Deep Carbon Observatory

A Decade of Discovery
This report was produced by Deep Carbon Observatory (DCO) Synthesis Group 2019 on behalf of the DCO Executive Committee, and would not have been possible without the support of the DCO Secretariat and Engagement Team.

**Synthesis Group 2019**

Marie Edmonds, Chair  
University of Cambridge, UK

Susannah Dorfman  
Michigan State University, USA

Kerstin Lehnert  
Columbia University, USA

Karen Lloyd  
University of Tennessee, USA

Craig Manning  
University of California, Los Angeles, USA

Craig Schiffer  
Carnegie Institution for Science, USA

Celina Suarez  
University of Arkansas, USA

Dimitri Sverjensky  
Johns Hopkins University, USA

Karen Lloyd  
University of Tennessee, USA

Craig Schiffries  
Carnegie Institution for Science, USA

Dimitri Sverjensky  
Johns Hopkins University, USA

Celina Suarez  
University of Arkansas, USA

Dimitri Sverjensky  
Johns Hopkins University, USA

Karen Lloyd  
University of Tennessee, USA

Craig Schiffries  
Carnegie Institution for Science, USA

**Executive Committee**

Craig Manning, Chair  
University of California, Los Angeles, USA

John Baross  
University of Washington, USA

Tara Bryndzia  
Shell International Exploration & Production, Inc., USA

David Cole  
The Ohio State University, USA

Isabelle Daniel  
Université Claude Bernard Lyon 1, France

Donald Dingwell  
University of Munich, Germany

Marie Edmonds  
University of Cambridge, UK

Peter Fox  
Rensselaer Polytechnic Institute, USA

Robert Hazen  
Carnegie Institution for Science, USA

Russell Hemley  
University of Illinois at Chicago, USA

Kai-Uwe Hinrichs  
University of Bremen, Germany

Claude Jaupart  
Institut de Physique du Globe de Paris, France

Adrian Jones  
University College London, UK

Karen Lloyd  
University of Tennessee, USA

Bernard Marty  
Centre de Recherches Pétrographiques et Géochimiques France

Eiji Ohtani  
Tohoku University, Japan

Paula Olsiewski  
Alfred P. Sloan Foundation, USA

Terry Plank  
Lamont-Doherty Earth Observatory, USA

Rob Pockalny  
University of Rhode Island, USA

Craig Schiffries  
Carnegie Institution for Science, USA

Nikolay Sobolev  
Russian Academy of Sciences, Russia

Vincenzo Stagno  
Sapienza University of Rome, Italy

**Secretariat**

Robert Hazen  
DCO Executive Director, Carnegie Institution for Science, USA

Craig Schiffries  
DCO Director, Carnegie Institution for Science, USA

Andrea Mangum  
DCO Program Manager, Carnegie Institution for Science, USA

Jennifer Mays  
DCO Science Program Associate, Carnegie Institution for Science, USA

Michelle Hoon-Starr  
DCO Science Program Assistant, Carnegie Institution for Science, USA

**Engagement Team**

Rob Pockalny  
Team Leader, University of Rhode Island, USA

Katie Pratt  
Communications Director, University of Rhode Island, USA

Darlene Trew Crist  
Engagement Counselor, Crist Communications, USA

Josh Wood  
Digital Content Manager, University of Rhode Island, USA

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Cover image: Gas sampling at Lastarria Volcano (northern Chile) during the Trail by Fire expedition (trailbyfire.org). Credit: Yves Moussallam, Lamont-Doherty Earth Observatory, USA.

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Deep Carbon Observatory

A Decade of Discovery

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Deep Carbon Science
The Deep Carbon Observatory launched in 2009 with an ambitious plan to understand how carbon inside Earth—deep carbon—contributes to and affects the global carbon cycle. Carbon is one of the most important elements of our planet: carbon-based fuels provide much of our energy; carbon is an essential element of life; and excess carbon in our atmosphere presents one of the greatest planetary challenges of our time. The amount of carbon in the easily accessible surface environment, however, is only a tiny fraction of the carbon in Earth. Before DCO, remarkably little was known about the physical, chemical, and biological properties of Earth’s deep carbon.

Core support from the Alfred P. Sloan Foundation allowed an international multidisciplinary collaboration of scientists to come together and explore fundamental questions about carbon inside Earth: How does carbon move between Earth’s interior and atmosphere? How much and in what forms does deep carbon exist? What are the limits to Earth’s deep microbial life? And, lastly, where did Earth’s deep carbon come from and how did life begin?

DCO has made huge progress over the last decade. A network of more than 1200 scientists from 55 nations is now in place and working together to find answers to these questions. The DCO Science Network has produced more than 1400 peer-reviewed manuscripts, shedding light on the quantities, movements, forms, and origins of deep carbon, providing openly available data that will keep future deep carbon scientists busy for the next decade or more.

DCO scientists conducted field investigations across continents and deep into the ocean floor. They carried out field measurements in remote and inhospitable regions of the world: deep in the oceans, on the summit of active volcanoes, and in the deserts of the Middle East. They investigated how carbon behaves deep in Earth’s interior with natural samples, such as diamonds, as well as laboratory experiments mimicking the extreme temperatures and pressures of Earth’s interior, and theoretical models of deep carbon transport and temporal evolution. Where instrumentation and models were lacking, DCO scientists developed new instrumentation and new models to meet the challenge.

Throughout these studies, DCO invested in the next generation of deep carbon researchers, students and early career scientists, who will carry on the tradition of exploration and discovery for decades to come.

This report documents DCO’s ten years of investigation and highlights a number of important discoveries.
Ten Transformational Discoveries in a Decade of Deep Carbon Research

1. The deep biosphere is among the largest ecosystems on Earth (pages 40–43)
   Life in the deep subsurface totals 15,000 to 23,000 megatonnes (million metric tons) of carbon, about 250 to 400 times greater than the carbon mass of all humans on the surface, and inhabits a biosphere nearly twice the volume of all the world’s oceans. DCO scientists found the deepest, lowest-density, and longest-lived subseafloor microbial ecosystem ever recorded. By exploring Earth’s deep biosphere, DCO scientists have changed our understanding of the limits of life at extremes of pressure, temperature, and depth, and have explored how microbes sustain life using abiotic fuel.

2. Rocks and fluids in Earth’s crust provide clues to the origins of life (pages 40–41)
   DCO scientists found amino acids and complex organic molecules in rocks on the seafloor. These molecules, the building blocks of life, were formed by abiotic synthesis and had never before been observed in the geologic record. Studies suggest they form as by-products of serpentinization in the presence of carbon from Earth’s interior. Scientists also found pockets of ancient saline fluids rich in hydrogen, methane, and helium many kilometers deep in continental crust, providing evidence for the existence of early, protected environments capable of harboring life.

3. Much of the volcanic carbon flux seeps out of fractures and faults unassociated with eruptions (pages 27–29)
   Volcanoes and volcanic regions are outgassing carbon dioxide (CO₂) into the ocean-atmosphere system at a rate of 280–360 megatonnes per year. This estimate includes, as well as carbon emitted during eruptions, the CO₂ contribution from widespread diffuse degassing of CO₂ out of fractures and faults in volcanic regions and the mid-ocean ridge system. Volcanic and tectonic regions together emit two orders of magnitude less carbon than that associated with anthropogenic activities, such as the burning of fossil fuels.

4. Volcanic CO₂ flux may be used to forecast eruptions (page 28)
   The volume of carbon dioxide outgassed by some volcanoes increases days to weeks before eruptions, raising the possibility of forecasting volcanic eruptions. DCO researchers measured volcanic outputs around the globe. At Mount Etna, Italy, for example, one of Earth’s most significant sources of volcanic carbon, they found the amount of CO₂ emitted typically increases by 5–8 times about two weeks before a large eruption. Such changes may hold the key to timely warnings of imminent volcanic activity to improve safety of local communities.

5. The deep carbon cycle through deep time reveals long-term stability of atmospheric CO₂, punctuated by large perturbations (pages 33–34)
   DCO scientists have reconstructed Earth’s deep carbon cycle from the deep geologic past to the present day. This new, more complete picture of the planetary ingassing and outgassing of carbon shows a remarkably stable system over hundreds of millions of years and reinforces the importance of continental breakup and associated volcanic activity as a dominant mechanism of planetary outgassing. DCO scientists added to this picture by investigating past disturbances to Earth’s climate system following large volcanic eruptions and asteroid impacts to learn how Earth responds to such events.
Earth harbors a wide range of previously unknown carbon-bearing minerals (pages 34–37)

DCO scientists discovered new forms of carbon deep in Earth’s mantle through experiment and observation, including new, dense forms of carbonates in the deep mantle. These discoveries allow a better understanding of the carbon “storage capacity” of the deep mantle and the role of subduction in recycling surface carbon back to Earth’s interior. DCO scientists also quantified and modeled carbon mineral diversity on Earth, allowing prediction of previously unknown mineral species and establishing an entire new mineral classification system. Network analysis and advanced data science tools provide scientists unprecedented insight into the diversity of carbon-bearing minerals in the crust of our planet. Studies cast new light on the record of major changes in our planet’s history such as the rise of oxygen and the waxing and waning of supercontinents.

Abiotic methane forms in the crust and mantle of Earth (pages 37–40)

The process of serpentinization leads to the formation of abiotic methane in many different environments on Earth. DCO scientists developed and used sophisticated analytical equipment to differentiate between biotic and abiotic formation of methane. Field and laboratory studies of rocks from the upper mantle document a new high-pressure serpentinization process that produces abundant abiotic methane. The formation of methane through geologic processes provides fuel for microbial life.

Diamond inclusions provide evidence of an ocean of water within the mantle and high-pressure materials never seen before in natural samples (pages 31–32)

Tiny mineral inclusions in diamond show traces of water dispersed throughout Earth’s transition zone, and allow glimpses of high-pressure minerals previously only synthesized in the laboratory. Inclusions in super-deep diamonds provided evidence of an amount of water equivalent to the mass of the entire surface ocean dispersed in an area of the mantle known as the transition zone, between 440 and 660 kilometers below the surface. Some super-deep inclusions are minerals that exist only at the high pressures of the lower mantle, proving carbon cycling by plate tectonics over the history of Earth.

Fluids move and transform carbon deep within Earth (page 36)

DCO scientists discovered that the solubility of carbon-bearing minerals, including carbonates, graphite, and diamond, is much higher than previously thought in water-rock systems in the mantle. Experiments and fundamental theory led to a revolutionary new model for water in deep Earth and the discovery that diamonds can easily form through water-rock interactions involving organic and inorganic carbon. This model predicted the changing chemistry of water found in fluid inclusions in diamonds and yields new insights into the amounts of carbon and nitrogen available for return to Earth’s atmosphere over geologic time.

Two-thirds of Earth’s carbon may be in the iron-rich core (page 34)

DCO research suggests that two-thirds or more of Earth’s carbon may be sequestered in Earth’s core as a form of iron carbide. This “missing carbon” brings the total carbon content of Earth closer to what is observed in the sun and helps us to understand the origin of Earth’s carbon from stellar material.
Melts Carbon-bearing sediments Photosynthesis and decomposition Photosynthesis, respiration, and diffusion Silicate weathering Volcanic degassing

The mantle contains carbon in reduced and oxidized forms, in fluid and mineral states.
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Terrestrial Biosphere
Ocean
Atmosphere
Ocean
Sediment
Lithosphere
Upper Mantle
Core
Lower Mantle

CONTINENTAL ARC
MID-OCEAN RIDGE
ISLAND ARC

Carbon in Deep Earth

RESERVOIRS OF CARBON AT APPROXIMATE RELATIVE SIZES (DIAMETER IS A LOG SCALE)
FLUXES OF CARBON
History and Strategy

In 2007 Robert Hazen of the Geophysical Laboratory, Carnegie Institution for Science, presented his origins-of-life research to a group of potential donors in New York City. He outlined the chemical steps by which life might have emerged on Earth from a deep, hot, carbon-rich volcanic environment on the seafloor.

A few months later, Hazen was contacted by Jesse Ausubel, a program manager with the Alfred P. Sloan Foundation. Ausubel had seen Hazen’s presentation in New York and wanted to discuss the potential for developing a new, large-scale research program on the origins of life. Through further discussions, they broadened the topic from the origins of life to a comprehensive and multidisciplinary exploration of carbon—the backbone of life—in Earth’s crust, mantle, and core. Subsequently, the Sloan Foundation offered Hazen funding for a workshop where experts in a range of disciplines could explore the needs and opportunities in deep carbon research.

Russell Hemley, director of the Geophysical Laboratory (2007–2013), who endorsed and contributed to the program concept, offered to host the meeting at the Carnegie Institution for Science in Washington, DC. The resulting Deep Carbon Cycle Workshop was held 15–17 May 2008. Attended by 115 scientists from institutions worldwide, the workshop focused discussion on five major topics:

1. The nature and extent of deep carbon reservoirs, from crust to core.
2. The nature and magnitude of carbon fluxes among these reservoirs, as well as between surface and subsurface reservoirs.
3. The nature and extent of deep microbial life.
4. The possible role of deep crust and mantle processes in abiotic organic synthesis.
5. The possible impact of the deep carbon cycle on societal concerns regarding climate and energy.

The workshop sessions and discussions identified many scientific opportunities, as well as several fundamental advances necessary to effectively investigate the proposed new research avenues. The meeting report concluded that “the only effective way to move this important and virtually unexplored scientific field forward is to first lay a foundation for fundamental understanding by establishing new instrumental facilities, investigating materials synthesis and characterization at extreme conditions, developing thermochemical and kinetic databases, pursuing theoretical applications, and establishing procedures for studying deep life.”

The workshop’s success demonstrated the vast potential for a transformative large-scale research program. In 2009 Hazen, in partnership with Hemley, applied for and received additional funding from the Sloan Foundation to launch this new research venture—soon known as the Deep Carbon Observatory, a name coined by Hemley during the workshop. They established a Secretariat at the Geophysical Laboratory to serve as the program’s central coordination and administrative hub. They also established an international Founders’ Committee—which was replaced by an Executive Committee at the beginning of 2011—to guide the program’s scientific objectives and activities.

DCO’s scientific framework evolved during the program’s first several years into its ultimate configuration of four science communities: Deep Life (DL), Reservoirs and Fluxes (RF), Deep Energy (DE), and Extreme Physics and Chemistry (EPC). The Founders’ Committee and Secretariat initially established three scientific “directorates”: Deep Life, Reser-
voirs and Fluxes, and Energy, Environment, and Climate. These became four directorates at the end of 2010 when the Energy, Environment, and Climate directorate split into two groups: Deep Energy and Physics and Chemistry of Carbon. In May 2012 the Physics and Chemistry of Carbon directorate was renamed as Extreme Physics and Chemistry. The directorates—later renamed “science communities”—were each led and guided by a Scientific Steering Committee.

In 2012 DCO expanded to include new teams focused on Engagement and Data Science, which served members of all four science communities. The Engagement Team facilitated community building and shared DCO’s scientific results with the community and the public. The Data Science Team combined informatics, data management, library science, network science, computer science, and domain science to enable the analysis and analytics of DCO data.

In 2015 DCO added a Modeling and Visualization Forum to augment the work of the four science communities. In 2016, seven years into the ten-year program, DCO formed two new committees to prepare for DCO’s approaching culmination: Synthesis Group 2019 (SG2019) and Task Force 2020 (TF2020). SG2019 was established to synthesize and integrate research conducted across DCO’s four science communities into a coherent whole, to realize a new understanding of deep carbon science and fully capture DCO’s achievements. TF2020 explored possible structures and organizations to continue supporting deep carbon science in 2020 and beyond, resulting in the Institut de Physique du Globe de Paris hosting a central coordination system for deep carbon science to ensure the continuation of this community and its many multidisciplinary scientific endeavors.

DCO’s central strategy involves connecting hundreds of participating scientists at research institutions around the world. DCO fosters the deep carbon community by holding meetings and workshops, providing direct scientific research funding, supporting an international leadership and program management structure, and providing community-wide resources in engagement and outreach, modeling and visualization, and data science. These and many other DCO activities have cemented the deep carbon community and contributed to DCO’s scientific success.

(Above) DCO’s four science communities collaborated in cross-community activities that brought the communities together in a decade of discovery.

(Below) DCO held four international science meetings, which gave the scientific community the opportunity to share findings, assess progress, and plan for future research. Shown here are the attendees at the third International Science Meeting at the University of St. Andrews, Scotland, in March 2017.
More than two dozen researchers from 10 countries participated in DECADE, which included representatives from all countries operating major national volcano observatories. DECADE outfitted 12 of the world’s most prodigiously outgassing volcanoes with permanent gas composition monitoring stations and launched campaigns to some of the world’s most remote volcanoes. These new stations add to existing monitoring networks operated by organizations such as the United States Geological Survey (USGS), the Istituto Nazionale di Geofisica e Vulcanologia (INGV), the University of Palermo, Italy, and the Observatorio Vulcanológico y Sismológico de Costa Rica (OVSCORI), among others. Through partial support from DECADE, there are now approximately 30 collaboratively operated gas-monitoring stations on volcanoes across five continents.

DECADE scientists flew state-of-the-art drones equipped with miniaturized gas-sensing devices, which measure carbon dioxide, sulfur dioxide, and hydrogen sulfide concentrations, over dangerous and remote volcanoes, including some that had never been characterized for their gas emissions. They used satellites to verify data collected by sensors at active and “dormant” volcanoes. This work has produced dramatic improvements in global time-series data on volcanic gas emissions, with the potential for forecasting volcanic eruptions.

DECADE scientists established the DECADE Portal, (decade.iedadata.org), an online map-based data access and exploration tool that facilitates data discovery.

**Members of DECADE gathered for a workshop in Washington, DC, 29 April–4 May 2018, to create a new estimate of global volcanic carbon degassing.**
and access for volcanological research, networking multiple globally distributed data resources, including the Global Volcanism Program database (volcano.si.edu), EarthChem (earthchem.org), the sample registry SESAR (geosamples.org), and the Italian MaGa database for natural gas emissions (magadb.net). DECADE scientists held regular meetings and workshops, designed to train members of the wider community, explore new techniques, and synthesize data.

A workshop held at the Carnegie Institution for Science, Washington, DC, in May 2018 focused on bringing together all volcanic carbon flux data worldwide, and estimating the global volcanic carbon flux into the atmosphere, with associated uncertainties. A number of synthesis papers arose from this workshop. The DECADE community established a special issue of Geochemistry, Geophysics, Geosystems (G-Cubed) to publish synthesis and research-based volcanic and tectonic carbon outgassing papers.

The second major subgroup of the RF Community formed when some 18 researchers from eight countries on four continents teamed up with their students and postdocs to form DMGC. They carried out a remarkable series of studies on the origins of diamonds and the mineralogy and evolution of Earth’s mantle, as revealed by diamond inclusions. Discoveries ranged from finding the equivalent of an ocean’s worth of subducted water in Earth’s transition zone to demonstrating that organic material from the surface penetrates deep into the lower mantle through subduction.

DMGC scientists collaborated with the Gemological Institute of America, providing a unique opportunity for scientists to study the inclusions (imperfections) of rare, large diamonds worth millions of dollars. For scientists, such “imperfect” diamonds are extremely valuable because they are unique geologic samples, offering a snapshot of the environment in which the diamonds formed. These inclusions, which can be isotopically dated, helped scientists understand how Earth’s
Early career researchers took part in four International Diamond Schools. The schools reflected DCO’s commitment to ensuring the next generation of deep carbon research. Inclusions in diamond, such as the red garnet visible here, are windows into Earth’s interior. Inclusions helped DCO scientists discover minerals known to exist only at the high pressure of the lower mantle, and prove that carbon has been cycled back into the Earth’s interior through plate tectonics over the course of our planet’s history.

interior has evolved through geologic time, under the influence of large-scale planetary processes. Tiny pockets of highly saline fluids found in these diamonds demonstrate that they formed from subducted slab components. Other inclusions are made entirely of iron metal, giving a glimpse of the highly reducing conditions of Earth’s deep mantle.

DMGC shared its advances in diamond research through four International Diamond Schools. The schools brought together early career researchers for intensive, hands-on training that incorporated geology, exploration, and gemology to ensure that the next generation of deep carbon scientists is well equipped to continue this research.

After a decade of research, analysis, and sharing of results, RF scientists have formed a wide, collaborative community. Achievements over the past decade are providing a springboard for future scientific endeavors. DECADE is poised to continue its volcano monitoring work, having installed monitoring equipment around the globe with local personnel trained to continue its operation and generation of data. DMGC will continue its investigations to learn more about what diamonds can tell us about the origins, forms, and movement of carbon between Earth’s reservoirs. The RF Community’s legacy of online models, shared databases, and publications will serve to underpin further investigations of the global carbon cycle and how it has changed and will continue to change over time.

A complete list of Reservoirs and Fluxes Community members can be found online at deepcarbon.net/rf.
The Extreme Physics and Chemistry Community at a Glance

**Decadal Goals**

- Seek and identify possible new carbon-bearing materials in Earth and planetary interiors.
- Characterize the structural and dynamic properties of materials and identify their reactions and transformations at conditions relevant to Earth and planetary interiors.
- Develop, extend, combine, and exploit experimental tools to investigate carbon-bearing samples in new regimes of pressure, temperature, and composition.
- Develop, extend, and improve databases and simulations of deep carbon material properties, reactions, and transport for integration with the 4D Deep Carbon in Earth Model.

Through novel instrumentation and challenging experiments, the Extreme Physics and Chemistry (EPC) Community sought to understand forms of carbon at the extreme temperatures and pressures within Earth’s interior. EPC scientists made huge strides in understanding the physical properties and chemical behavior of the myriad forms of mineral phases and fluids containing carbon deep in our planet. Researchers identified important new mineral compounds and structures, observed how minerals deep within Earth’s interior reorganize their atoms under varying pressure and temperature conditions, and compiled their results into databases and models, laying a solid foundation for future research.

EPC operated as a constellation of 22 research teams, each targeting unique components of the community’s decadal goals. Initially functioning largely as separate entities, over the course of the DCO these teams evolved into a collaborative, multidisciplinary community committed to sharing data, creating open access online databases, and building robust modeling and discussion forums. They also developed novel experimental tools to mimic in the laboratory the extreme conditions inside Earth.

EPC leadership galvanized their community of scientists at five meetings, where all community members were in-
vited and participants undertook long-term planning and provided input on ongoing and planned research initiatives. Such convocations resulted in EPC-focused thematic sessions at international meetings and ongoing opportunities for the exchange of ideas. EPC sessions regularly took place at the annual American Geophysical Union (AGU) and Goldschmidt meetings, and during the 2017 joint meeting of the Japan Geosciences Union and AGU.

Replicating the extreme conditions of Earth’s interior, through experiment or simulation, presents a grand challenge. EPC researchers tackled it by developing new, and exploiting existing, technologies and software platforms to create high pressure/temperature environments in the laboratory or on a computer. They used devices such as diamond anvil cells, apparatus that exerts great pressure by squeezing a sample between two diamonds coupled with lasers that then heat the compressed crystals, to simulate the wide range of pressures and temperatures in Earth’s mantle and core. They then analyzed the compressed carbon-bearing samples by a variety of advanced analytical techniques—using X-rays, neutrons, electrons, and lasers to study the properties of the new carbon-bearing phases that form at high pressures and temperatures. EPC scientists developed unique, close collaboration between modelers and experimentalists, which led to productive interactions and some of the community’s most novel and highest impact papers.

Data from these advanced experimental techniques fueled novel modeling efforts. EPC scientists developed and refined the Deep Earth Water (DEW) model, a critical step for understanding fluid transport and reactivity in Earth’s mantle, including the formation of diamonds and organic carbon species in subduction zone fluids (see page 36). Many community members also became active users of ENKI, a collaborative, web-based model-configuration and testing portal that provided researchers tools in computational thermodynamics and fluid dynamics.

EPC theorists developed an advanced, open-source computational infrastructure for multi-physics modeling (TerraFERMA, terraferma.github.io) to explore the transport of reactive fluids and magmas. To ensure that these computational tools would outlive the DCO itself, EPC co-sponsored a series of training schools to link traditional thermodynamic modeling with molecular dynamics.

EPC’s new capacities for theoretical modeling also strengthened the community’s interactions with the other...
three DCO communities. For example, modeling results are helping to confirm the fate of subducted organic compounds as carbon is recycled through the upper mantle and track the transformation of organic compounds into deep energy resources.

Many of EPC’s contributions are recorded in an AGU monograph, *Carbon in Planetary Interiors*. Among its many findings, the community identified and characterized 100 new crystal structures in Earth’s interior, including new data on the structure, elastic properties, and chemical behavior of a wide range of phases at extreme conditions. Their work provided new insight into pathways for carbon atoms to “find one another” so they can associate, aggregate, and assemble in geologic systems. Such pathways play an important role in diamond formation, petroleum exploration, carbon sequestration, and determining the origins of graphite and diamond in the geologic record. The community also helped constrain the stability of hydrocarbons at high pressures and temperatures and better defined the role that pressure plays in carbon reactions in aqueous fluids.

Post 2019, the EPC Community is in a strong position to continue to thrive and grow. The community consists of a network of colleagues who share knowledge, resources, and data with a contingent of early career scientists. With a large and diverse publication legacy, the community will build upon its analytical and experimental techniques, modeling innovations, and data repository to continue to uncover the range of carbon forms that exist at the extreme conditions found inside Earth and other planetary bodies.

A complete list of Extreme Physics and Chemistry Community members can be found online at [deepcarbon.net/epc](http://deepcarbon.net/epc).
The Deep Life Community at a Glance

Decadal Goals
• Determine the processes that define the diversity and distribution of deep life as it relates to the carbon cycle.
• Determine the environmental limits of deep life.
• Determine the interactions between deep life and carbon cycling on Earth.

The Deep Life (DL) Community engaged a diverse and international group of scientists in field studies, laboratory experiments, and bioinformatics to describe the deep biosphere and its impact on global carbon cycling. This research community successfully approximated the size of the deep biosphere, including where, how much, and what kinds of life exist in the deep subsurface, with its extremes of pressure, temperature, and low nutrient availability. They also shed light on the microbial cycling of carbon, sulfur, and iron in the subsurface, how deep fluids affect the structure and function of microbial communities, and how temperature and pressure limit life within the deep subsurface biosphere.

More than 400 scientists from 34 countries made up the DL Community, including experts in oceanography, biology, biogeochemistry, microbiology, and geobiology. To investigate the deep biosphere, these multidisciplinary collaborators constructed models and used sophisticated instrumentation to explore a massive ecosystem extending several kilometers deep beneath Earth’s surface.

DL Community members were involved in more than 100 projects, both on land and at sea. Sampling missions targeting the marine subsurface took them to the Atlantis Massif in the Atlantic Ocean, where they explored the role of serpentinization (a process through which mantle rocks are hydrated, forming the mineral serpentine and liberating molecular hydrogen) in fueling deep life; to the Nankai Trough off the coast of Japan in the Pacific Ocean, where they investigated the temperature and pressure limits on microbial life in the marine subsurface; to the coast off the Shimokita Peninsula where the most deeply buried microbial life has been discovered 2.4 kilometers below the ocean floor; and to the Lost City Hydrothermal Vent field in the mid-Atlantic to better understand how deep carbon fuels microbial communities.

DL scientists augmented research at sea with what they learned on land. This research included expeditions to geyser fields in the western mountains of the United States, a series of groundwater wells that make up the Coast Range.
Ophiolite Microbial Observatory in actively serpentinitizing terrain in northern California, subduction zones in Costa Rica, the rocky desert of the Sultanate of Oman, the deep mines of South Africa and Canada, and deep boreholes in Finland.

The Census of Deep Life (a central DL project) undertook a global census of deep subsurface microbes. The contributing scientists took advantage of major advances in DNA sequencing technology to identify individual subsurface microbial groups, map their locations and the conditions under which they exist, and determine their roles in the deep carbon cycle. They conducted more than 100 molecular surveys of deep biosphere communities on samples from the marine and continental subsurface.

Like all of DCO’s communities, the DL Community operated in an open way, sharing innovative techniques and novel findings with the broader scientific community. They took on the challenge of improving metadata standards in deep life research (the way in which samples are identified and archived) by building a Deep Biosphere ontology. They also set up a bioinformatics strategy for detecting and removing contamination in marker gene studies. Both developments will serve to advance future discoveries.

The Deep Life Community collected microbial life in both the ocean subsurface and continental interior, which helped define and quantify the extent and composition of the deep biosphere. As one example of more than 100 projects undertaken by this 400+ member community, work aboard the world’s largest scientific research vessel, D/V Chikyu, helped them determine the limits of life within the ocean subsurface.

The DL Community hosted a series of targeted workshops and launched training initiatives, further ensuring its legacy. One example was an emphasis on training early career scientists in specialized cultivation techniques, including tools to investigate microbial population size, community composition, and the role that physicochemical properties play in subsurface life.

A workshop designed to jump-start research in extreme biophysics focused on the structures, dynamics, and activities that enable biomolecules and biomolecular assemblies of extremophiles to function under extreme temperature and pressure conditions. This workshop sparked funding by the US National Science Foundation for a Research Collaboration Network, “The Molecular Limits of Life,” which will continue well beyond 2019. Not only will this network improve understanding of the molecular limits of life, its work has implications for improvements in food and pharmaceutical preservation.

**DL by the numbers**

- **414** scientists
- **36** countries
- **103** projects
- **376** publications
Deep Life scientists collected samples of the deep biosphere on land and at sea. Subsequent analysis allowed them to quantify life in the deep subsurface—15,000 to 23,000 million metric tons of carbon—and inhabiting a biosphere nearly twice the volume of all the world’s oceans. (Left) Deep Life scientists collected samples on land, from places such as the Coastal Range Ophiolite, California, pictured here. (Right) Shown here is a scientist collecting Baltic Sea sediments to assess how microbial communities vary in form and chemistry on diets of organic carbon from marine and terrestrial sources.

and medical technologies, with the potential for new developments in nanotechnology and energy science.

Other DL research will also continue past 2019. A new Center for Deep Life Investigation in China, based at Shanghai Jiao Tong University, was launched in 2018. This center is providing a platform for continued international collaboration and instrumentation development by the Deep Life Community. In early 2019, the Cluster of Excellence: The Ocean Floor—Earth’s Uncharted Interface was launched at the MARUM Center for Marine Environmental Sciences at the University of Bremen in Germany, initiating a new chapter in ocean-floor research. This international, interdisciplinary initiative, involving many DCO partners, is focusing on the geochemical, geobiological, and geodynamic processes at and within the ocean floor.

A complete list of Deep Life Community members can be found online at deepcarbon.net/dl.

Deep Life Project Leaders
Kai-Uwe Hinrichs, Co-chair University of Bremen, Germany
Mitchell Sogin, Co-chair Marine Biological Laboratory, USA

Scientific Steering Committee
Doug Bartlett University of California, San Diego, USA
Rick Colwell Oregon State University, USA
Steven D’Hondt University of Rhode Island, USA
Fumio Inagaki Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan

Tom Kieft New Mexico Institute of Mining and Technology, USA
Mark Lever ETH Zürich, Switzerland
Beth Orcutt Bigelow Laboratory for Ocean Sciences, USA
Matt Schrenk Michigan State University, USA
Fengping Wang Shanghai Jiao Tong University, China
Roland Winter Technical University Dortmund, Germany
Decadal Goals

- Use field-based investigations of representative terrestrial and marine environments to determine the quantities, movements, forms, and origins of abiotic gases and organic species in Earth’s crust and uppermost mantle.
- Implement revolutionary instrumentation to discriminate abiotic from biotic methane gas and other organic compounds in terrestrial and marine settings.
- Quantify the physicochemical conditions that produce hydrogen and abiotic forms of methane gas, as well as more complex organic compounds.
- Integrate advances in understanding with a box model for carbon.

The Deep Energy (DE) Community advanced significantly our understanding of the origin and formation of hydrocarbons and complex organic species. DE researchers exploited advanced instrumentation that allowed them to determine if methane gas formed abiotically or as a result of biological processes, and to understand the geologic formation of methane and higher hydrocarbons through processes related to serpentinization.

The DE Community studied the mechanisms by which methane and higher hydrocarbons form, in particular the abiotic methane generation pathways that rely on carbon and hydrogen derived from slow geologic processes such as serpentinization. To distinguish abiotic methane from that produced from microbial processes, Deep Energy scientists employed analytical techniques using isotopologues of methane.
methylene, which may discriminate sources. (An isotopeologue is any of a group of compounds that differ only in their isotopic composition; for example, water and heavy water.) DE scientists undertook studies of fluid-bearing hydrocarbons from Precambrian cratons, the large, ancient, stable blocks of Earth’s crust that form the continental cores.

DE scientists conducted field campaigns worldwide. Samples collected included drill-cores from the deep ocean floor at the Atlantis Massif, methane and carbonated peridotite samples from the Samail Ophiolite, chunks of oceanic crust and upper mantle in the Sultanate of Oman, and rocks from geothermal wells and steam vents in Iceland, Greece, and Costa Rica. Deep submarine sites in South Africa and the Nankai Trough off the coast of Japan provided the opportunity for investigating relationships between seismic events and microbial communities. In labs around the world, DE collaborators analyzed this abundance of samples, conducting experiments to elucidate how methane and other compounds form, move, and transform inside Earth.

Experimentalists tested the formation of abiotic methane using various methodologies. They synthesized abiotic methane and higher organic molecules in the laboratory, providing a framework for identifying possible sources in natural samples. They then brought natural peridotite and chromite-rich rock samples into the lab and used them as catalysts for generating abiotic methane. Still other experiments focused on the impact of depth, pressure, and space limitations on the production and transformation of methane and other forms of deep carbon.

Such complex experiments required equally sophisticated analytical equipment capable of replicating the conditions found in natural settings. Scientists used techniques such as diamond anvil cells, Raman
spectroscopy (which detects changes in the color of light to probe the arrangement and strength of chemical bonds), and X-ray diffraction (which reveals the symmetry and crystal structure of compounds). Deep Energy scientists also developed new instrumentation. Notable developments included the Panorama mass spectrometer, which makes it possible to measure relative abundance of rare methane isotopologues, and a pressurized underwater sample handler, which collects and preserves microbial, aqueous, and gas samples in the field for further analysis in laboratory settings. In addition, the tunable infrared laser direct absorption spectrometer is a low-cost portable instrument for measuring ratios of methane isotopologues, making it useful for testing the origin of methane in the field.

The structure and breadth of the DE Community provided many opportunities for researchers looking at different aspects of a research question to share samples, analyses, and results. Deep Energy scientists collaborated with colleagues from other communities, especially EPC and DL, on deep fluids and serpentinization. The collaborations drove the initiation of large field-based projects such as the Oman Drilling Project and investigations at the Atlantis Massif core complex.

Community-wide meetings afforded scientists opportunities to share data in informal settings. These meetings fostered strong community building, enhancing collaborative research across geographic, cultural, and multidisciplinary boundaries. The DE Community prepared a special issue of *Frontiers in Earth Science* to share recent advances in understanding how the slow, deep carbon cycle controls the habitability of Earth over geologic timescales. Papers included in the volume explore topics ranging from the forms and origins of deep carbon to its implications for the origins of life on Earth.

This decade of discovery will serve as a strong foundation for the DE Community to carry on its work. The integration of field studies and laboratory experiments involving many early career scientists at every level bodes well for future collaboration, as does the multidisciplinary aspect of this research.

A complete list of Deep Energy Community members can be found online at [deepcarbon.net/de](http://deepcarbon.net/de).

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**Deep Energy Project Leaders**

Isabelle Daniel, Chair  Université Claude Bernard Lyon 1, France  
Edward Young, Co-chair  University of California, Los Angeles, USA

**Scientific Steering Committee**

Magali Ader  Institut de Physique du Globe de Paris, France  
Chris Ballentine  University of Oxford, UK  
Peter Clift  Louisiana State University, USA

David Cole  The Ohio State University, USA  
Nils Holm  Stockholm University, Sweden  
Long Li  University of Alberta, Canada  
Tullis Onstott  Princeton University, USA  
Magali Pujol  Total, France  
Pablo García del Real  Fugro USA Marine, Inc., USA  
Igor Tolstikhin  Kola Scientific Center of Russian Academy of Sciences, Russia
Cross-Community Activities

DCO pioneered new ways of collecting, analyzing, and sharing data to enhance interdisciplinary research. DCO’s Data Science Team and Modeling and Visualization Forum worked with scientists from all four science communities (Extreme Physics and Chemistry, Reservoirs and Fluxes, Deep Life, and Deep Energy), collaborating on projects requiring data science expertise and creating visualizations of Earth that were unimaginable only a few years ago.

From its inception, DCO recognized that new, cutting-edge instrumentation was needed to answer many of its scientific questions. Early investments in instrument development made it possible for DCO scientists to make unique measurements to investigate deep Earth processes. To supplement analytical measurements and experimental research, DCO scientists explored field sites around the globe. They shared innumerable rock, fluid, and gas samples, and the resulting datasets with wider communities to continue to expand what is known about carbon deep within Earth.

**Novel Instrumentation Provides Windows into Unseen Worlds**

DCO invested heavily in developing new instrumentation to distinguish abiotic from biological sources of methane. Novel instrumentation is critical in addressing fundamental questions about how methane is produced in deep and shallow environments in Earth. DCO scientists developed a unique gas-source multiple-collector isotope ratio mass spectrometer, the Panorama mass spectrometer, specifically to tackle this challenge. Among the first projects funded by DCO, Panorama was installed at the University of California, Los Angeles, USA, in 2015. At the Massachusetts Institute of Technology, USA, a parallel effort to distinguish origins of methane used tunable infrared laser direct absorption spectroscopy to measure doubly substituted methane isotopeologues (combinations of different carbon as well as hydrogen isotopes). A third team at the California Institute of Technology, USA, designed and built a new mass spectrometer, which allowed them to estimate the temperatures at which thermogenic and biogenic methane form. Collectively, these instruments are making transformational advances in our understanding of the origin and provenance of methane gas and are revolutionizing the field of stable isotope geochemistry.

The oldest life-forms on Earth may have originated in the deep oceans under high pressure. To understand the origins of life, researchers look to today’s high-pressure microbial communities. To expand the scope of high-pressure microbial research, and make high-pressure samples available to a broader swath of the research community, DCO supported the custom development of PUSH50, the 50 milliliter (mL) Pressurized Underwater Sample Handler. PUSH50 enables scientists to retrieve and transport biological samples under constant pressure up to 100 MPa and 160°C. It allows microbes that live and grow under high pressures to be moved from field site to the lab, or from lab to lab, without experiencing fatal decompression. Before development of this technique, it was nearly impossible to measure the diversity of high-pressure microbial life. Another research group at the Institut de Physique du Globe de Paris is developing a novel absorption spectrometer that uses a tiny fiber-optic waveguide as the sample chamber. The instrument is being designed for deployment in the deep ocean to detect methane from hydrothermal springs and seeps on the seafloor.

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To address the technological difficulties in retrieving deep-sea samples, DCO supported the development of PUSH50, a device that maintains deep-sea samples at high pressure so they can be recovered under in situ deep-sea conditions and studied in the laboratory without decompression.
The development, deployment, and application of new instrumentation to measure volcanic gas fluxes underpins much of the success of the DECADE group of the RF community. An important DECADE achievement has been the refinement and deployment of the MultiGAS sensor consisting of an infrared spectrometer and electrochemical sensors. It can measure parts per million (ppm) levels of volcanic gases precisely, allowing researchers to quantify the ratio between carbon and sulfur in volcanic gas plumes. By combining this ratio with independent measurements of sulfur dioxide flux (a gas that is much easier to measure spectroscopically than CO$_2$), the volcanic CO$_2$ flux can be determined. The instruments, if installed at the crater rim, produce minute-by-minute time series of volcanic gas composition and CO$_2$ flux, allowing new discoveries to be made concerning how CO$_2$ flux varies before eruptive activity. This monitoring of volcanic gas composition makes it possible in some cases to forecast eruptions, creating a potentially lifesaving tool. Multiple iterations of the MultiGAS sensor have improved its portability and size and even allowed it to be mounted on an unmanned aerial vehicle (drone). This work revolutionizes what we know about the variability of volcanic emissions and may play a role in eruption forecasting in the future.

To help researchers quantify and constrain the source of carbon in volcanic gas emissions, DCO provided partial support for Rutherford Appleton Laboratory, UK, to develop a prototype field-deployable Laser Isotope Ratiometer to fingerprint the isotopic composition of outgassed carbon dioxide in volcanic emissions. Field measurement of the carbon isotopic composition of volcanic gases reveals clues to the provenance of carbon outgassed from volcanoes (e.g., mantle, subducted components, crust) and hence how carbon cycles from the surface environment to the mantle and back again.

DCO supported development of a groundbreaking ultrafast laser instrument system for in situ thermodynamic measurements of tiny samples (an order of magnitude smaller than the width of a human hair) of carbon-bearing minerals and fluids under extreme conditions of temperature and pressure. This prototype enables scientists to determine properties of the sample such as its thermal conductivity, lattice parameters, and how compressible it is, in previously unattainable pressure-temperature regimes, up to 55 gigapascals (about 540,000 times atmospheric pressure at the surface), similar to Earth’s lower mantle. This development expedites vital measurements and eliminates the need for large samples, which are difficult to synthesize and manufacture experimentally at high temperatures and pressures. Scientists then use the thermodynamic properties of the samples to map the potential carbon-bearing phases present in Earth’s interior by working out which ones are stable at various pressure and temperature conditions.

DCO researchers installed a MultiGAS sensor at Rabaul Volcano, Papua New Guinea, to gather emissions data that may help forecast future eruptions. After the research was completed, the equipment was given to the Rabaul Volcanological Observatory to continue data collection.
**Data Science Advances**

**Scientific Discoveries**

Data science paved the way for new insights about the interactions, synergies, and dependencies of the total planetary carbon cycle. DCO’s Data Science Team provided the resources and knowledge for much of this progress. DCO researchers used a dedicated computer cluster at Rensselaer Polytechnic Institute, as well as the expertise of DCO’s Data Science Team there, who offered guidance on how to incorporate state-of-the-art computational algorithms and analytics.

This focus on data science resulted in new, comprehensive, potentially long-lasting databases, offered new ways to look at old data, and integrated emerging data science approaches into several DCO projects. For example, scientists applied network theory (similar to the analysis used to discover Facebook connections) to mineralogy and predicted the number of carbon-bearing minerals on Earth that are currently unknown to science. This work also led researchers to discover a group of 208 mineral species that form either principally or exclusively as a result of human activities, bolstering the call for an “Anthropocene Epoch” in the history of Earth.

DCO researchers also deployed big data and multidisciplinary expertise to document the diversity and distribution of more than 500 minerals of carbon in Earth’s crust and upper mantle. The analysis revealed patterns and trends in mineral evolution with time, through their associations with one another and with the environments in which they are found. The “Carbon Mineral Evolution” initiative created a deep-time data infrastructure to quantitatively understand Earth’s carbon mineralogy through 4.5 billion years of Earth’s history.

In addition to advancing scientific understanding and discoveries, DCO leaves a legacy of open-access databases and metadata best practices. These comprehensive datasets cover a range of topics including diamonds, volcanic gas fluxes and compositions, and a global mineral inventory. All are openly accessible and available for future scientific purposes. For example, the DECADE volcanic gas data portal accesses both the Smithsonian Institution’s Global Volcanism Database and the EarthChem database, allowing investigators to visualize volcanic gas data interactively and to download other linked geochemical datasets (e.g., melt inclusion compositions eruption data). Diamonds purchased for DMGC studies have been registered in the global IGSN (International Geo Sample Number) system to make them accessible for future research.

**Modeling and Visualization Bring Earth to Life**

The challenge of conceptualizing the deep reservoirs and forms of Earth’s carbon lies in the vast length scales and divergent timescales of the planet’s carbon cycle. DCO researchers used modeling and visualization to go inside Earth in a virtual way, using experimental findings and calculations to mimic planetary processes. They employed a variety of modeling approaches to investigate carbon forms, reactions, and movements within Earth through geologic time. They developed models simulating geodynamics, geochemistry, and tectonic reconstructions as well as timescales (from snapshots of the present day to the entirety of Earth’s history). Researchers at the Johns Hopkins University and OFM Research, both in the USA, integrated existing thermodynamic models of magmas (a software package designed to facilitate thermodynamic modeling of phase equilibria in magmatic systems, MELTS) and fluids (Deep Earth Water model, DEW). They were then able to model the mass transfer, speciation, and transport of carbon and other chemical elements as supercritical fluids in Earth.

DCO researchers documented the diversity and distribution of 500 minerals of carbon, using big data approaches and the expertise of many disciplines. Shown here is the manganese carbonate mineral rhodochrosite.
The EarthByte group at the University of Sydney, Australia, created a virtual plate tectonic deep carbon laboratory, which revolutionized the study of mantle-crust-atmosphere interactions over deep time. A range of deep carbon problems have been tackled using this framework, such as reconstructing the CO₂ flux from different magmatic-tectonic settings; and simulating the hydrogen flux produced by serpentinization of the seafloor over geologic time.

University of Oxford, UK, modelers constructed a carbon transport model (Subduction Magmatism Finite Element Code, SubMaFEC), which simulates the physical and chemical transformations of subducting slabs and the melting process, allowing it to compute the controls on the transport of carbon and other volatiles through the system. Lastly, a planetary-scale “box model” of carbon pathways in deep Earth incorporates new DCO discoveries.

DCO’s Modeling and Visualization Forum at the University of California, Davis, USA, worked with researchers across the four communities to create displays and manipulate their data in virtual reality environments. Researchers can now work virtually with mineral networks to see how minerals interact and co-locate with each other, visualize volcanic gas plumes, construct and manipulate molecules using a nanotech construction kit, and model subduction zones. These virtual reality tools give scientists a new perspective on their datasets, allowing them to manipulate data in three dimensions and conduct virtual experiments.

Field Studies Provide a Global Perspective

DCO scientists journeyed to some of the most remote yet scientifically valuable regions on the planet. From establishing global volcano monitoring systems to collecting sediment, rocks, and gases from Earth’s vast seafloor, DCO scientists exploited innovative techniques and technologies in the field to find clues to the nature of carbon deep inside Earth.

Scientists traveled to Costa Rica and Panama as part of a field-sampling program to investigate connections between microbiology, volcanic systems, and the cycling of living and dead carbon as one of Earth’s plates subducts beneath another. Early career scientists from across all four of DCO’s science communities planned and executed a sampling program called Biology Meets Subduction to take a holistic view of carbon cycling at a volcanic arc.

In the Oman desert DCO scientists conducted a drilling project at the Samail Ophiolite, the world’s largest and best-exposed subaerial block of oceanic crust and upper mantle. This exposed “deep ocean substrate” afforded scientists a rare opportunity to observe and understand carbon uptake in mantle rocks—the process of serpentinization—and how microbial ecosystems exist and interact with geologic fluids in such extreme environments. This is but one example of how DCO leveraged collaborations with many organizations such as the US National Aeronautics and Space Administration, the Japan Agency for Marine-Earth Science and Technology, the International Continental Drilling Program, the International Ocean Discovery Program, and many others.

Scientists drilled deep within Earth’s crust beneath the oceans and the continents. By drilling 2.5 kilometers into the seafloor and sampling microbes from continental mines and boreholes more than 5 kilometers deep, DCO scientists constructed models of the ecosystem deep within the planet. This scientific synthesis reflects numerous field expeditions,
including several as part of the International Ocean Discovery Program.

The DECADE group conducted campaigns to some of Earth’s most remote volcanoes (see pages 10–11) and outfitted some of the world’s most active volcanoes with permanent gas composition monitoring stations. One of these campaigns, Trail by Fire, involved a five-month survey of active volcanoes in the Nazca Plate subduction zone from Peru to Southern Chile. DECADE also facilitated a new program to use drones (Unmanned Aerial Systems) with miniaturized gas-sampling equipment to collect volcanic gas measurements at Manam and Rabaul volcanoes in Papua New Guinea. These field investigations add appreciably to the scientific lexicon of deep carbon science.

The tools, datasets, and databases resulting from DCO cross-community initiatives open the door to a wide range of advances in carbon science and the understanding of Earth as a system.
The DCO science communities made fundamental discoveries across four strands of deep carbon science: quantities, movements, and forms of carbon in deep Earth, and their relation to the origins of life on Earth.

Quantities and Movements of Carbon in Earth
DCO scientists have made transformational discoveries about the quantities of carbon in Earth’s deep reservoirs, and how carbon moves between the planet’s interior and surface. Carbon moves between Earth’s mantle, crust, and atmosphere through a combination of mantle convection and plate tectonics as well as by the associated processes of volcanism, melting, and degassing. Volcanism moves carbon through eruption or the shallow intrusion of carbon-bearing magma into the crust, while heating of carbon-bearing rocks causes degassing. Plate tectonics acts to regulate the amount of carbon in our atmosphere and oceans through volcanic and metamorphic (temperature- and pressure-related) outgassing of carbon dioxide, and through removal by subduction, where one tectonic plate containing various forms and quantities of carbon (e.g., carbonate, organic matter) sinks back into the mantle. The mantle contains almost one million times more carbon than the ocean and atmosphere combined, so fluxes of carbon from this vast internal carbon reservoir play a critical role in regulating the temperature and atmosphere of Earth’s surface environment over geologic timescales and have driven evolution and extinction of life on Earth. It is worth noting here that over the past one hundred years, our planet’s geologic carbon emissions have been dwarfed (by 40–100 times) by those produced by anthropogenic activities such as the burning of fossil fuels. These deep reservoirs and fluxes of carbon, despite their importance for Earth’s climate and habitability, were poorly known before the DCO program.

Volcano studies are unlocking inner Earth secrets
Volcanoes are conduits for carbon transport from Earth’s interior to the atmosphere. DCO scientists measured the flux of carbon dioxide emitted from 34 of the world’s most prolific gas-emitting volcanoes. Using these new data, they refined estimates of the total flux of carbon from volcanic outgassing, broken down into different tectonic settings. They now estimate that volcanoes and volcanic regions are outgassing CO$_2$ into the ocean-atmosphere system at the rate of 260–380 megatonnes per year (1 megatonne [Mt] is equivalent to $1 \times 10^9$—one billion—kilograms, or one million metric tons). This estimate includes the CO$_2$ contribution from widespread “diffuse degassing” of CO$_2$ out of fractures and faults in volcanic regions, volcanic lakes, and the CO$_2$ output of the mid-ocean ridge system. To put this figure into context, 260–380 megatonnes of CO$_2$ equals about one-fifth or less (14 to 21 percent) of the CO$_2$ emitted by

DCO has refined estimates of the quantities of carbon in Earth’s deep reservoirs, and how carbon moves between the planet’s interior and surface. Arrows indicate the direction of the carbon fluxes. Numbers are estimates of carbon fluxes in megatonnes per year.
the US transportation sector alone in 2017 (according to 2017 data collected by the United States Environmental Protection Agency).

The DECADE subgroup of the Reservoirs and Fluxes Community (see pages 10–11, 23) focused on the problem of quantifying the flux of carbon from volcanoes and volcanic regions. The vast amount of research conducted by DECADE scientists shows that volcanic carbon outgassing is concentrated at certain areas, including the enormous rifts that cross the continents (e.g., the East African Rift) and calderas (topographic depressions over magma chambers caused by magma evacuation during large eruptions). Other areas of concentrated outgassing are in low-silica lava lakes or “open vents,” such as Mount Etna, Italy, Nyiriagongo in the Democratic Republic of Congo, and Ambrym in Vanuatu. These kinds of volcanoes exhibit “persistent degassing,” which means they emit volcanic gases containing carbon continuously and prodigiously over decades, or even up to millennia in some cases, making their contribution a key part of the transfer of deep carbon to Earth’s atmosphere.

When DECADE scientists discovered that the CO₂ flux from some volcanoes increases days to weeks before eruptions, they raised the possibility that these patterns might be used to forecast volcanic eruptions. At Mount Etna, for example, one of Earth’s most significant sources of volcanic carbon near highly populated areas, the amount of CO₂ emitted increases by 5–8 times about two weeks before a large eruption. At Villarica volcano, Chile, the ratio of carbon to sulfur in the volcanic plume increased by 6–12 times two months before an explosive eruption. Similar patterns have been recognized at Stromboli, Italy, Poas and Turrialba, Costa Rica, and Masaya, Nicaragua. Such changes may hold the key to safe and timely warning of imminent volcanic activity.

DCO researchers have pioneered the development of novel vehicular platforms for MultiGAS and other sensors to monitor volcanoes. In 2017 scientists detected volcanic CO₂ from space for the first time using NASA’s OCO-2 satellite-mounted sensor to detect CO₂ from an eruption at Yasur Volcano on Tanna Island in Vanuatu. These progressions pave the way for future development of more precise space-based sensors for volcanic CO₂ monitoring. DECADE scientists are now using unmanned aerial vehicles (UAVs or drones) to access otherwise inaccessible volcanic vents and are achieving high-precision measurements of gas flux and composition. An expedition to Papua New Guinea brought together five independent groups working with UAVs at volcanoes in 2019, which resulted in successful characterization of the CO₂ flux from Manam and Rabaul volcanoes, as well as setting the stage for future developments in instrumentation and measurement strategy. Such technological developments are laying a foundation for more complete coverage and comprehensive understanding of the volcanic carbon contribution to the global carbon budget, and how to use these carbon signals to forecast eruptions.

**Carbon outgassing from other sources adds up**

Tectonically active continental regions (e.g., mountain belts like the Himalayas in Tibet, and the Apennines in Italy) emit CO₂ produced by metamorphic reactions that release carbon in fluids, by the degassing of unerupted magma bodies in the shallow crust, or by the direct degassing of the mantle along large faults. Mountain belts such as the Himalayas may also act as carbon sinks, storing carbon in deeply buried metamorphic rocks. The CO₂ budget of mountain belts is difficult to estimate; very small amounts of CO₂ seep up through faults and fractures into the atmosphere over large regions in some cases. In some areas, most notably in Italy, the fluxes of CO₂ have been painstakingly measured over large areas by integrating spot measurements of CO₂ flux. DCO researchers created a new database of volcanic and nonvolcanic carbon gas

DCO scientists measured carbon dioxide emissions from more than 30 of the world’s most prolific gas-emitting volcanoes and provided a new estimate of the total flux of carbon from volcanic outgassing.
emissions to make global estimates of fluxes from these sources (magadb.net). This database includes more than 850 gas composition and flux measurements for locations all over our planet. These global datasets make clear that tectonic degassing is concentrated in extensional regimes, where large-scale faults give rise to an enhanced crustal permeability, allowing deep crustal or mantle gases to reach the atmosphere, as in the eastern Himalayas, central Italy, central and eastern Europe, and the continental rift systems.

For a complete picture of the global carbon budget, DCO scientists also sought to determine the seafloor carbon budget. To estimate how much carbon is emitted as magma forms new oceanic crust along the 80,000 kilometers of Earth’s spreading ridges, DCO scientists turned to cutting-edge microanalysis, which revealed new insights into carbon associated with basalts erupted on the seafloor. Basalts contain crystals that host tiny inclusions of trapped liquid magma called quenched melt. Upon cooling, the inclusions preserve dissolved carbon and water that otherwise would be degassed during eruption. Scientists analyzed these tiny melt inclusions, which have roughly the width of a human hair, for their volatiles and other elements using secondary ion mass spectrometry (a technique used to analyze the concentrations of elements precisely in small volumes of a sample). These studies reveal that fluxes of CO₂ from the mid-ocean ridge system on the seafloor are of the same order of magnitude as the flux from volcanoes on land, between 21 and 92 megatonnes per year. The flux of CO₂ is not constant everywhere along the mid-ocean ridge system, however. A hundredfold variability in outgassing is observed at different spreading centers around the world, which largely reflects differences in the carbon content of the underlying mantle: some regions of carbon-rich mantle give rise to particularly high CO₂ fluxes out of Earth’s interior to the atmosphere. The flux of carbon from mid-ocean ridges remains, however, a tiny fraction (much less than 1 percent) of the total amount of carbon being released due to anthropogenic activities such as the burning of fossil fuels.

Swallowing carbon back into deep Earth
When one tectonic plate slides beneath another, carbon from the ocean-atmosphere system returns to the interior of Earth. This process, called subduction, is important be-
cause the balance between volcanic and tectonic carbon outgassing and the removal of carbon by subduction controls the amount of carbon present in the atmosphere and oceans and consequently, the temperature and habitability of Earth's surface environment. In modern Earth, weathering, formation of carbonates on the seafloor, burial of organic carbon, and subduction remove carbon at rates similar to the flux of carbon added to the atmosphere by volcanoes and tectonics. This means that in today's subduction zones, the amount of carbon going down roughly equals the amount coming out and that these processes have kept the size of the surface carbon reservoir (and our climate) in delicate balance over tens to millions and billions of years. However, during several periods in Earth's history (about 7 times over the past 500 million years) this balance has been perturbed through large volcanic eruptions (“large igneous provinces” erupting more than 0.5 million cubic kilometers of magma), which have degassed enormous amounts of carbon. In some instances, these events triggered rapid climate change and mass extinction.

Carbon inputs to subduction zones consist of both carbon-bearing sediments and carbonated oceanic crust. Ocean drilling, largely through the International Ocean Discovery Program (iodp.org), shows scientists what kind and how much sediment and carbonated crust is going down into subduction zones. DCO scientists discovered that the relative amounts of inorganic and organic carbon within the down-going slab varies from place to place on the seafloor. This variability is related to the subduction zone's proximity to the continents, ocean circulation patterns, and the latitude, making each subduction zone unique.

DCO scientists also have explored the fate of carbon after it descends on the tectonic conveyor belt to the mantle. They conducted experiments mimicking Earth's interior to understand how subducting slabs sink into the mantle and then heat up. They found that carbon in the slab may dissolve efficiently into the dense fluids produced when hydrous minerals in the subducting slab (e.g., serpentine) break down. When released from the sinking slab, the carbon-bearing fluids migrate upward and escape in the “forearc” in methane seeps (which often manifest as hot and cold springs on the submarine continental shelf or on land) or as carbon dioxide gas from arc volcanoes. Before DCO work on subduction carbon budgets, little was known about the mass balance of carbon between these environments.

Early career scientists leading an ambitious and multidisciplinary field campaign in Costa Rica, called Biology Meets Subduction, uncovered an important piece of the subduction carbon budget puzzle. By sampling tens of springs in the Costa Rican forearc and volcanic arc, they found that a large amount of carbon (around 10–20 percent of what is emitted from the volcanoes in the arc) may be leaving the slab beneath the forearc. Instead of reaching either the atmosphere or the ocean through seeps and springs, or the deep mantle, the carbon is “sequestered” deep underground, forming calcite deposits. This finding means that less carbon than was previously estimated may return to the deep mantle at subduction zones and is instead stored in the overlying crust. It is likely that different subduction zones, each with its own thermal structure and geometry, return different proportions of carbon from the slab to the deep mantle.

These studies have shown that while carbon outgassing (through volcanoes and tectonics) largely balances carbon replenishment (by subduction) through geologic time, there is significant spatial and temporal variability in the carbon subduction budget. This variability may allow us to understand perturbations to Earth's climate system in the past. For example, in the warm Cretaceous Period about 100 million years ago, the total length of subduction zones was much greater than it is today, which meant there were many more “arc” volcanoes emitting CO\textsubscript{2} into the atmosphere. In addition to the igneous provinces generated by hot spots during the Cretaceous, it is likely that there was a larger proportion of “continental” subduction zones. There, magmas may have
interacted with stored crustal carbonates in the overlying plate, releasing carbon into the atmosphere and causing short-lived imbalances in the geologic carbon cycle, which led to periods of warm climate.

**Diamonds divulge Earth’s deep mysteries**

Some of DCO’s greatest achievements involve diamond research, which has accelerated dramatically as a direct result of the program. DCO integrated several existing groups, forming a wider network that supported early career researchers, shared techniques, and drove forward novel methodologies. Diamond, as well as being a striking gemstone, is an elemental form of carbon that is stable in the mantle. DCO scientists in the DMGC subgroup of the Reservoirs and Fluxes Community (see pages 10–12), have made some astounding discoveries working with diamonds and their inclusions.

Not only do diamonds have commercial value, but the scientific secrets they harbor are priceless. DCO researchers have shown in a sequence of groundbreaking studies that diamonds may form in at least three different ways. When carbonated melts (liquid hot magma carrying dissolved carbon) infiltrate the oxygen-poor conditions of the mantle, they may be transformed to diamonds in a process called redox freezing. Some other diamonds may originate in water-rich fluids that contain dissolved salts and organic acids (carbon-bearing compounds with acid properties, capable of donating a proton, or hydrogen ion). Shifts in the pH of such fluids may cause direct precipitation of diamonds in the mantle. A third way that diamonds may form is through direct precipitation from carbon-bearing metallic iron melt in the lower mantle. In all cases, diamonds may grow around and trap bits of mantle rock that provide tantalizing clues to their origins and to the nature of deep Earth.

Diamonds provide unique “windows” into the storage and transport of deep carbon over more than 3.5 billion years of geologic time. Diamonds can be erupted near or onto Earth’s surface through kimberlite eruptions, which are explosive volcanic events originating several hundred kilometers deep within Earth’s mantle. DCO researchers discovered that individual diamonds may have a long and complex growth history, with episodic growth periods for a
single diamond occurring over as much as 2 billion years. Through studies of mineral and fluid inclusions in diamonds and their isotopic composition, scientists can now infer how carbon recycles from the surface environment back into the mantle, and the nature of the carbon-rich fluids that gave rise to diamond formation.

“Super-deep” diamonds originate from the lowermost upper mantle, the transition zone (between 440 and 660 kilometers deep) and perhaps also from the lower mantle (more than 660 kilometers deep). DCO scientists discovered tiny and exceedingly rare inclusions of ringwoodite in a Brazilian diamond (ringwoodite is the most abundant mineral of the transition zone, but because it forms only under high temperatures and pressures, was previously found only in meteorites or synthesized in the laboratory). Water makes up about 1.4 percent of the inclusion’s weight, lending credence to an about 30-year assumption that Earth’s transition zone might hold “several oceans’ worth” of water. Scientists also investigated sulfide inclusions in diamonds and found isotopic evidence of sulfur with an incredible history: it had erupted through volcanoes high into Earth’s stratosphere more than 2 billion years ago, then accumulated on the seafloor in sediments, and was later subducted back into Earth’s mantle where it became part of a growing diamond. These studies have helped scientists again prove the two-way exchange of carbon and other volatiles between Earth’s surface and interior.

DCO scientists studied large, gem-quality diamonds of the type included among the British Crown Jewels (e.g., the Cullinan and Koh-i-noor diamonds) known as megacryst diamonds. Inclusions consist of metallic phases, with significant quantities of dissolved carbon. These metal inclusions are associated with high-pressure mineral phases such as majorite garnet and calcium silicate perovskite (a mineral thought to be common in Earth’s deep mantle but never seen before in a natural sample). In other diamonds, scientists observed calcium silicate perovskite directly for the first time. These groundbreaking observations shed light on the chemical state of the deep mantle. It has long been predicted that the availability of oxygen decreases with depth in the mantle, stabilizing iron in its native state. The discovery of metallic iron in deep diamonds now confirms this prediction and provides insight into how the planet may have differentiated. These studies also highlight a new mechanism for diamond formation: they may precipitate directly out of a metallic liquid.

**Melts in Earth’s interior**

A primary way that carbon moves through the interior of our planet and is transported to the surface environment is through the melt (molten rock or metal) phase. DCO researchers have been studying various kinds of melts, each found in a different region of Earth’s interior and all playing key roles in the deep carbon cycle. Early in Earth’s history, for example, iron-rich melts segregated from the silicate portion of Earth and formed a core 3400 kilometers in diameter. DCO researchers captured a snapshot of this process in a pioneering investigation of metallic inclusions in ultradepth, gem-quality diamonds.

DCO scientists also have made great progress in understanding how carbon is carried by silicate melts in the mantle and crust over a wide range of temperature and pressure. Well-calibrated thermodynamic models for various conditions relevant to Earth’s present and past describe how carbon dissolves in melts in the crust and where carbon escapes into the atmosphere through volcanism. DCO scientists achieved seamless modeling of water-rich melts and fluids from mantle to crustal depths by interfacing MELTS software with the Deep Earth Water (DEW) model (see page 36).

Not all melts in Earth are iron- or silicate-based. Through experimentation, DCO researchers discovered that carbonatite melts may be ubiquitous in the mantle. These melts, created by small degrees of melting of a carbon-rich region of the mantle, may consist of recycled slab material. They are formed near the subducting slab, and also deep in the melting regions beneath ocean island volcanoes and mid-ocean ridges. These melts are important carriers of volatiles and a
range of exotic trace elements. Where carbonatite melts occur in quantity and intrude into the crust, they can give rise to economically valuable concentrations of rare earth elements.

Models of carbon movements and storage in Earth

Plate tectonic reconstructions have provided a platform for a set of powerful new models to describe how Earth’s deep carbon cycle has changed through geologic time. These models apply new understanding derived from DCO experimental and theoretical studies over the past decade to Earth’s dynamic past. The models describe how the constant motion of Earth’s tectonic plates changes the layout of continents, the number of outgassing volcanoes, and the height and length of mountain belts. The software modeling tool GPlates, for example, makes possible interactive visualization of plate tectonics, providing a framework to model the lengths of subduction zones, mid-ocean ridges, and mountain belts through the Phanerozoic (the past half billion years or so). GPlates can also be used to estimate carbon outgassing and ingassing, as well as the mass of carbon that may be locked up as marine carbonates. DCO scientists have shown, for example, that CO₂ degassing from continental rift environments (similar to the East African rift today) may have been much more important in the past than they are now. Studies show that in two periods of Earth’s history, one between 160 million and 100 million years ago and one beginning 55 million years ago, rift-related degassing may have amounted to more than three times today’s values and may have caused global warming. Another study quantified the role of mid-ocean ridges in sequestering carbon and delivering it to subduction zones over the past 400 million years, which may induce cyclicity in atmospheric CO₂ levels.

The burial of carbonates on the seafloor, and their subsequent subduction, is the principal mechanism by which carbon is removed from the surface reservoir and therefore bears on our understanding of global climate. The importance of deep-sea carbonate deposition has increased substantially over the past 100 million years. Deposition rates increased following the evolution of calcareous plankton, the gradual increase in the carbonate compensation depth in the oceans (the depth above which carbonate may precipitate), and increased weathering rates caused by the uplift of the Himalayas between 50 million and 30 million years ago. GPlates models show that increasing accumulation of deep-sea carbonates since the Cretaceous is linked closely to global cooling in the geologic record and represents a previously unquantified aspect of the global carbon cycle.

DCO scientists also took into account the fact that Earth has not always evolved at a consistent rate. The steady-state carbon storage and transport model cannot account for “catastrophic” events at various times throughout Earth’s history. DCO scientists evaluated how such perturbations led to shifts in the carbon cycle. They studied continental flood basalts (immense volcanic eruptions of basalt, which have occurred a handful of times in the past 500 million years). These basalts outgassed thousands of megatonnes of carbon, creating a warm atmosphere and ocean, which led to anoxia that may have lasted for millions of years. Large-scale shifting of the continents also may have led to “tipping points” in climate, plunging Earth into icehouse or greenhouse conditions. Asteroid impacts may have vaporized oceans and carbon-bearing sediments at times in Earth’s long history, and, depending on their size, may have had similar effects on flood basalt eruptions, causing mass extinction and climate...
DCO scientists have considered these events and their possible effects on the global carbon cycle in the past and in the future.

Forms of Carbon in Earth
Carbon exists in diverse solids and liquids in the interior of Earth. These materials may include combinations of carbon with oxygen (e.g., carbonate minerals, carbonatite magmas, and carbon dioxide), elemental carbon (e.g., graphite and diamonds), and combinations of carbon with iron (e.g., carbides and carbon-bearing iron melts). Other materials form through combination with hydrogen (e.g., kerogen, coal, petroleum, methane, and its clathrates) or other elements (silicon, sulfur, nitrogen, and more). In studying the forms of carbon at extreme conditions, DCO researchers characterized states (structures and properties) and transformations (conditions, rates, and mechanisms) of carbon-bearing materials at extreme conditions. Over the last decade, this research led to remarkable discoveries about the forms of carbon in Earth.

The iron-rich core may hold a large part of Earth’s total carbon budget
A fundamental question that DCO scientists sought to answer was where is the carbon in Earth? The core of Earth is largely made of iron alloy. The inner core (with a radius of around 1220 kilometers) is solid iron alloy, with smaller amounts of other siderophile (iron-loving) elements. It has long been known that particular types of seismic waves (the waves generated by large earthquakes) travel more slowly through the inner core than expected for solid iron, suggesting that the inner core is less dense than pure iron. To explain the density of the core, a small fraction of a light element or elements is required (which may be carbon but may also involve some oxygen, hydrogen, or silicon). DCO scientists have made important discoveries concerning the nature and form of carbon held within the core. In laboratory experiments, DCO researchers demonstrated that the speed of seismic waves through a form of iron carbide, Fe7C3, is consistent with observed seismic wave speeds through Earth’s inner core, which makes this phase a strong candidate for the dominant mineral of the inner core. The outer core, in contrast, is liquid, made of molten iron alloy. It was already well understood that convection of this molten liquid generates Earth’s magnetic field, thereby protecting all life on Earth from cosmic rays that would otherwise strip away the protective layer of atmospheric ozone. The liquid iron alloy of the outer core may hold more carbon than the solid iron core; in fact, scientists believe that up to one percent by mass of the outer core may be carbon. These findings, taken together, suggest the core may hold two-thirds or more of the planet’s carbon, locked away there since the earliest stages of our planet’s geologic evolution. This “missing carbon” brings the total carbon content of Earth closer to what is observed in the sun and helps us to understand the origin of Earth’s carbon from stellar material. Researchers are continually refining understanding of how much carbon may exist in the core by undertaking increasingly complex experiments to look at the effects of other volatiles, such as sulfur, on the solubility of carbon in iron alloys.

Discovering the nature of carbonates and CO2 at high pressure
Although likely to be much less carbon-rich than the core, Earth’s vast rocky mantle is the second largest reservoir in Earth for carbon. The mantle is largely composed of silicates (minerals made up of negatively charged silicon-oxygen frameworks charge-balanced by cations such as magnesium, calcium, and iron). In pockets and veins between these silicates, the mantle holds carbon in various forms, ranging from water-, carbon-, and silica-rich fluids and minerals including pure carbon forms (graphite and diamond), carbides, carbonates, and solid CO2 ices. The form of the carbon-bearing material present in any particular part of the mantle depends to a large degree on the availability
of oxygen. Where oxygen is available, carbonate minerals or melts abound; where oxygen is absent, hydrocarbons, carbides, or diamonds occur. The immense range of carbon forms in the interior of Earth is largely due to the action of plate tectonics. Oxidized carbon from the surface of Earth returns to the deep interior by subduction, which in turn stirs up the mantle.

DCO researchers have made enormous advances in understanding the range of structures and properties of carbonates in the silicate mantle. Armed with such knowledge, scientists now understand the fate of subducted carbon, leading to better informed projections of the amount of carbon that may exist in the deep mantle. One such discovery concerns the “coordination” of carbon in mantle minerals. Coordination refers to the number of atoms of a particular type, oxygen in this case, that surround a carbon atom. At low pressures, carbon exists either as molecular CO₂, which forms a linear O-C-O molecule, or as carbonate, where three oxygen atoms surround a carbon in a single plane. DCO researchers have discovered, through experiments, that at high pressures another configuration is possible: a tetrahedral structure in which one carbon atom is bonded to four oxygen atoms by single bonds, forming a 3-D pyramidal shape. This tetrahedral configuration is common in silicates, where four oxygens surround a silicon atom. The discovery of tetrahedral carbon in carbonates raises the exciting possibility that at mantle depths greater than about 1800 kilometers, carbon might substitute for silicon in common minerals of the lower mantle. This suggests that the “storage capacity” of the lower mantle for carbon is greater than once thought.

Studies of the high-pressure forms of carbonates are particularly important when considering the fate of subducted slabs in the mantle. DCO researchers have carried out experiments to understand what happens to the carbonate mineral dolomite at pressures in the lower mantle (dolomite is an important component of down-going slabs containing both magnesium and calcium). They found that while the magnesium component reacted with iron to produce diamond, iron carbide (Fe₃C), and magnesium iron oxide (Mg,Fe)O, the calcium component of the carbonate persisted in a high-pressure form. This work suggests that slab carbonates could, in theory, persist down to the lower mantle. Indeed, inclusions of calcium carbonate (CaCO₃) have been found in deep diamonds. Together these studies provide good evidence that at least some carbon is transported from the surface all the way to the deep mantle through the action of plate tectonics.

DCO scientists also found that other forms of oxidized carbon may occur in the mantle of Earth and possibly other planets. At the high pressures and temperatures of planetary interiors, the stable form of CO₂ may be a solid ice that would be an important carbon reservoir. Solid CO₂ may exist deep within Earth’s mantle, transported there by subduction, and it is a likely constituent of the interiors of other planets such as Saturn and Jupiter. DCO scientists have quantified the range of polymorphs and properties of solid forms of CO₂. It can exist in a crystalline form under conditions of the core-mantle boundary. Some high-pressure tetrahedral forms of “dry ice,” called phase V (CO₂-V), exhibit high density and hardness. It is even possible that these phases could form solid solutions with silicate minerals, a configuration that may exist in the interior of some rocky planets. In other high-pressure experiments, DCO scientists found that another form of oxidized carbon, H₂CO₃, may

Using statistical relationships between mineral localities and frequency of occurrence, DCO researchers estimated the total number of carbon-bearing minerals at the surface of Earth, including 145 species of carbon-bearing minerals yet to be discovered. They launched the Carbon Mineral Challenge to citizen scientists, who identified 30 of these “missing” minerals, including this one: triazolite.
exist in solid form in the interiors of some icy planets, and may exist in dissolved form (as carbonic acid) in subduction zones in Earth.

Creating a Deep Earth Water model

In addition to solid forms, carbon exists in fluid form deep inside Earth. Until recently, understanding how carbon is carried in deep, water-based fluids has been an unresolved scientific goal, but that all changed in 2013 with the publication of a series of groundbreaking studies. A team of DCO theoreticians published first-principles calculations of the dielectric constant of water for high pressures and temperatures ([dewcommunity.org](http://dewcommunity.org)). These new findings, together with some fundamental experimental studies by DCO scientists, gave rise to the Deep Earth Water (DEW) model in 2014, which in turn has led to some of the most important scientific advances of the DCO program.

The DEW model opened the door to modeling carbon transport in ionic fluids and water-rock interactions at depths as great as 200 kilometers in the mantle. A critical advance made possible by the DEW model is a new understanding of how diamonds form in Earth’s mantle. The extraordinary richness and diversity revealed by this new picture of mantle water-rock interaction suggests that diamonds may form in deep fluids merely because of a shift in the pH (acidity) of the fluids. In another scenario, complex hydrocarbons—that is, oil—may form from reactions involving acetate, perhaps producing fuel for deep microbial life.

DCO researchers have discovered, through experiments and theoretical DEW modeling, that carbon may exist as various species with oxygen and with hydrogen, and in combination (complexes) with other major elements in deep fluids (e.g., magnesium with carbon). Thus, the migration of carbon in deep fluids is closely linked to the migration of many other chemical elements. Another first-principles study produced the surprising result that carbon dioxide, as the molecule CO₂, is probably only a minor form of carbon in deep fluids, contrary to decades of previous studies. Instead, H₂CO₃, a complex of CO₂ and H₂O, is likely to be abundant. This new finding turns existing thinking on its head.

A radical new outcome of the DEW modeling shows that the amount of carbonate that is soluble in these high-pressure fluids is much higher than previously thought. This provides a mechanism for releasing carbon from the slab and carrying it to the mantle wedge and perhaps, ultimately, back to the atmosphere through volcanic outgassing. It has become clear that carbon plays an outsized role in subduction zone fluids, not only for mediating the transport of other elements, but perhaps also for setting the redox state of the mantle wedge. This discovery is an important piece of the puzzle in the development of a generic subduction zone model. It is supported by observations of carbonate dissolution and precipitation in exhumed subduction zones, and by the composition of fluid inclusions in diamonds in ultra-high-pressure subduction zone rocks.

The DEW model also sheds light on an enduring scientific mystery: Why is Earth’s atmosphere so rich in nitrogen when compared with Venus and Mars? DEW modeling shows that under the conditions in Earth’s mantle, nitrogen should exist in aqueous solutions as N₂; because planets cannot hold onto the gas in their interiors, nitrogen pumps out into the atmosphere through volcanism.

Carbon mineral diversity and evolution through Earth’s history

In addition to the core and mantle, DCO scientists have studied the forms and diversity of carbon-bearing minerals near Earth’s surface, in the crust. A team of researchers has cataloged the number of carbon-bearing mineral species and the localities in which they are found. They have discovered statistical relationships between the number of localities in...
which mineral species are found, and the frequency at which they are found, making it possible to estimate the total number of carbon-bearing minerals at the surface of Earth. These relationships also hold true for other, non-carbon-bearing minerals. Based on these predictions, DCO issued a Carbon Mineral Challenge (mineralchallenge.net) to amateur mineral collectors in 2015 to find the 145 species of carbon-bearing minerals predicted but yet to be discovered, with specific indicators to the sort of locality in which they may be found. Responding to the challenge, citizen-scientists discovered 30 new minerals, including two, abellaite and parisite-(La), whose compositions were predicted.

Novel network analysis tools developed by DCO researchers and data scientists have allowed simultaneous visualization of multiple variables from large mineralogical datasets. These new approaches, using big data methods (e.g., data network analysis) for the first time in this field, have led to entirely unforeseen insights and discoveries. The network diagrams allow researchers to see clearly which minerals coexist with one another, and how these associations may “evolve” through geologic time, in response to variables such as the rise of oxygen in Earth’s atmosphere, the assembly of supercontinents (with associated orogenic belts), and the appearance of carbonate-producing organisms in the Phanerozoic.

This research makes use of novel Data Science methods to interrogate databases of mineral occurrences and rarity and an entirely new system of mineral classification that will revolutionize museum collections. The Natural History Museum of Vienna has opened a new exhibit based on this new classification; others at the Museum of Natural History in New York and the University of Arizona are in planning stages. This new picture of how minerals evolve in tandem with Earth’s system is much more than just a classification. It has a much wider reach, with implications for new understanding of the timing and locality of ore deposit formation, as well as links to climate and to the evolution of life on Earth.

Abiotic Methane and Links to Life’s Origins

Methane and other hydrocarbons are not only important sources of energy for society but also may have catalyzed and nurtured Earth’s earliest forms of life. Hydrocarbons may be stored in Earth’s deep reservoirs on long timescales but also transported on rapid timescales as they seep from Earth’s interior into the atmosphere. Methane, along with hydrogen and higher hydrocarbons, can be major constituents of fluids in the crust and mantle, and these fluids may reach the surface of Earth in modified forms. The DCO community has identified a large number of field sites where methane is being released to the ocean-atmosphere system, including deep boreholes, continental seeps, and hydrothermal vents. Understanding the origin of such fluids is important for assessing potential future sources of energy and for understanding the link between the biological realm and the geosphere. Scientists have long understood that hydrocarbons deep within Earth can be the product of thermal decomposition of organic matter or digestion of organic compounds by microorganisms. However, important discoveries made by DCO scientists center on the realization that, under certain conditions of temperature, pressure, and composition, methane and more complex
hydrocarbons can form abiotically, that is, with no involvement of biomolecules.

**How does methane form?**

Methane seeping through oceanic crust into the oceans at the seafloor may be produced by thermogenic processes (e.g., the breakdown of organic matter during heating), as a by-product of the action of living microbes, or by geologic processes (e.g., reactions associated with serpentinization in the presence of carbon). Studies show that in some cases all of these sources contribute to methane production.

Serpentinization is a geologic low-temperature reaction involving heat and water in which mantle rocks oxidize ($\text{Fe}^{2+}$ converts to $\text{Fe}^{3+}$) and hydrolyze. The mantle underlying the ocean crust is made of peridotite, which is a solid rock made up of the minerals olivine and pyroxene (both are iron- and magnesium-bearing silicates). In places such as slowly spreading mid-ocean ridges (“core complexes” such as the Atlantis Massif, near the Mid-Atlantic Ridge), peridotite outcrops on the seafloor and seawater circulates through it. The peridotite reacts with the seawater and converts to a mixture of serpentine, brucite, magnetite, and other minerals. This reaction is important because it produces hydrogen and may produce methane (abiotically) if carbon is present (e.g., produced from the degassing of magma). The hydrogen provides fuel for microbial life on the seafloor and in the crust and sediments.

It is thought that methane may form through a series of generalized Fischer-Tropsch reactions, which produce methane and perhaps higher hydrocarbons through reaction of hydrogen and carbon dioxide. However, these reactions are sluggish at the conditions of fluid circulation through peridotite exposed on the seafloor, despite the large amounts of methane observed in hydrothermal fluids at sites of active serpentinization. Discoveries by DCO scientists supply a potential answer to this conundrum: reactions may shift toward methane production if the reactions take place in a confined pore space, driven by the adsorption of water onto the pore walls.

**New instrumentation to distinguish abiotic methane**

Given the many ways that methane can be produced in geologic environments, a fundamental question arises: Can we distinguish biotic sources of methane from abiotic sources? The development of methods to solve this problem is a major DCO achievement. DCO scientists at the University of California, Los Angeles, used the Panorama mass spectrometer to separate two rare mass-18 isotopologues (combinations of different carbon and hydrogen isotopes) of methane, which can be used to distinguish abiotic and biotic methane. A team at the California Institute of Technology is working on similar analytical advances to isolate the isotopologues of methane using a custom mass spectrometer called the Thermo IRMS 253 Ultra. Both instruments are now commercially available as a result of the partnership between these companies and the DCO. A parallel effort at the Massachusetts Institute of Technology measures the isotopologues in methane samples using tunable infrared laser direct absorption spectroscopy.

Methane stable isotope geochemistry may be used as a fingerprint for how the molecules were formed. For example, methane produced by microbial processes has very different proportions of mass-18 doubly-substituted isotopologues than methane formed by other processes. Variations in the concentration of these rare isotopic species of methane are temperature-dependent, so could in some cases provide information about the temperature of formation. Researchers have found, however, that the ratios between these doubly-substituted isotopologues are not always in equilibrium; in such cases the calculated temperatures are spurious, although they still may provide valuable information about the source of methane. Isotopologue analyses of methane provide constraints on the generation of methane in diverse settings, including the Lost City hydrothermal system, the deep mines in the Precambrian cratons in Canada and South Africa, mud volcanoes from Taiwan, and various continent-bound ultramafic (high-magnesium) igneous complexes.

Methane produced at mud volcanoes in the Nankai Trough off the eastern coast of Japan has been analyzed for its proportions of doubly-substituted isotopologues using infrared spectroscopy. The analysis showed that almost all of the methane from these particular mud volcanoes comes from microbes, which may have survived for millions of years beneath accumulated seafloor sediments, under increasing pressure, and with limited carbon and energy...
sources. This research raises intriguing questions about the origins of the vast reserves of methane trapped in hydrates and clathrates in the world’s oceans.

**Scientific drilling to understand serpentinization**

DCO researchers have drilled into the continents and dived deep into the oceans to understand the environments favoring serpentinization, both today and in the past. These global studies are shedding light on the origins of these carbon-bearing fluids, and in consequence possibly the origins of life on Earth.

An ophiolite (oceanic crust brought to the surface by plate tectonics) in the Sultanate of Oman, is the world’s best exposed and most accessible extensive outcrop of oceanic crust and upper mantle. There, DCO scientists are engaged in an ambitious drilling project to study how the igneous rock peridotite, which makes up a large proportion of the subducting slab, takes up carbon. Already the project has revealed that the peridotite hosts a large reservoir of carbon that was dissolved from a subducting slab and deposited in a mantle wedge. This deposition leads to large increases in rock volume, resulting in extensive fracturing. Drilling through this ophiolite offers an unparalleled opportunity to study carbonation of peridotite and better understand carbon sequestration by ultramafic rocks.

In the Atlantic Ocean, the Lost City hydrothermal field is a unique environment where mantle peridotite has been exposed on the seafloor, a so-called core complex. Expeditions there have allowed scientists to observe mantle rocks being actively altered by seawater and serpentinized, sustaining diverse microbial communities fueled by the hydrogen and methane produced by water-rock interaction. Located west of the Mid-Atlantic Ridge on the Atlantis Massif (about 20 kilometers away from the spreading center), the Lost City has towering hydrothermal chimneys, which pump serpentinizing vent fluids out into the ocean. This site has mantle peridotite outcropping on the seafloor, a result of tectonic faulting and uplift. The landscape is dramatic: cliffs of peridotite seep fluids, which feed the growth of pale and delicate carbonate towers. The high-pH fluids trigger carbonate precipitation upon mixing with seawater and serve as important energy sources for microorganisms that thrive in the porous chimney walls. Drilling and coring have provided samples of the serpentinization process in action, as drills use a new type of sensor that records methane, oxygen, pH, oxidation reduction potential, temperature, and conductivity.

Drilling at Lost City has answered important questions regarding the process of serpentinization and its ability to produce hydrogen and methane in the presence of carbon, and to serve as a source of fuel for microbial life. DCO researchers have found that the rate of serpentinization varies with pressure, temperature, pH, and mineral and fluid chemistry. The rate of abiotic methane production arising from serpentinization probably also varies, controlled by the availability of catalysts such as platinum-group metals.

A series of wells drilled into the Coast Range Ophiolite in northern California, a section of ancient seafloor, has led to discoveries about microbial diversity in serpentinizing fluids. Serpentinization releases hydroxyl ions, which give rise to highly alkaline fluids and present challenges to life. Studies show that only a few key bacterial taxa are capable of survival in such environments.

**Origins of life**

If abiotic methane can be produced in serpentinizing environments, what about other hydrocarbons and organic molecules? What about life? Hydrothermal vents at mid-ocean ridges have long been proposed as potential sites for the origin of life. DCO researchers conducted laboratory experiments to find out whether it is possible to synthesize the building blocks of life using the reactions between the prod-

Expeditions to the Lost City hydrothermal vent field have allowed DCO scientists to observe mantle rocks being actively altered, sustaining diverse microbial communities fueled by the hydrogen and methane produced by water-rock interactions. Studies here and at other locations around the globe are shedding light on the origins of carbon-bearing fluids with implications for the origins of life.
uct of serpinetization (hydrogen) and CO$_2$ derived from magma building the oceanic crust. They synthesized a wide range of hydrocarbon compounds, including $n$-alkanols, $n$-alkanoic acids, $n$-alkenes, $n$-alkanes, and $n$-alkanones, all components of living cells. Other studies have revealed an abundance of complex organic carbon compounds in serpinetized ultramafic rocks. These compounds may derive from past microbial activity within the oceanic crust, potentially supported by the by-products of serpinetization.

For decades, scientists have pondered whether amino acids, the building blocks of life, could arise spontaneously from sequences of chemical reactions in a water- or rock-dominated environment. Researchers in the DCO community made an important breakthrough when they discovered abiotic synthesis of amino acids and other complex organic molecules in the pores of ultramafic rocks deep beneath the seafloor in the Atlantis Massif. Scientists speculate that these amino acids may be incorporated into the fluids issuing from hydrothermal vents. Until recently, abiotic amino acids, created by terrestrial geochemical processes independent of life, had not been discovered preserved in Earth’s geologic record. The amino acids are thought to have formed during the serpinetization process, whereby mafic minerals in the rocks were hydrated in the presence of CO$_2$. This important discovery has raised questions about the possibility of life on other rocky planets and moons, which may host serpinetizing systems.

Other discoveries point to microbial life appearing much earlier in Earth’s history than previously thought and in a slightly different environment, this time on land. DCO researchers found microbial biosignatures and minerals matching modern hot spring environments (such as Yellowstone National Park, USA) in 3.5-billion-year-old rocks of the Pilbara Craton in Australia.

**Deep biosphere**

Studies of the terrestrial and marine subsurface reveal remarkable and extensive subsurface microbial ecosystems. These deep and dark biological reservoirs may extend to several kilometers beneath the seafloor and perhaps deeper in the continental subsurface. Some of the microbes that live here, instead of using the sun’s light as a source of energy, rely on energy from geofuels (hydrogen and methane) or abiotically formed organic matter to drive the synthesis of molecules essential for life and reproduction. Other types of microbes in the subsurface make use of small amounts of photosynthetically derived carbon that trickles down into the subsurface, making them possibly the most

DCO discoveries point to microbial life appearing on land much earlier in Earth’s history than previously thought. DCO researchers found microbial biosignatures and minerals matching modern hot spring environments (such as Champagne Pool, Wai-O-Tapu, New Zealand shown here) in 3.5-billion-year-old rocks of the Pilbara Craton in Australia.
energy-efficient organisms on the planet. Microbial cells of vast evolutionary diversity in the subseaﬂoor and deep subsurface continental crust perform carbon transformations that over billions of years have remodeled Earth and fostered the emergence of complex life-forms. Perhaps as many as $10^{12}$ different kinds of microbes yield astounding genomic and functional diversity that enables the adaptation of single-celled organisms to nearly any environment on Earth, including those at high pressures and temperatures and those with extreme energy limitations. DCO researchers have spent a decade exploring this vast and poorly understood biotic fringe.

With insights from hundreds of samples under the continents and seas, DCO researchers approximate the volume of the deep biosphere at 2 billion to 2.3 billion cubic kilometers, almost twice the volume of all oceans, as well as the carbon mass of deep life in the subsurface. Life in deep Earth totals 15,000 to 23,000 megatonnes of carbon, about 250 to 400 times greater than the carbon mass of all humans on the surface. The deep biosphere constitutes a “subterranean Galapagos” comprising members of all three domains of life: bacteria and archaea (microbes with no membrane-bound nucleus), and eukarya (microbes or multicellular organisms with cells that contain a nucleus as well as membrane-bound organelles). Two types of microbes—bacteria and archaea—dominate deep Earth. DCO scientists predict about 70 percent of Earth’s bacteria and archaea—dominate deep Earth. DCO scientists predict about 70 percent of Earth’s bacteria and archaea—dominate deep Earth. DCO scientists predict about 70 percent of Earth’s bacteria and archaea live in the subsurface. Among them are millions of distinct types, most yet to be discovered or characterized. This so-called microbial dark matter dramatically expands our perspective of the tree of life.

Deep microbes are often very different from their surface cousins, with life cycles on near-geologic timescales, subsisting in some cases on nothing more than energy in the form of hydrogen from rocks. The genetic diversity of life below the surface is comparable to or exceeds that above the surface. While subsurface microbial communities differ greatly between environments, certain genera and higher taxonomic groups are ubiquitous—they appear planetwide. Microbial community richness relates to the age of marine sediments where cells are found—suggesting that in older sediments, food energy has declined over time, reducing the diversity of the microbial community.

DCO scientists have discovered subseaﬂoor microbial communities in coal-bearing sediments as deep as 2.5 kilometers below the ocean ﬂoor, which play important ecological roles in biogeochemical carbon cycling over geologic time. In other types of environments, biomass may actually increase with depth as they near hot spots of chemosynthetic energy, such as serpentining rocks, or near hydrothermal vent ﬂuids.

Microbes face significant challenges inhabiting these dark and deep environments, having to compete for energy, resources, and space. They also have to develop adaptations to cope with extreme pressures and temperatures. The absolute limits of life on Earth in terms of temperature, pressure, and energy availability remain unknown. The records continually get broken. A front-runner for Earth’s hottest organism in the natural world is Geogemma barossii, a single-celled organism thriving in hydrothermal vents on the seafloor. Its cells, tiny microscopic spheres, grow and replicate at 121°C (21 degrees hotter than the boiling point of water at atmospheric pressure). Microbial life can survive up to 122°C, the record achieved in a lab culture. The record depth at which life has been found in the continental subsurface is approximately 5 kilometers; the record in marine waters is 10.5 kilometers beneath the ocean surface, a depth of extreme pressure. For example, at 4000 meters depth, the pressure is approximately 400 times greater than at sea level.

Other DCO researchers studied how extremes of pressure affect the fundamental processes responsible for sustaining life. Much of life on Earth has to deal with high pressures in one way or another; life in the oceans, for example, survives beneath a water column of several kilometers. Microbes living in the ocean at the bottom of the deepest trenches, however, live at a pressure that is still only one-third of the pressure conditions experienced by the deepest microbes in the crust. It has been shown, in laboratory experiments, that even the structure of a microbe’s DNA may be modiﬁed at such pressures. Much remains unknown regarding the speciﬁc mechanisms microbes employ to mitigate high pressure, but it is likely that strains of microbes have evolved
adaptive mechanisms to survive better at high pressures. DCO researchers have shown that pressure-adapted _Shewanella oneidensis _may even be able to survive brief periods at the pressures expected to occur during meteorite impacts, raising the possibility that microbes could survive space travel and colonize other planets.

DCO researchers devised ingenious ways to sample microbes that live in these deeply buried environments. DCO’s 50 mL Pressurized Underwater Sample Handler (PUSH50, see page 22) expands the scope of high-pressure microbial research and grows the research community that can access and investigate high-pressure subsurface samples.

Microbial life also has been found deep within the continents, hosted by ancient fluids. Researchers sampling fluids seeping out of deep mines in continental regions have discovered that aqueous, carbon-bearing fluids may become trapped in the crust for periods of geologic scale, more than a billion years in some cases. Over time, the fluids become enriched in hydrogen and methane produced by microbial activity or reactions between hydrogen and oxidized carbon. These processes may account for a large mass flux of carbon and hydrogen through the crust, similar in scale to that produced from water-rock reactions in the oceans. The gold and diamond mines of the Witwatersrand Basin in South Africa, for example, allow access to fluids from depths as great as 3.4 kilometers, hosted by ancient rocks more than 3 billion years old. These studies have highlighted isolated microbial communities eking out a living using dissolved hydrogen gas and inorganic carbon released by the rocks, with little or no input of organic carbon from the surface.

These deep microbial communities may have been isolated for millions of years. In Finland, microbial life has been sampled from the Oulokumpu borehole at depths as great as 2.3 kilometers. It is not just simple, single-celled organisms that live in such deep and dark environments: nem-
atodes have been found living in fractures 0.9 to 3.5 kilometers deep in mines in South Africa, within fluids with ages up to a few thousand years.

**Life in slow motion**

Microbes transform the carbon landscape of Earth’s subsurface by, very slowly, eating or breathing carbon-bearing compounds. Microbes may even enter dormant, or nongrowing, states for protracted periods. One study, conducted in the ocean floor sediments of the South Pacific, revealed that subsurface microbes may survive for millions of years in an extreme low-energy state of suspended animation and subsist by slowly consuming nearby carbon compounds. Geologically slow processes such as the radiolysis of water (the splitting of water into hydrogen and hydroxide) mediated by radioactive decay (which supplies ionizing radiation) and serpentinization, (which produces hydrogen and methane from the hydration of oceanic crust in the presence of carbon), may provide energy sources sufficient for respiration of microbes. Turnover times for such microbe populations in marine sediments may range up to thousands of years.

**Growing deep microbes in the lab**

Culturing deep-sourced microbes in the laboratory made possible direct observation of their metabolic processes and effects on their environment. Yet, culturing these microbes, which live in such extremes of temperature and pressure and paucity of nutrient supply, poses immense challenges. Many microbes in the deep subsurface may depend on interactions with each other or on specific growth conditions that cannot be replicated in a laboratory. To overcome these limitations, researchers use laboratory enrichments to coax a microbe of interest to become the dominant organism in a mixed natural population. A study with one common subsurface microbe cultured in this way, *Bathyarchaeota*, shows that such organisms use as an energy source lignin, a component of terrestrial woody plants. These microbes may be some of the most important actors in the carbon cycle as they remove terrestrial organic carbon from the surface, accounting for up to 45 percent of carbon in some marine sediments. This research has important implications for future use of these and similar microbes to derive energy from biofuels. Other examples are the *Altiarchaeales*, which can be found in natural enrichments in cold springs, and *Frackibacter*, which was identified in pure culture from fracking fluids.

DCO studies also have relevance for society’s attempts to sequester carbon in subsurface reservoirs. As part of a carbon sequestration project in Iceland, Carbfix, DCO scientists have shown that injecting CO₂ into basaltic rock initially causes the deep microbe population to decline, but some microbes thrive, feeding on the nutrients leached from the rocks by the CO₂-rich fluid. These microbes may slow the sequestration process by using up the mineral components that would otherwise combine with CO₂ to form immobile carbonate. Studies of deep microbial life are clearly integral to any future efforts to understand and plan carbon sequestration on larger scales.
In such large-scale endeavors, which generate abundant data and sample sets, knowledge is limited by our ability to understand what we observe.

Deep Earth sampling
Sites may be too hot, too cold, too deep, too dangerous, or too remote for scientists to sample and study. Repeated and detailed observations are challenging, or even impossible, under extreme conditions. DCO has conducted remarkable scientific investigations of some of the most challenging environments on Earth: deep under the seafloor and beneath the terrestrial subsurface, in acidic volcanic fluids, at high-altitude volcanic plumes, in mines cutting through ancient continental rocks, and in the tiniest inclusions inside minerals. These observations, astonishing as they are, only scratch the surface of what may be possible to obtain in the future.

By their very nature, such studies are rare glimpses into a tiny fraction of the entire system—snapshots in time and space. An illustrative example is how DCO researchers use inclusions, trapped in mantle mineral phases (usually diamonds), as their primary source of in situ information for understanding how carbon is transformed in the mantle. These diamond inclusions provide a window into deep Earth that otherwise is inaccessible. Only sparse regions of the mantle (mainly in the upper, lithospheric mantle) are sampled. As a result, the amounts of carbon involved in oxidation-reduction reactions and the conditions under which the reactions take place are poorly understood. As sampling and analytical technology improves, along with the advent of open access cataloguing of samples in a systematic way, coverage will improve and understanding of the heterogeneity of the observable Earth will grow. Other pressing questions concern inaccessible parts of the planet. For example, it is not possible to measure directly how much carbon is in Earth’s core; instead researchers must devise other methodologies.

Field studies have provided DCO with many of its most important discoveries and insights. Knowledge is limited here by the types of measurements that can be made consistently over time, a problem solved only through developing and deploying new technologies. Automated, high-precision carbon isotopic measurements at volcanoes, for example, are on the horizon, as are much lower detection limits for satellite-based observations of volcanic degassing. Together these tech-
Techniques hold promise for markedly improving understanding of volcanic degassing and eruption forecasting.

One important reality that DCO scientists have had to address is that given current technology, access, and funding limits, it is impossible to measure carbon flux from every erupting volcano on Earth. Given these limitations, how many monitoring stations are sufficient to gain an accurate estimate of flux? This issue of “how many measurements are enough?” applies across the field of deep carbon science. Large field projects, such as the Oman Drilling Project and the Atlantis Massif Expedition, while offering unprecedented insight into pristine environments, life, and the deep carbon cycle, also face the challenge of “how much is enough?” Repeatability and reproducibility of observations and measurements underpin robust scientific method. DCO scientists have devised strategies to ensure that they avoid biased sampling. For example, scientists sampled deep mine fluids not only in one continental craton, but in many, in an attempt to avoid local bias and seek global answers. As another example, the DECADE group has measured CO₂ fluxes from more than 30 volcanoes worldwide in an attempt to capture the spread and also the systematics controlling the carbon outgassing flux. To validate their approach, they employed statistical techniques to show that the top 20 outgasers dominate volcanic flux. In some areas a certain amount of bias is inevitable: single cores or a small number of cores cannot hope to achieve a complete picture of the subsurface.

In such large-scale endeavors, which generate abundant data and sample sets, knowledge is limited by our ability to understand what we observe. Modeling and laboratory experimentation are key for supplementing and enhancing understanding of field observations.

**Modeling**
Modeling brings unique challenges that often exemplify limits to knowledge. DCO developed models suggesting how deep carbon reservoirs and fluxes between them change over deep time. Plate tectonic reconstructions and numerical models have both successfully reconstructed melting at subduction zones. To gain a picture of the whole, models must assemble a family of observations for different parts of a system, with many inherent uncertainties derived from sparse observation or analytical error. Other challenges exist in identifying the first-order mechanisms that control processes and those we can ignore, to avoid making models too complex, while minimizing trade-offs.

Cores drilled from the subsurface of the ocean floor provide insight into Earth’s composition and the processes that allow life to survive at extreme pressures and temperatures.
in different parameters. Extrapolations to longer time intervals, or wider spatial scales, or across different types of model parameters, introduce further uncertainty.

Selecting reasonable modeling strategies ultimately matters. Scientists must hope that not every process is important for capturing the key dynamics of a system and that observations of a phenomenon are representative; which may be true in some cases, but not in others. Big questions remain to be answered through either field studies or modeling. For example, how many large igneous provinces must be studied in detail to understand how they affect the deep carbon cycle? How many sediment sections on the seafloor must be sampled to understand how microbial cell counts or microbial community composition and activity varies with depth? How many subduction zones must be studied to obtain a more complete picture of carbon cycling between the shallow and deep Earth?

**Experimentation**

Recently developed technology has allowed scientists to reach new limits of temperature and pressure in the laboratory, but these horizons must be expanded even further to better understand natural systems. A key part of this expansion is the pursuit of systems containing minerals and deep Earth fluids in which the fluid chemistry is measured directly, ideally in situ. Remarkably few such data are currently available. Consequently, these experiments constitute a new frontier for future deep carbon science. DCO scientists also opened another frontier related to the identification of species in deep Earth fluids. Current models indicate a much greater complexity of carbon-bearing species in deep fluids than was realized before the DCO. Experiments in the future should focus on identifying the species in deep fluids, both organic and inorganic. Again, remarkably few such studies exist at present. In fact, the paucity of data is so great that experiments at extremes of temperature and pressure are not the most crucial. Instead, experiments at relatively modest pressure/temperature conditions representative of subducting plates beneath arc volcanics would bridge a crucial gap in current knowledge.

In experiments, scale is vitally important. Is it possible, for example, to conduct meaningful experiments on high-pressure mineral composition and structure in micrometer-scale capsules? Can the intricacies of microbial metabolism be deduced from observations in a smaller, controlled experimental microcosm or pure culture? One area in which enormous progress has been made, but for which much remains unknown, is the form and amount of carbon contained in Earth’s core. It is now believed that a form of iron carbide may be an important solid phase in the core. Limits to knowledge stem from incomplete experimental coverage over the extreme range of pressure, temperature, and composition in deep Earth. For simplified compositions and for complex iron-alloys containing nickel and two or more light elements, our understanding of their properties is still limited to relatively low pressures and temperatures, far below the relevant ranges of the core. A lack of samples from the core compounds the experimental challenge.

Experimentation casts light on the flux of carbon removed from subducting slabs, which may then be returned to the atmosphere through volcanoes or diffuse degassing. Here it is necessary to understand the solubility of carbon in subduction zone fluids under a range of conditions, and combine this with detailed field studies to understand carbon distribution in high-grade orogenic rocks—fossil subduction zones that have been thrust up onto Earth’s surface. However, much more than carbon solubility alone must be
studied and understood. Carbon solubility is linked chemically to the solubilities of the major rock-forming elements through aqueous complexes of carbon and other elements such as magnesium, calcium, and iron. Consequently, to gain a full understanding of carbon mobility in deep fluids, experiments and models must target the full complexity of these fluids. In addition to these considerations, the pressures and temperatures under which deep fluids and melts become completely miscible—the true supercritical realm—must be studied in great detail to understand the deep cycling of carbon. Current knowledge of this realm is woefully inadequate.

**Surprises and perturbations**

Much of the modeling and experimentation across DCO has assumed “steady state,” or perhaps transitions from a range of steady states through geologic time as larger-scale Earth differentiation and geodynamics dictate. Earth has experienced, however, dramatic departures from steady state in its past, often violently. Asteroid impacts and large flood basalt eruptions have wiped out significant fractions of life and altered geochemical conditions on Earth. Earth’s climate has plunged into ice ages and hothouse climates after passing tipping points. There are lessons to be learned here for understanding the impacts of the rapid climate change of the present day.

The range of life on Earth today is largely the result of its violent past—vast eons of slow change and evolution, punctuated by catastrophe. DCO activities to address the impact of catastrophic events on life and on deep carbon cycling included a workshop and special issue of *Elements* magazine “Catastrophic Perturbations to Earth’s Deep Carbon.” Clearly, many unknowns remain: How different might Earth look today if these events had not taken place? Why do some types of organisms survive such events, while others get wiped out? How will the current anthropogenic carbon perturbations affect Earth’s system?

Over this last decade of discovery, DCO scientists have often approached the limits of human knowledge and, in many cases, made significant inroads to address these limits through innovation, creativity, and persistence. This experience is sure to serve the community of deep carbon scientists well as it encounters future limits and unknowns.

Large flood basalt eruptions, similar in style to this one in Iceland in 2014, have occurred at times through Earth’s history, causing large-scale perturbations to the deep carbon cycle and mass extinctions.
DCO has not only advanced fundamental understanding of Earth and its history, but has produced tangible societal benefits and legacies, including developing and supporting a global network of scientists.

Carbon is an element of central importance to human lives. Organic molecules are the basis of life on Earth (and perhaps other planets). Carbon in the oceans and atmosphere influences the global climate system. Mitigating the rapid increase in atmospheric carbon dioxide released by the burning of fossil fuels is a critical challenge. Carbon-based fuels, however, remain essential to the world’s economy through transport, communications, and all aspects of everyday life. A move to carbon-neutral fuels and energy sources is unavoidable and is the focus of much research, including studies in carbon sequestration and alternative energy resources. DCO’s scientific legacies lay the foundation for meeting these societal challenges.

Supporting Scientists of the Future

DCO has supported and enhanced the careers of many early career scientists by providing support, mentoring activities, and networking and educational opportunities such as summer schools and workshops. DCO created a forum of early career researchers, which has helped secure funding and new jobs for scientists at the early stages of their careers. DCO has built an enduring legacy in a diverse, dynamic, interactive community of more than 1200 deep carbon researchers around the globe. A new, integrative scientific field called deep carbon science has emerged with a momentum of its own, driven by a new cross-disciplinary community of scientists.

Volcano Monitoring and Eruption Forecasting

At active volcanoes scientists deploy a range of sensors in an attempt to forecast eruptions that may affect surrounding communities. Noxious gas emissions affect human health, and landslides, ash fall, and pyroclastic flows can cause serious physical damage and loss of life. Until about a decade ago, scientists typically monitored volcanoes only using networks of seismometers to sense the many earthquakes that occur as magma moves toward the surface. The advent of au-
Automated geochemical sensors to monitor volcanic outgassing has added a new dimension to volcano monitoring. It is now clear that magma approaching the surface releases volatile molecules such as carbon dioxide, hydrogen sulfide, and water, which make their way to the surface of Earth ahead of the magma. DCO scientists have established that carbon dioxide flux increases weeks to months before significant eruptions at some monitored volcanoes, raising the possibility of using geochemical information to forecast eruptions.

**Mitigating Climate Change and the Energy Transition**

Understanding the forms and nature of carbon inside our planet has implications for resource management and future energy solutions. The Samail Ophiolite in Oman, for example, represents a natural analogue for carbon sequestration, where carbon (from magmatic gases, in this case) is taken up by high-magnesium (ultramafic) rock to form a carbonate-containing rock called listwanite. This carbonation process may someday be exploited to offset carbon emissions caused by the burning of fossil fuels. DCO scientists in Oman are working to understand how to accelerate the carbonation process and shorten the natural timescale for sequestration of carbon. At the Iceland CarbFix project, another natural experiment in sequestration, DCO investigators are injecting carbon-bearing fluids into basalt and observing their conversion to solid carbonate phases.

Methane hydrates are solid, ice-like combinations of methane and water; more than 5000 gigatonnes of carbon (roughly ten times the amount of carbon in Earth's atmosphere) is held in this form in low-temperature environments such as the seafloor or in permafrost. Methane hydrates represent a huge reservoir of carbon, comparable to that held in petroleum and natural gas reserves. As well as carbon, methane hydrates hold significant quantities of hydrogen and may, in the future, be a source of cheap hydrogen-based energy when combined with carbon sequestration technologies. Methane hydrates may become unstable under conditions of warming oceans, which, combined with additional atmospheric impacts of anthropogenic climate change, could lead to runaway global warming. By deciphering the crystal structure of methane hydrates and quantifying their stability, DCO scientists have significantly contributed to understanding the physical and chemical characteristics of methane hydrates, which is critical to estimating their role in future climate change.

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DCO research into new forms of carbon materials is leading to discoveries in physics and advanced technology. One example is the discovery of new forms of polymeric carbon dioxide at high pressures, with carbon bonded to four oxygen atoms in a solid crystalline framework. Studies such as this may lead to breakthroughs in addressing carbon sequestration problems by understanding how carbon might be held in the deepest parts of Earth's silicate mantle.

Superconductor research has drawn heavily on deep carbon science experimental approaches. Observation of a new low-temperature superconducting phase in diamagnetic carbon disulfide under high pressure may prove highly valuable in a range of industrial applications. Advances in materials science surrounding graphene, nanodiamonds, and carbon nanotubes address the important societal challenge to develop lightweight and strong materials.

DCO has supported the founding of spin-off companies and the development of instruments with significant poten-
tial for societal benefit. The Panorama mass spectrometer at the University of California, Los Angeles, and the tunable infrared laser direct absorption spectrometer at the Massachusetts Institute of Technology, capable of unprecedented measurements of isotopic bond ordering in methane gas, are providing scientists with data to determine the origins of various sources of methane. These instruments have important implications for ongoing and future research. Similarly, the Laser Isotope Ratiometer, a sensor to measure isotopes of carbon in the gas phase, helps advance understanding of ecosystem dynamics and quantification of the carbon budget of the atmosphere. These instruments, developed and supported by DCO, have potential application for future missions to other planets, moons, and asteroids.

**Scientific and Educational Legacies**

DCO has provided a legacy of knowledge that will advance deep carbon science research for years to come. In addition to 1400 peer-reviewed publications, DCO scientists were responsible for seven special issues of journals, providing in-depth discussion of specific topics of deep carbon research. These included special issues of *American Mineralogist*, *Elements*, *Engineering*, *Frontiers*, *G-Cubed*, and the *Journal of the Geological Society of London*. Two collections—*Carbon in Earth* (Reviews in Mineralogy and Geochemistry, volume 75, 2013) and *Deep Carbon: Past to Present* (Cambridge University Press, 2019)—shared DCO research findings with the broader scientific community. The Extreme Physics and Chemistry Community also compiled an AGU monograph, *The Physics and Chemistry of Carbon in Planetary Interiors*, to consolidate new knowledge of how carbon functions under conditions of extreme pressure and temperature.

DCO also shared its knowledge and resources with the interested public, appealing to a fundamental curiosity about how the planet works. DCO science has been featured in documentary films in the United States and overseas, such as the Nova documentary *Life’s Rocky Start* (2016), the Netflix’s documentary *The Most Unknown* (2018), and the Science Channel’s documentary *Dark Origins of the Moon* (2018). In an effort to share what has been learned over the last decade, two widely accessible popular science books have been written: *Symphony in C*, by Robert Hazen (W.W. Norton & Company, 2019) and *The History of Carbon from Crust to Core*, by Simon Mitton (Cambridge University Press, 2019).

The program has amassed and makes available a wide range of educational materials, including extensive data and sample collections, lectures, videos, infographics, and review articles for use at both undergraduate and graduate levels. Over the last decade, DCO has produced press releases that have collectively reached more than a billion people. Topics included finding the temperature limits to life, discovery and quantification of the deep biosphere, the origins of methane, and progress in forecasting volcanic eruptions. DCO scientists have produced TED Talks and given public lectures and interviews with numerous media organizations, with the goal of sharing new understanding of the role of carbon in keeping the planet habitable.
To secure a strong future for deep carbon science, DCO established Task Force 2020, a committee charged with identifying structures and organizations that will keep the DCO legacy alive by proposing new ventures capitalizing on DCO’s international network of scientists and building upon their scientific achievements. The committee concluded that an international and interdisciplinary approach is essential to the success of this endeavor, along with access to global datasets, field sites, and instrumentation.

Technological advances have led to new, high-precision instruments that are costly to design, build, calibrate, and maintain. Successfully integrating and using such advanced instrumentation requires international cooperation for developing accessibility and user protocols, standards, and data formats. Similarly, sample curation and storage requires international consistency and networking to ensure accessibility and reproducibility.

Beginning in 2020, the Institut de Physique du Globe de Paris will host a central coordination system for deep carbon science to ensure support of a coherent community and facilitate the design of ambitious, multidisciplinary international projects. A newly configured executive board organized a meeting in October 2019 in conjunction with the culminating DCO conference, to help ensure a smooth transition. Support for this initiative is strong, as shown by a global survey of current DCO members.

With the culmination of the initial decadal program, DCO scientists have already secured grants of more than $120 million (with additional proposals pending) to carry deep carbon science into the future. These new projects illustrate the wide scope of deep carbon research and the scale that is necessary to make progress.

DCO leaders created a sustainable successor to DCO international science meetings by launching a biennial conference series, the Gordon Research Conference on Deep Carbon Science, which provides an ongoing forum for sharing new deep carbon research findings and developing future research directions. Also, a new biennial Gordon Research Seminar on Deep Carbon Science organized by and for young investigators will be held in conjunction with future Gordon Research Conferences. The seminar succeeds the DCO workshops and summer schools for early career scientists.

The first Gordon Research Conference on Deep Carbon Science, held in June 2018, brought together researchers from around the world to share the latest findings about deep carbon and its impact on planetary processes. The next deep carbon conference is scheduled for June 2020.

The Ocean Floor—Earth’s Uncharted Interface is a seven-year grant from the German Research Foundation. Kai-Uwe Hinrichs, University of Bremen, Germany, is one of several leaders. This new interdisciplinary Cluster of Excellence aims to initiate a new chapter in ocean-floor research. The project will focus on deciphering the processes controlling the transport of biogenic particles to the ocean floor and their transformation under changing climate conditions; balancing the transfer of carbon and other elements between the ocean floor and seawater; understanding how ocean-floor ecosystems react to environmental changes; and using climate models to tackle questions related to warmer future oceans.

Science for Clean Energy (S4CE), a European Horizon 2020 program, led by Alberto Striolo and Adrian Jones, both at University College London, UK, involves a number of DCO...
members. S4CE aims to develop, test, and implement the emerging technologies required for detecting, quantifying, and mitigating the risks of subsurface geo-energy operations, many of which are concerned with the origin, transport, and storage of carbon-based fluids. These operations include geothermal energy, enhanced gas recovery, carbon sequestration, and unconventional operations.

*Earth’s First Origins* is a NASA grant awarded to Karyn Rogers, Rensselaer Polytechnic Institute, USA. This project will tackle the question of how, and in what order, the ingredients for life on Earth came together. The five-year project seeks to uncover the conditions on early Earth that gave rise to life by identifying, replicating, and exploring how prebiotic molecules and chemical pathways could have formed under realistic early Earth conditions. This broad and far-reaching study will consider the onset of plate tectonics, as well as the formation of the oceans and atmosphere and their fundamental links to life.

*Clever Planets* (Cycles of Life Essential Volatile Elements in Rocky Planets) is an interdisciplinary, multi-institutional group of scientists led by Rajdeep Dasgupta, Rice University, USA, and funded by a grant from NASA. This interdisciplinary group is working to unravel the conditions of planetary habitability in the solar system and other exoplanetary systems. Their research focuses on the origin and cycles of life-essential elements (carbon, oxygen, hydrogen, nitrogen, sulfur, and phosphorus) in young rocky planets. They hope to identify where habitable niches are most likely to occur, which planets are most likely to be habitable, and when in their evolutionary history such conditions of habitability are most likely. This group is part of NASA’s Nexus of Exoplanetary Systems Science research network.

*Earth 4D* is a five-year Canadian Institute for Advanced Research grant awarded to Barbara Sherwood Lollar, University of Toronto, Canada, and fellow program director Jack Mustard, Brown University, USA, and a dozen colleagues and collaborators. Earth 4D will try to transform this idea of subsurface science to include all aspects of the subsurface, focusing not just on carbon, but on the flux and transport of water and elements necessary for life. What researchers discover about Earth will inform the investigation of planetary processes and the search for life on Mars and other potentially habitable planets.

*CarboPaT* (Carbonates at High Pressures and Temperatures) is a German research consortium launched in 2015 with support from the German Research Foundation for six years. CarboPaT studies phase relations, crystal chemistry,
physical properties and reactions of carbonates at conditions relevant to the transition zone and the lower mantle to answer questions such as how much carbon is stored in deep Earth. This research requires a multidisciplinary approach and state-of-the-art equipment for making measurements at the extreme conditions of Earth’s interior. Foundation funding makes it possible for scientists to design new experimental techniques essential for their work. Björn Winkler, Goethe University, Germany, leads the consortium.

ENIGMA, Evolution of Nanomachines in Geospheres and Microbial Ancestors, is a five-year grant from NASA with the goal of understanding how proteins originated and evolved through deep time, and whether similar instances of biochemistry emerging from geochemistry could have occurred on other planetary bodies. Paul Falkowski, Rutgers University, USA, leads the project, which includes DCO members Robert Hazen, Shaunnna Morrison, Joy Buongiorno, all at Carnegie Institution for Science, USA, Donato Giovannelli, University of Naples Federico II, Italy, and Karen Lloyd, University of Tennessee, USA. The project was inspired in part by the work of the DCO Deep Life Community to understand how deep life came to be and how it evolved. The new work is looking at different minerals to understand how the chemistry of mineral surfaces could trigger biochemical reactions that may have jump-started life.

The work of the Deep Life Community also will continue at the International Center for Deep Life Investigation established at Shanghai Jiao Tong University in 2019. Led by Xiang Xiao and Fengping Wang, both at Shanghai Jiao Tong University, China, the Center provides a platform for continued international collaborations that seek to address key scientific issues relating to the deep biosphere.

Collectively, these and other initiatives will serve as the cornerstone for future discoveries in deep carbon science.

(Above) Science for Clean Energy is a project led by DCO scientists aiming to better understand carbon sequestration. Experiments involving carbon-rich fluids are being carried out at an Icelandic geothermal power plant.

(Below) The International Center for Deep Life Investigation established at Shanghai Jiao Tong University, China, in 2019 will continue the work of the Deep Life Community, extending studies of deep microbial life.
Supporting a Decade of Discovery

The Alfred P. Sloan Foundation pledged $50 million over ten years to establish and operate the Deep Carbon Observatory. This generous support was leveraged by more than $600 million of support from other organizations around the world. It also allowed for the creation of a global network of scientists collaborating on some of the most fundamental questions about how Earth works.

DCO established a network that connected people and resources across scientific disciplines, with a view to addressing old problems in new ways. This approach engaged a network of collaborators at academic institutions, commercial organizations, government agencies, and professional societies from around the world.

DCO is deeply grateful to the Alfred P. Sloan Foundation for a decade of unwavering support, which made DCO’s success possible. Special thanks are also due to the Carnegie Institution for Science, which hosted the DCO Secretariat and provided valuable leadership, vision, and support since the program’s inception.

DCO also acknowledges the contributions of many other groups and organizations that have supported, facilitated, or nurtured the study of deep carbon. Advances in deep carbon science were made through the collective efforts of many contributors, including the following organizations:

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US National Aeronautics and Space Administration
US National Science Foundation

A close-up view of a section of the Samail Ophiolite in Oman, the world’s largest and best-exposed subaerial block of oceanic crust and upper mantle. The field of view is about 15 centimeters across.
The Deep Carbon Observatory is a global community of more than 1200 scientists who have spent the last decade investigating the quantities, movements, forms, and origins of carbon inside Earth.

deepcarbon.net