National Aeronautics and Space Administration

NASA Astrobiology Institute 2016 Annual Science Report

Team Report:

Origin and Evolution of Organics and Water in Planetary Systems,

NASA Goddard Space Flight Center

Origin and Evolution of Organics and Water in Planetary Systems

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NASA Goddard Space Flight Center

Principal Investigator:
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Team Overview

The Goddard Team targets the Origin and Evolution of Organics and Water in Planetary Systems, in short – *Why is Earth Wet and Alive*? We address this central question through an integrated program of (a) pan-spectral astronomical observations of comets, circumstellar disks, and exoplanet environments, (b) models of chemical evolution and dynamical transport in the early Solar System, (c) laboratory studies of extraterrestrial samples, and (d) realistic laboratory and numerical simulations of inaccessible cosmic environments.

Synergistic integration of these areas is essential for testing whether delivery of life's building blocks – exogenous water and prebiotic organics – enabled the emergence and development of the biosphere. As humankind plans searches for life elsewhere in the Solar System, our Team develops (e) instrumental protocols to search for life's fundamental molecules – the informational polymers without which "life as we know it" would not exist.

Our research encompasses five themes:

- From Comets and Asteroids to Planets: Organics as a Key Window into Emergent Earth
- Organic Compounds in Authentic Extraterrestrial Materials: The Ultimate Rosetta Stones
- Laboratory Simulations of Formative Processes in Cosmic Ice and Dust Analogues
- From Molecular Cores to the Protoplanetary Disk: Our Interstellar Organic Heritage
- Analytical Protocols for Detection and Diagnosis of Life's Molecular Compounds

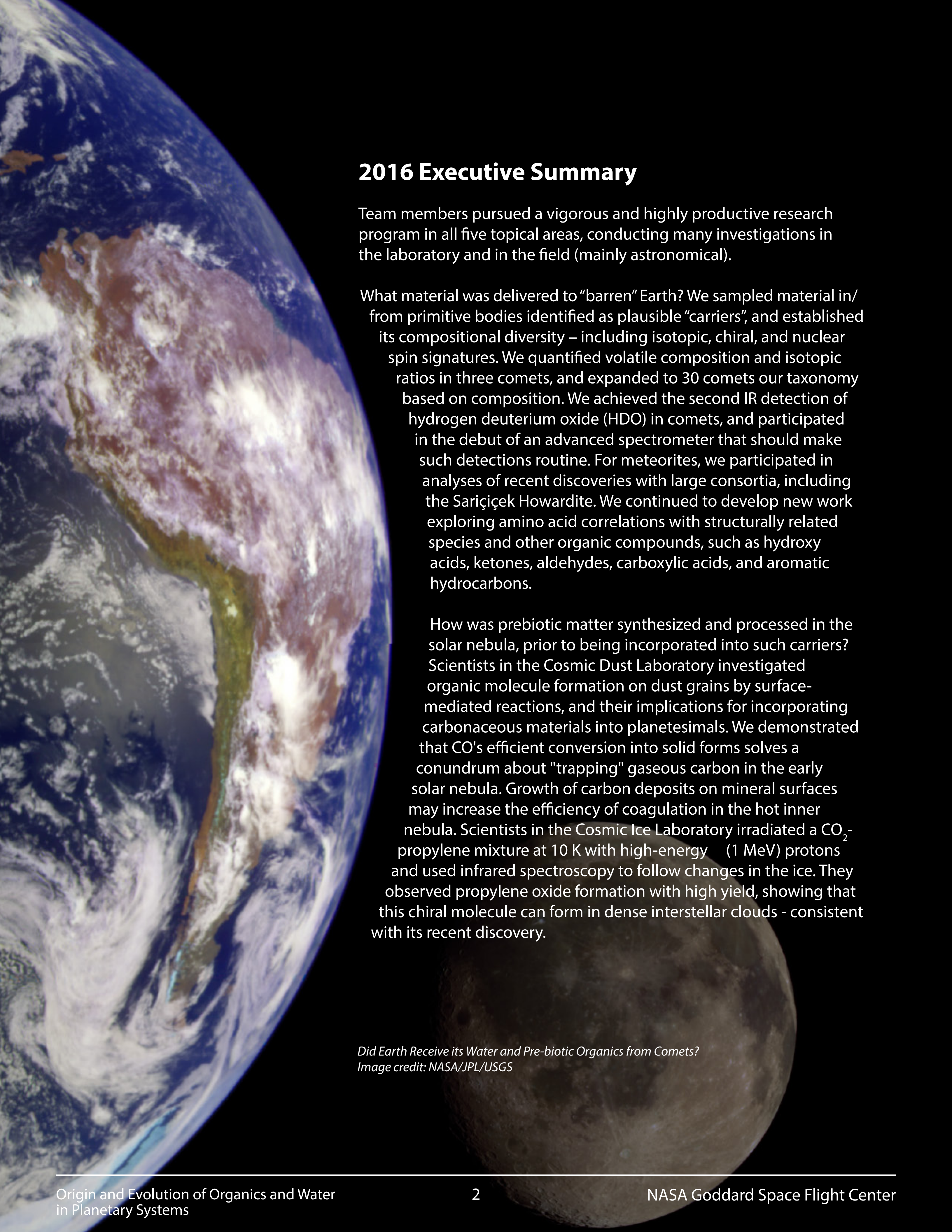
Team Website: https://astrobiology.gsfc.nasa.gov

2016 Executive Summary

Team members pursued a vigorous and highly productive research program in all five topical areas, conducting many investigations in the laboratory and in the field (mainly astronomical).

What material was delivered to "barren" Earth? We sampled material in/from primitive bodies identified as plausible "carriers", and established its compositional diversity – including isotopic, chiral, and nuclear spin signatures. We quantified volatile composition and isotopic ratios in three comets, and expanded to 30 comets our taxonomy based on composition. We achieved the second IR detection of hydrogen deuterium oxide (HDO) in comets, and participated in the debut of an advanced spectrometer that should make such detections routine. For meteorites, we participated in analyses of recent discoveries with large consortia, including the Sariçiçek Howardite. We continued to develop new work exploring amino acid correlations with structurally related species and other organic compounds, such as hydroxy acids, ketones, aldehydes, carboxylic acids, and aromatic hydrocarbons.

How was prebiotic matter synthesized and processed in the solar nebula, prior to being incorporated into such carriers? Scientists in the Cosmic Dust Laboratory investigated organic molecule formation on dust grains by surface-mediated reactions, and their implications for incorporating carbonaceous materials into planetesimals. We demonstrated that CO's efficient conversion into solid forms solves a conundrum about "trapping" gaseous carbon in the early solar nebula. Growth of carbon deposits on mineral surfaces may increase the efficiency of coagulation in the hot inner nebula. Scientists in the Cosmic Ice Laboratory irradiated a CO_2-propylene mixture at 10 K with high-energy (1 MeV) protons and used infrared spectroscopy to follow changes in the ice. They observed propylene oxide formation with high yield, showing that this chiral molecule can form in dense interstellar clouds - consistent with its recent discovery.



Did Earth Receive its Water and Pre-biotic Organics from Comets?
Image credit: NASA/JPL/USGS

How was prebiotic matter synthesized and processed in the interstellar medium prior to being carried into the solar nebula? Geoffrey Blake (CalTech) led the discovery of the first chiral molecule in space: propylene oxide (CH_3CHCH_2O), opening the possibility that the chirality of interstellar molecules could be measured in the future, for comparison with meteorites and biology. Blake and colleagues imaged rings of molecular emission in the DM Tau disk associated with the CCH radical and the cyclic molecule cyclopropenylidene (c-C_3H_2) (Bergin et al. 2016). This work suggests that a rich hydrocarbon chemistry, driven by ultraviolet photons, can occur in outer layers of such disks. Isotopic fractionation ratios are a powerful tool for determining the origin of Solar System organic materials; Goddard Center for Astrobiology (GCA) scientists described nitrogen $^{14}N/^{15}N$ fractionation chemistry in molecular clouds and protostellar disks, and discussed the connection with corresponding ratios measured in primitive meteorites and comets.

Can we define new instrument protocols to extend our knowledge of the complexity of organic compounds in mission targets relevant to astrobiology? Under the NASA Cooperative Agreement Notice 3, we developed protocols for amino acid detection through derivitization; they are now awaiting use on the Curiosity rover on Mars. In 2016, GCA scientists pursued the development of and protocol definition for an Orbitrap™-based testbed mass spectrometer that shows promise for future planetary missions. We continue to explore the potential application of novel nanopore-based detection and sequencing of informational biopolymers for future missions to Mars and ocean worlds such as Europa or Enceladus.

The Rosetta Stone, British Museum. Credit: Bettmann/CORBIS

Team Members

Jose Aponte
Ricardo Arevalo, Jr.
Geoffrey Blake
Boncho Bonev
William Brinckerhoff
Steven Charnley
Martin Cordiner
Michael DiSanti
Jason Dworkin
Jamie Elsila
Sara Faggi
Perry Gerakines
Erika Gibb
Daniel Glavin
Reggie Hudson
Natasha Johnson
Yi-Jehng Kuan
Karen Meech
Stefanie Milam
Tom Millar
Joseph Nuth
Lucas Paganini
Eric Parker
Anthony Remijan
Mark Sutton
Geronimo Villanueva

From Comets and Asteroids to Planets: Organics as a Key Window into Emergent Earth

GCA scientists quantified the diversity of chemical composition among comets, to assess their potential for delivering pre-biotic organic materials and water to young (barren) planets.

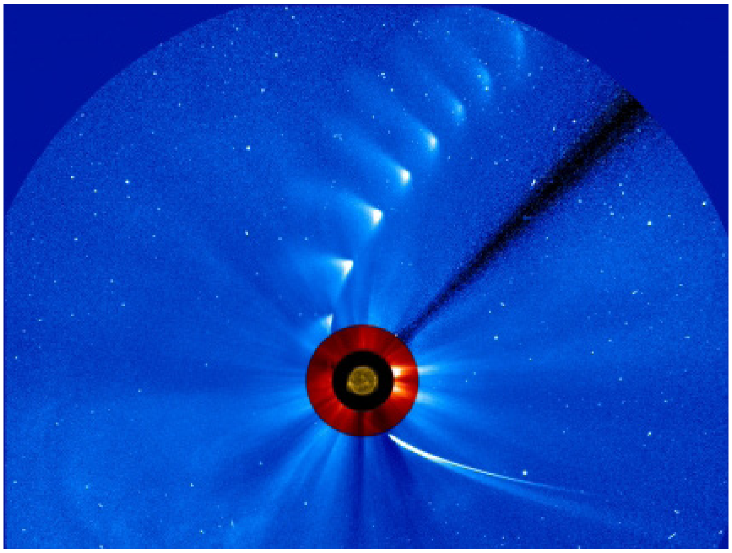


Fig. 1. Comet C/2012 S1 (ISON). Comet ISON comes in from the bottom right, disrupts completely near the Sun, and moves out toward the upper right, getting fainter and fainter. Time-lapse image from the ESA/NASA Solar and Heliospheric Observatory. Credits: ESA/NASA/SOHO/SDO/GSFC

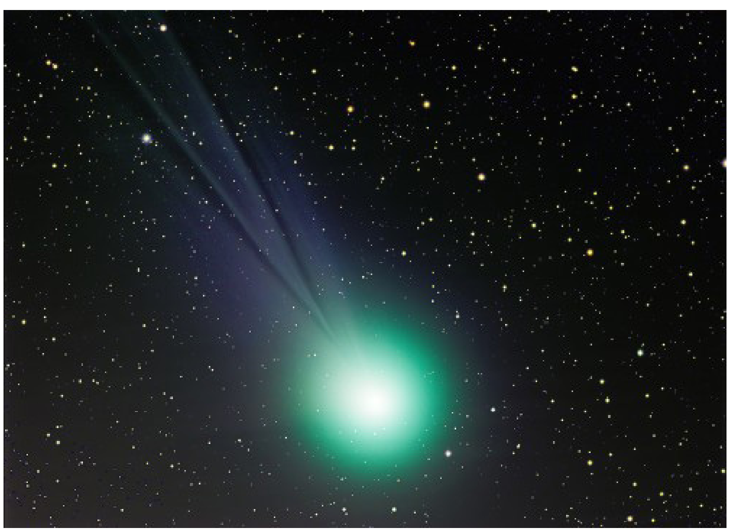


Fig. 2z. Comet C/2014 Q2 (Lovejoy) on 15 January 2015. The greenish coma is a signature of low-dust gas-rich content. The bright streaks trace the comet's tail of ionized gas, that follows the solar wind. Credit: Dark Horse Observatory 230_01.

Using high-resolution infrared spectroscopy at Keck-2 and the NASA-IRTF, DiSanti et al. (2016) measured production rates for H_2O and eight trace gases (CO, C_2H_6, CH_4, CH_3OH, NH_3, H_2CO, HCN, C_2H_2) in sun-grazing comet D/2012 S1 (ISON), over a wide range in heliocentric distance (1.21 to 0.34 AU). Stefanie Milam led studies of ISON's evolution/disruption at radio wavelengths (Keane et al. 2016). ISON's composition changed after disruption began, suggesting interactions between coma dust and gas.

The (D/H) isotopic ratio in cometary water is often compared with ocean water (VSMOW), to assess the role of comets in delivering water to Earth. Among 10 comets with detected HDO, the D/H ratio ranged from one to four times VSMOW. In ISON, D/H was <2.0 VSMOW (Gibb et al. 2016). Paganini et al. (2017) detected HDO and H_2O in C/2014 Q2 (Lovejoy) at 1.9 VSMOW - a factor of 2 larger than that measured by radio astronomers several weeks earlier (Biver et al. 2016), questioning whether Lovejoy 'aged' as it passed through perihelion or if the measurements were imperfect.

Milam participated in a radio study of isotopes (H, C, N, O, & S) in two comets (Biver et al. 2016), finding different D/H ratios in 2014 Q2 (Lovejoy) and 2012 F6 (Lemmon), suggesting radial migration from distinct comet-forming regions in the protoplanetary disk. Our continued studies of coma chemistry with Atacama Large Millimeter Array (ALMA) led to new discoveries regarding the distribution and excitation of CH_3OH, including the production of the first CH_3OH rotational temperature map in a cometary coma (Cordiner et al. 2016, 2017). New insights into the origin of cometary HNC (a tracer of nitrogen-rich, large organic molecules) were also obtained.

Organic Compounds in Authentic Extraterrestrial Materials: The Ultimate Rosetta Stones

We continued to focus on better understanding the origin of meteoritic amino acids and their chiral excesses. This year, we published a review paper describing the diversity of amino acid distributions across multiple groups of carbonaceous meteorites and how this diversity reflects parent body compositions (see Fig. 3). We continued investigating the correlation between amino acids and the structurally related amines, expanding on our previous work and publishing a paper on the analysis of a series of CR2, CM2, and CM1/2 chondrites. Our study of the origin of amino acids in Apollo lunar samples was published, demonstrating these compounds to be primarily terrestrial contamination with some meteoritic input. We participated in analyses of recent meteorite discoveries with large consortia; a publication on the Sariçiçek Howardite meteorite has been submitted. We continued to develop new work exploring amino acid correlations with structurally related species and other organic compounds, such as hydroxy acids, ketones, aldehydes, carboxylic acids, and aromatic hydrocarbons. We established a new collaboration to use NASA high-end computing models to explore the degradation of amino acids under meteoritic conditions.

We used our knowledge of prebiotic organic compounds to contribute to community discussions of biosignatures, participating in relevant workshops. We continue to leverage our expertise and facilities to develop novel instrumentation for future spaceflight, and helped develop a partnership that led to the flight of an Oxford Nanopore Biomolecule Sequencer on the International Space Station.

We leveraged NAI support in developing our analytical facilities to support the contamination control and contamination knowledge efforts of OSIRIS-REx asteroid sample return mission, which successfully launched in September. We continue to support the Sample Analysis at Mars instrument on the Curiosity rover via laboratory instrument analogs.

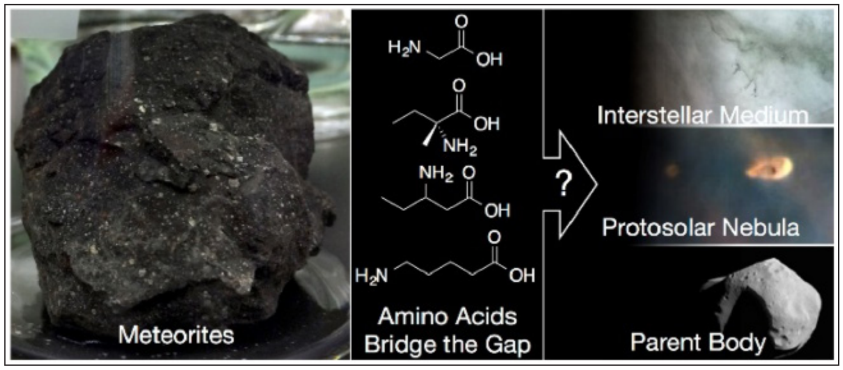


Fig. 3. Our research into amino acids and other organics in meteorites helps in understanding the origin and evolutionary history of these compounds that are relevant to life on Earth.

Fig. 4. Our Team contributed to the OSIRIS-REx asteroid sample return mission, which launched in September, 2016.

Laboratory Simulations of Formative Processes in Cosmic Ice and Dust Analogues

Natasha Johnson and Joseph Nuth in our Nucleation and Dust Chemistry Laboratory continued their research into the formation of organic molecules by surface-mediated reactions on dust grains. They investigated gas/solid carbon branching ratios and their implications for incorporating carbonaceous materials into planetesimals. They demonstrated that CO's efficient conversion into solid forms solves a conundrum about "trapping" gaseous carbon in the early solar nebula (Nuth et al. 2016). Laboratory simulations showed that reaction efficiencies vary according to substrate, temperature, and partial pressure of the gases used. The gases employed to date are carbon monoxide, nitrogen, and hydrogen, three of the more abundant gases available in the early solar nebula. Growth of carbon deposits on mineral surfaces may increase the efficiency of coagulation in the hot inner nebula.

Work in the Cosmic Ice Laboratory was motivated by the discovery of the first chiral interstellar molecule, propylene oxide, by GCA co-investigator Geoff Blake's team. However, this molecule's origins were unknown. Reggie Hudson, Mark Loeffler, and student intern Katarina Yocum reasoned that propylene oxide would likely be converted to propylene (a known interstellar molecule), when exposed to a source of O-atoms and energy (such as cosmic rays). They irradiated a CO_2-propylene mixture at 10 K with high-energy (1 MeV) protons and used infrared spectroscopy to follow changes in the ice. They observed propylene oxide formation, showing that this molecule can form in dense interstellar clouds. The reaction's yield was quite high (~10%) and the recorded low-temperature spectrum will permit future searches (Hudson et al. 2017a).

Perry Gerakines and Hudson continued the difficult work of measuring abundances for icy interstellar and solar system molecules, obtaining the first IR band strengths for amorphous N_2O (isoelectronic with the important molecule CO_2) (Hudson et al. 2017b) and CH_3SH, a molecule sometimes considered a biomarker (Hudson 2016).

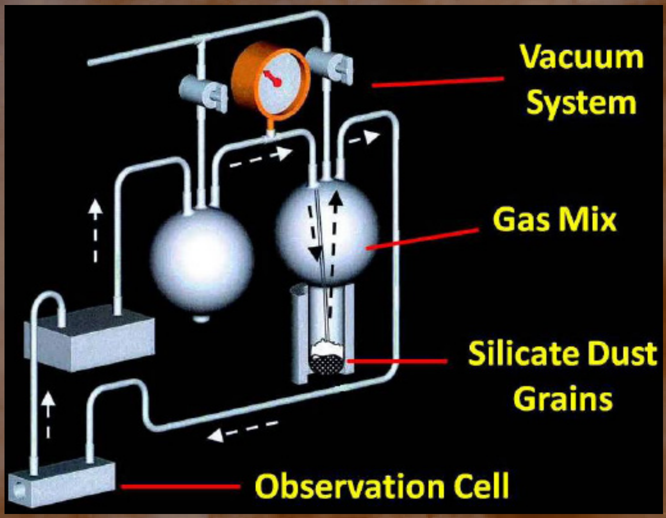


Fig. 5. Laboratory system for studying dust-catalyzed chemistry leading to organic molecules.

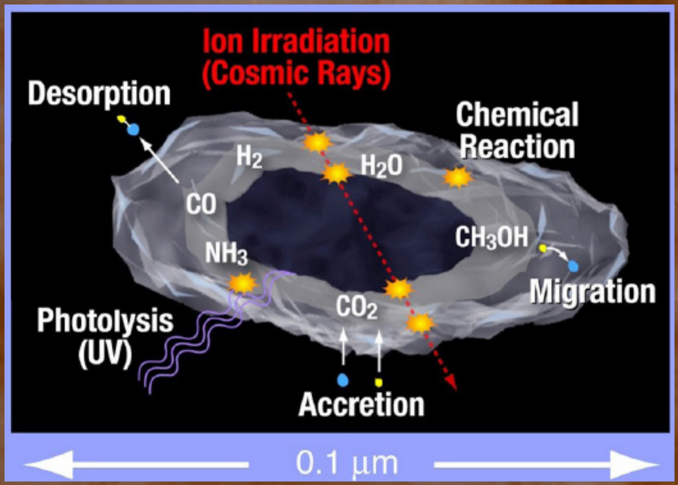


Fig. 6. Concept for forming propylene oxide and related organics on interstellar icy dust grains.

From Molecular Cores to the Protoplanetary Disk: Our Interstellar Organic Heritage

Gas-phase or solid-phase chemical reactions could have produced the organic molecules incorporated into the early Solar System. Steven Charnley led a theoretical study of organic chemistry in disks around young accreting protostars where the gas and dust undergoes rapid heating and cooling (Taquet et al. 2016). They showed that both chemistries can synthesize large organic molecules, and they identified outstanding questions.

Isotopic fractionation is a powerful tool for testing the origin of Solar System organic materials. Charnley, Milam, Cordiner and colleagues reviewed recent observations and theoretical models of chemistry affecting nitrogen fractionation ($^{14}N/^{15}N$) in molecular clouds and protostellar disks, and discussed the connection to meteorites and comets (Wirström et al. 2016).

Molecular *snowlines* demonstrate that ice-gas fractionation is an important feature of protoplanetary disks; the composition of accreted pre-cometary ices may reflect such processing. Using Herschel Space Observatory data, Geoffrey Blake and colleagues determined locations of the water snowline in four protoplanetary disks (Blevins et al. 2016). With ALMA, Blake and colleagues imaged molecular rings in the disk of protostar DM Tau, in light emitted by the CCH radical and the cyclic molecule cyclopropenylidene (c-C_3H_2) (Bergin et al. 2016). This work suggests that a rich hydrocarbon chemistry can occur in the outer layers of such disks.

Many molecules can exist in two forms (*enantiomers*) in which each molecule is the mirror image of the other. A defining characteristic of biological processes is *homochirality* in which the left-handed enantiomer is used exclusively. Amino acids extracted from primitive meteorites also show an excess of the left-handed form. Blake (CalTech) led a team of radio astronomers (McGuire et al. 2016) that discovered the first chiral molecule in space: propylene oxide (CH_3CHCH_2O). This discovery opens the possibility that the chirality of interstellar molecules could be measured in future and compared to that found in the Solar System and in biology, to constrain origins.

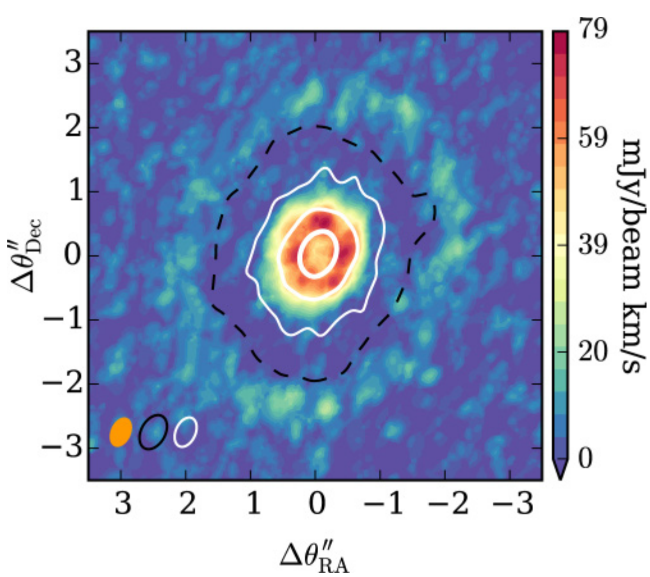


Fig. 8. An ALMA image of the hydrocarbon ring of CCH molecules in the disk of DM Tau (Bergin et al. 2016).

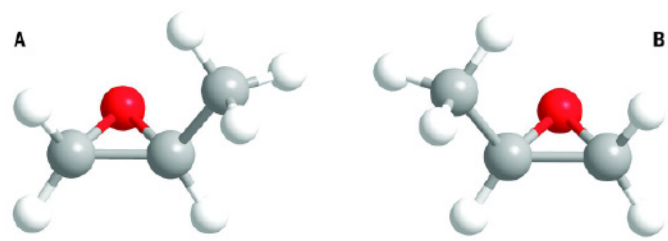


Fig. 9. The molecular structures of the two enantiomers of the chiral molecule propylene oxide (McGuire et al. 2016).

Analytical Protocols for Detection and Diagnosis of Life's Molecular Compounds

We continued to develop and test a range of laboratory protocols to improve the effectiveness of molecular analysis offered by future *in situ* instruments to identify potential biosignatures in complex planetary samples. NAI support was leveraged to quantify the benefits of selective ion enrichment and tandem mass spectrometry (or MS/MS) techniques during laser desorption analysis of Mars analogs, in support of the Mars Organic Molecule Analyzer (MOMA) investigation under development for the ExoMars rover mission. These protocols will allow MOMA to isolate and structurally characterize individual organic compounds detected in multiphase mineral assemblages by MOMA's ion trap mass spectrometer (Goesmann et al., 2017). Additionally, NAI supported the development of and protocol definition for an Orbitrap™-based testbed mass spectrometer that shows promise for future planetary missions. In collaboration with French team members, we are examining operational modes and efficient data acquisition and analysis schemes that will allow the performance of this ultrahigh resolution mass analyzer to be characterized as a function of challenging environmental conditions.

We continue to explore the potential application of novel nanopore-based detection and sequencing of informational biopolymers for future missions to Mars and ocean worlds such as Europa or Enceladus. GCA summer intern Mark Sutton, in collaboration with our astrobiology group and the laboratory of GCA-alumnus Dr. Aaron Burton of NASA JSC, conducted tests with a MinION™ nanopore device from Oxford Nanopore Inc. Experiments included attempting to sequence DNA from low-biomass Mars analog soil samples from the Atacama Desert and investigating how storage temperature affects flow cell performance. These results inform the viability of such technology on a remote planetary mission, and test the effectiveness of its use during human space exploration. The JSC-led Team (J. Dworkin is a co-I) recently deployed a MinION device on the International Space Station, pioneering this approach.

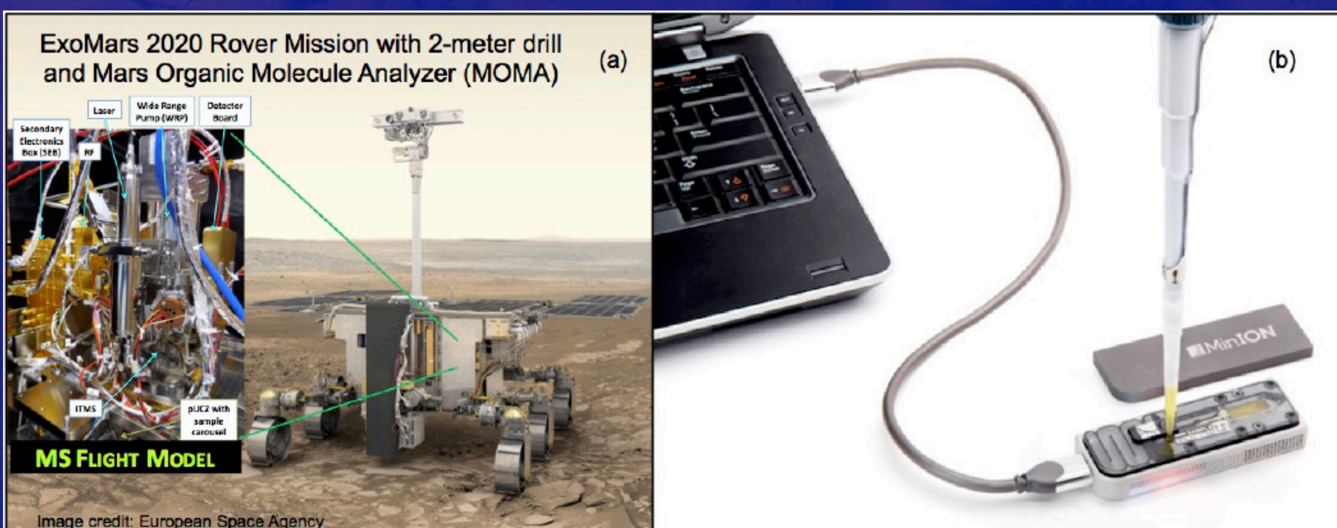


Fig. 7. (a) Development of analytical protocols for molecular analysis are being applied to the planned operation of the MOMA instrument on the ExoMars rover. (b) Nanopore informational polymer sequencing technology, such as the compact MinION device, is being examined for its compatibility with space flight application.

Origin and Evolution of Organics and Water in Planetary Systems: 2016 Publications

Aponte, J.C., McLain, H.L., Dworkin, J.P., Elsila, J.E. (2016). Aliphatic amines in Antarctic CR2, CM2, and CM1/2 carbonaceous chondrites. *Geochim. Cosmochim. Acta* 189, 296-311. DOI: 10.1016/j.gca.2016.06.018

Cordiner, M. A., Charnley, S. B., Mumma, M. J, Bockelée-Morvan, D., Biver, N., Villanueva, G., Paganini, L., Milam, S. N., Remijan, A. J., Lis, D. C., Crovisier, J., Boissier, J., Kuan, Y.-J., Coulson, I. M. (2016). Measuring the Distribution and Excitation of Cometary CH_3OH Using ALMA. *IAU Proc.* 29A, 233-236. DOI: 10.1017/S1743921316002957

DiSanti, M. A., Bonev, B. P., Gibb, E. L., Paganini, L., Mumma, M. J., Villanueva, G. L., Keane, J. V., Blake, G. A., Dello Russo, N., Meech, K. J., Vervack, Jr., R. J., McKay, A. J. (2016). En Route to Destruction: The Evolution in Composition of Ices in Comet D/2012 S1 (ISON) between 1.2 and 0.34 AU from the Sun as Revealed at Infrared Wavelengths. *Ap. J.* 820, 34 (20pp). DOI: 10.3847/0004-637X/820/1/34

Elsila, J.E., Aponte, J.C., Blackmond, D.G., Burton, A.S., Dworkin, J.P., Glavin, D.P. (2016). Meteoritic Amino Acids: Diversity in Compositions Reflects Parent Body Histories. *ACS Central Science* 2, 370-379. DOI: 10.1021/acscentsci.6b00074

Elsila, J.E., Callahan, M.P., Dworkin, J.P., Glavin, D.P., McLain, H.L., Noble, S.K., Gibson Jr, E.K. (2016). The origin of amino acids in lunar regolith samples. *Geochim. Cosmochim. Acta* 172, 357-369. DOI: 10.1016/j.gca.2015.10.008

Faggi, S., Villanueva, G. L., Mumma, M. J., Brucato, J. R., Tozzi, G. P., Oliva, E., Massi, F., Sanna, N., Tozzi, A. (2016). Detailed analysis of near-IR water (H_2O) emission in comet C/2014 Q2 (Lovejoy) with the GIANO/TNG spectrograph. *Ap. J.* 830:157 (17 pp). DOI: 10.3847/0004-637X/830/2/157

Friedrich, J.M., Glavin, D.P., Rivers, M.L., Dworkin, J.P. (2016). Effect of a synchrotron X-ray microtomography imaging experiment on the amino acid content of a CM chondrite. *Meteorit Planet Sci* 51, 429-437. DOI: 10.1111/maps.12595

Gibb, Erika L., Bonev, Boncho P., DiSanti, Michael A., Villanueva, Geronimo L., Paganini, Lucas, Mumma, Michael J. (2016). An Infrared Search for HDO in comet D/2012 S1 (ISON) and Implications for iSHELL. *Ap. J.* 816, 101 (6pp). DOI: 10.3847/0004-637X/816/2/101

Goetz, W., W. B. Brinckerhoff, R. Arevalo, et al. (2016). MOMA: the challenge to search for organics and biosignatures on Mars. *International Journal of Astrobiology.* 15 (03): 239-250. DOI: 10.1017/s1473550416000227

Hudson, R. L. (2016). Infrared Spectra and Band Strengths of CH_3SH, an Interstellar Molecule. *Physical Chemistry Chemical Physics*, 18, 25756. DOI: 10.1039/c6cp01475e

Hudson, R. L., Loeffler, M. J., Yocum, K. M. (2017a). Laboratory investigations into the spectra and origin of propylene oxide, a chiral interstellar molecule. *The Astrophysical Journal*, 835, 225. DOI: 10.3847/1538-4357/835/2/225

Hudson, R. L., Loeffler, M. J., Gerakines, P. A. (2017b). Infrared spectra and band strengths of amorphous and crystalline N_2O. *Journal of Chemical Physics*, 146, 0243304. DOI: 10.1063/1.4973548

Keane, Jacqueline V., Milam, Stefanie N., Coulson, Iain M., et al. (2016). Catastrophic Disruption of Comet ISON. *ApJ*. 831:207 (7pp). DOI: 10.3847/0004-637X/831/2/207

Kuchner, Marc J., et al. (2016). Disk Detective: Discovery of New Circumstellar Disk Candidates through Citizen Science. *The Astrophysical Journal*, Volume 830, Issue 2, article id. 84, 14 pp. DOI: 10.3847/0004-637X/830/2/84

Loeffler, M. J. and Hudson, R. L. (2016). What is eating Ozone? Thermal reactions between SO_2 and O_3: Implications for icy environments. *The Astrophysical Journal Letters*, 833:L9 (5pp). DOI: 10.3847/2041-8213/833/1/L

McGuire, B.A. et al. (2016). Discovery of the interstellar chiral molecule propylene oxide (CH_3CHCH_2O). *Science*, Volume 352, Issue 6292, pp. 1449-1452. DOI: 10.1126/science.aae0328

Miles, B., Roberge, A., & Welsh, B. (2016). UV Spectroscopy of Star-grazing Comets Within the 49 Ceti Debris Disk. *The Astrophysical Journal*, 824 (2), article id.126, 6pp. DOI: 10.3847/0004-637X/824/2/126

Nuth, J. A., Johnson, N. M., Ferguson, F. T., Carayon, A. (2016). Gas/solid carbon branching ratios in surface-mediated reactions and the incorporation of carbonaceous material into planetesimals. *Meteoritics & Planetary Science*, 51, 1310. DOI: 10.1111/maps.12666

Nuth, J. A., Johnson, N. M., Ferguson, F. T., Rietmeijer, F. J. M., Hill, H. G. M. (2016). Great new insights from failed experiments, unanticipated results and embracing controversial observations. *Chemie der Erde - Geochemistry*, 76, 1. DOI: 10.1016/j.chemer.2015.09.002

Paganini, L. and Mumma, M. J. (2016). A Solar-pumped fluorescence model for Line-by-line Emission Intensities in the B-X, A-X, and X-X Band Systems of $^{12}C^{14}N$. *Ap. J. Suppl. Ser.* 236:3 (13pp). DOI: 10.3847/0067-0049/226/1/3

Silverberg, S.M., Kuchner, M.J., Wisniewski, J.P., et al. (2016). A New M Dwarf Debris Disk Candidate in a Young Moving Group Discovered with Disk Detective. The Astrophysical Journal Letters 830, Issue 2, article id. L28, 5 pp. DOI 10.3847/2041-8205/830/2/L28

Smith, K.E., House, C.H., Dworkin, J.P. et al. (2017). Spontaneous Oligomerization of Nucleotide Alternatives in Aqueous Solutions. Orig. Life Evol. Biosph. 47(1):3-11. DOI:c10.1007/s11084-016-9484-3

Taquet, V., Wirström, E.S., Charnley, S.B. (2016). Formation and Recondensation of Complex Organic Molecules during Protostellar Luminosity Outbursts. *The Astrophysical Journal*, Volume 821, Issue 1, article id. 46, 12 pp. DOI: 10.3847/0004-637X/821/1/46

Wirström, E.S., Adande, G.R., Milam, S.N., Charnley, S.B., Cordiner, M.A. (2016). ^{15}N Fractionation in Star-Forming Regions and Solar System Objects. *Astronomy in Focus*, Volume 29A, 2016, pp. 271-274. DOI: 10.1017/S1743921316003033