered by Nakamura et al. (2005) [1], are unique extraterrestrial materials that represent large sizes of high carbon contents. The mineralogical and isotopic investigations of UCMMs by [2] have revealed the association of extreme D-rich organic matter with both crystalline and amorphous silicates, which appears to be compatible to cometary origin. However, there have been only two UCMMs reported so far, and little has been known about the nature of UCMMs. In this study, for an UCMM, which was found in ~200 MMs collected in 250 kg of the surface snow near the Dome Fuji Station, Antarctica, we have carried out the systematic studies applying isotope microscopy, focused ion beam (FIB) extraction, scanning transmission X-ray microscopy (STXM) and transmission electron microscopy (TEM) observation to study the origin and formation of UCMMs.

### Experimental:

A polished thick section of a UCMM was used in this study. Isotope imaging of the UCMM was performed by a Hokudai isotope microscope system (Cameca ims-1270 SIMS with SCAPS). A Cs<sup>+</sup> primary beam in an aperture illumination mode was used to achieve uniform secondary ion emission from a sample area. The normal incident electron gun was used to compensate for sample charging. A tungsten strap was deposited on the surface of the UCMM, and an FIB section with ~100 nm thickness was extracted from the UCMM by a JIB-4501 FIB-SEM microscope at Ibaraki Univ. C-, N-, and O- X-ray absorption near edge structure (XANES) spectra of the FIB section were acquired using STXM at the beamline 5.3.2.2., Advanced Light Source, Lawrence Berkeley National Laboratory.

### Results and discussion:

The <sup>12</sup>C/<sup>14</sup>N and <sup>32</sup>S distributions in carbonaceous matters from the UCMM show that the carbonaceous matter has the heterogeneously-distributed N- and S-rich signatures relative to the surrounding epoxy. The isotope-ratio images for hydrogen, carbon and nitrogen of the FIB section show that there is no significant difference in isotopic compositions of the UCMM from those of epoxy within analytical uncertainties ( $\delta D = \sim +100$  per mil with a error of plus or minus 300 per mil,  $\delta^{13}C = \sim 0$  per mil with a error of plus or minus 70 per mil,  $\delta^{15}N = \sim +100$  per mil with a error of plus or minus 110 per mil).

A STXM carbon map shows that organic carbon is distributed all over the FIB section. Using a nitrogen map, organic N-rich and poor regions are identified, respectively. N-XANES spectra of N-rich regions exhibit intense peaks of imine, nitrile, and amide, while that of N-poor region shows a less characteristic spectrum. Aromatic C=C are likely assigned to pyridine in the N-rich regions, while that in the N-poor region is similar to those of typical chondritic and/or IDP organics [3].

The N-rich regions within a large range of the UCMM with a sufficient S/N has not been generally observed in chondritic organic matter and IDPs. It is noted that the N-XANES spectral patterns of the N-rich regions are very similar to those observed from the three samples of Comet 81P/Wild 2 dust particles, one of which was an organic globule [4, 5]. Nitrogen isotopic composition of the Comet Wild 2 organic globule is indistinguishable from terrestrial values [4], which is consistent to that in this study. In addition, that the N-rich and N-poor regions co-exist with a sharp boundary within the particle is intriguing. This may

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indicate that there exists more than one precursor for extraterrestrial organic matter. Further studies on the possible relationships of the UCMM with IDPs and meteorites from the comprehensive perspectives of mineralogy, isotope, and organic chemistry will be expected.

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## Hydrogen isotopic composition of the water in CR chondrites Hydrogen isotopic composition of the water in CR chondrites

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Many chondrites experienced aqueous alteration, as revealed by the presence of phyllosilicates that are often associated with carbonates, magnetite, sulfides, and sulfates. The timing and duration of the alteration has been constrained by Mn-Cr dating of carbonates; physical constraints on the alteration (e.g. temperature) have been assessed through O isotopes of individual components [e.g., 1]. These data suggest that the alteration of chondrites took place over extended periods of time, and probably occurred almost entirely in asteroidal rather than nebular settings [e.g., 2]. However, our understanding of the conditions of alteration remains imperfect. For example, the origin, composition, and evolution of the fluids during alteration remain poorly constrained. The modification induced by the fluids on the pristine characteristics of the original constituents of the chondrites is only partially understood. In addition to allowing a better understanding of asteroidal alteration, the isotopic composition of asteroidal water is a key parameter to better understand the asteroid-comet continuum and is an important input in nebular models [e.g., 3].

Aqueously altered chondrites are composed of two main hydrogen (H) bearing phases: organics and hydrated minerals. Phyllosilicates and silicates in some aqueously meteorites are enriched in deuterium (D) relative to SMOW [e.g., 4,5], but the enrichments are smaller than in the respective organics [6]. An interstellar origin was attributed to the asteroidal water based on its D enrichment [4]. However, different hypothesis must be tested. Were the D enrichments in water inherited from the molecular cloud or nebula, or do they represent a later signature produced through some secondary reprocessing?

CR chondrites are considered to be the most primitive chondrites in our collections. The thermal and aqueous alteration experienced by QUE 99177, MET 00426, EET 92042, GRA 95229, Renazzo and Al Rais CR chondrites was assessed through multi-technique characterization (Raman, IR, EPMA, SIMS) of the carbonaceous matter and hydrated mineral phases in them. Each of the chondrites escaped long duration thermal metamorphism and experienced some fluid circulation [7, 8]. In particular, the extent of aqueous alteration experienced by QUE 99177 and MET 00426 may have been previously underestimated. The H isotopic compositions of the altering fluids were measured in situ, by SIMS, in fine-grained phyllosilicates and individual coarse-grained hydrated silicates. The main observations are that (i) the water is systematically enriched in D in each CR chondrite (up to  $dD_{water} = 1980$ permil); (ii) the isotopic composition of the water is characterized by highly variable D-enrichment at the micrometer scale; (iii) there is no clear trend observed in the isotopic composition of the water (maximum D-enrichment, range of variation) along the aqueous alteration sequence in the studied CR chondrites.

The high variability of the isotopic composition of the water/OH in CR chondrites is most easily reconciled with a secondary origin of the D-enrichments than with the presence of preserved pristine D-rich ices. Chondrites and comets may have sampled different water reservoirs. The water present in the CR chondrites probably formed in the inner Solar System [7, 8].

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## Where is all the CO in Protostellar Systems? Where is all the CO in Protostellar Systems?

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The material falling into protostellar systems is a mixture of gas plus organic coated silicates and carbonaceous dust grains. CO is the most abundant molecular species after H<sub>2</sub> and its place in protostellar nebulae has been monitored for many years. As carbon coated grains enter the high temperature regions of the inner nebula or encounter high temperature shocks, copious quantities of CO should be generated as silicates are vaporized or annealed. Similarly carbonaceous grains in the oxygen rich environment of the hot inner nebula, in lightning discharges or in nebular shocks should generate CO. Finally, carbonaceous grains incorporated into growing planetesimals should continuously emit CO, especially as radioactive heating begins to melt their interiors. If the mass of carbonaceous materials is of the same order of magnitude as the oxygen rich dust a significant increase in the concentration of CO should be observed. Where is this excess CO?

Considerable work has been done on the potential for Fischer-Tropsch type reactions to occur on grain surfaces in protostellar nebulae, starting with the work of Anders and colleagues between 1967 - 1980 (e.g. Hayatsu and Anders, 1980) and proceeding through more recent work by Llorca and Cassanova (2000) or Hill and Nuth (2003) and Nuth et al., (2008). It appears that such processes are efficient enough to remove the excess CO that should be generated during the formation of planetary systems. This implies the existence of a large-scale carbon cycle that could be converting both carbonaceous grain coatings as well as more graphitic solid grains into organic materials, thus seeding many newly formed planetary systems with the seeds of life.

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