

DCO Energy, Environment and Climate Workshop
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Houston, Texas

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Energy, Environment and Climate Directorate White Paper

The Energy, Environment and Climate (EEC) directorate of the Deep Carbon Observatory (DCO) held its founding meeting on July 21-22, 2010, meeting at Shell's Bellaire Technology Center (BTC) in Houston, TX. A total of thirty-four (34) scientists (see Appendix for the participants list) from academia, industry and government/National Laboratories in the U.S.A. and the U.K. met to set the thematic goals, priorities and strategies for the directorate following the example of the other two DCO directorates (Reservoirs and Fluxes and Deep Life). The organizing committee consisted of Detlef Hohl (Shell, chair), Christian Mailhiot (Lawrence Livermore National Laboratory, chair), Russell J. Hemley and Connie Bertka (Carnegie Institution of Washington, CIW), Steven Bergman and Joe Westrich (Shell). The meeting followed a format used in the US Department of Energy (DoE) for innovation generation. The participants were all asked to come prepared with their own proposals/views for strategic/priority research directions in EEC and identify specific short-term pilot projects that can be conducted in the next 1-3 years. They were asked to describe the underlying scientific challenges and open issues, knowledge gaps, the proposed scientific approach and the potential impact on deep carbon science and main stakeholders, specific projects and share this with the group in a set of topical breakout sessions. The organizing committee provided a theme framework for the meeting, suggesting all strategic research directions categorized under:

- Abiogenic vs. biogenic origin of hydrocarbons (theme 1) or
- Physics and chemistry of deep carbon (theme 2) or
- Impact of deep carbon science on surface & near surface (theme 3)

Theme 3 is where the directorate derived its name from, while much of the content and challenges revolved around theme 2. Several participants therefore suggested the directorate be more appropriately named "Physics and Chemistry of Carbon" as the third logical discipline building block of DCO next to "Reservoirs and Fluxes" and "Deep Life".

Day 1 started with a plenary session. Connie Bertka presented history, background and status of the DCO. The scientific plenary session consisted of 1/2 hour presentations by T. Bryndzia, Bob Buruss, David White, Wendy Mao and Don DePaolo (see Appendix, the presentations are available on <http://dco.ciw.edu>). For

the idea-generating breakout sessions on day 1 and day 2, the participants split into the three theme groups with the intent to gather all information and input needed to draft the corresponding section for the EEC white paper. The meeting ended with a summary plenary session on day 2. The three theme groups provided the section below for the white paper shortly after the meeting.

One of the main goals of the DCO is to understand the present-day distribution of carbon throughout Earth (core, mantle, and surface) as a result of processes active during planetary accretion and the subsequent thermal and chemical evolution of Earth. During Earth's formation, volatiles were incorporated by accreting planetesimals. Initially, the growth of small planetesimals did not involve significant heating; toward the end stages of the generation of (possibly multiple) magma oceans. The solubility of carbon and other volatiles in the magma ocean and the depth of the magma ocean determine how much carbon remains within the mantle and how much is outgassed to the atmosphere as the magma ocean cools. The themes of this workshop revolved around an understanding of these processes. How important are abiotic processes in forming hydrocarbons? What are the physical processes that govern the carbon distribution, and what are the physicochemical properties of C-bearing materials? How do these processes affect Earth's surface, hydrosphere, and atmosphere?

Each of the topics covered in this workshop interfaces with other parts of the DCO: The first section, abiogenic and biogenic origins of hydrocarbons is clearly closely related to the Deep Life and Reservoirs Directorates, but concentrates on the chemistry and biochemistry of hydrocarbon production. The Physics and Chemistry of Carbon is also closely related to each Directorate, but emphasized the microscopic origins of behavior that manifests itself in the meso- and macroscopic processes identified in the other Directorates. Finally, the Impact of Deep Carbon Science on the Surface draws on all of the DCO data and focuses on the synthesis and ramifications of DCO science to societal needs.

1. Hydrocarbon Origins

It is generally accepted that the origin of methane and related light hydrocarbons found in surface and near-surface reservoirs is due to one of two mechanistic pathways: microbial-based digestion of organic matter or by thermal degradation of organic compounds. This long-held view has been challenged by reports of high-temperature methane-rich fluids venting from sediment-poor mid-ocean ridges, hydrocarbon seepages from terrestrial regions dominated by ultramafic rocks, methane-bearing fluids from Precambrian shields, and fluid inclusions in mantle and igneous rocks. Geochemical indicators, such as $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ratios, and carbon and hydrogen isotope compositions of methane, heretofore thought to be adequate for distinguishing methane of different origins, have been brought into question for certain hydrocarbon occurrences. Despite the introduction of new isotopic systematics such as use of noble gases to improve our ability to identify

fluid source and processes operating on carbon-bearing species, there is still a need to quantify the fundamental processes that regulate the chemical and isotopic signatures that could be used to unambiguously differentiate biogenic from abiogenic sources of hydrocarbons such as methane.

In the context of the carbon cycle the origin and behavior of both oxidized and reduced carbon species are certainly better understood for near-surface reservoirs compared to the deep Earth where the distribution and behavior are poorly constrained. It is clear, however, that a fundamental knowledge of deep Earth carbon is necessary because of its potential impact on geodynamic processes and because of the influence of the deep carbon cycle on surface processes such as secular variations in atmospheric composition and the rate of production of hydrocarbon deposits. This issue of communication of deep carbon with the surface and its potential chemical and isotopic modification only magnifies the need to be able to differentiate deep sources (abiogenic) from those derived at or near the surface (biogenic).

• **Local and global importance/flux/mass of abiogenic HC's:**

Abiogenic light hydrocarbons (HC's) have been recognized in a wide variety of geologic settings such as serpentinized mafic and ultramafic rocks, deep marine black and white smoker vents, alkaline igneous rock complexes where fluid inclusions contain C₁₋₆ HC, and greenschist and higher grade metamorphic rocks contain complex aqueous-CO₂-HC fluids. The volumes of these occurrences are apparently dwarfed by HC derived from organic reactions, although the precise fluxes and relative proportions have been poorly constrained. Mixing and fractionation of multiple sources are recognized for many economic HC accumulations. In order to better understand the overall Carbon cycle, an improved global flux model separating abiogenic and biogenic sources is required. Key challenges include:

1. Identifying the mechanism/s of abiogenic HC production which might include.
 - a. Fischer-Tropsch Type (FTT) pathways involving the reduction of CO and/or CO₂;
 - b. Polymerization processes of methane in Earth's deep mantle giving rise to higher alkanes; and
 - c. Methane produced via reaction of spent kerogen and graphite with water in high grade metamorphic rocks in Earth's deep crust.
2. The source, age and relative degree of isolation (residence) of fluid systems.
3. The accumulation and transport processes involved for dispersed abiogenic HC.

In addition to conventional HC reservoirs, gas hydrates, as a dispersed reserve, are identified as a high priority area that may be impacted by

abiogenic contributions, for example in the Gulf of Mexico. HC gas hydrates occur within minimally buried sediments in a variety of continental slope and deep marine settings but their volumes, fluxes, origin, and extent are poorly understood. These gas hydrates are a potential significant *Energy Source* yet their sudden decomposition may produce *Abrupt Climate Change* as suggested for the 55 Ma Paleocene-Eocene Thermal Maximum. The CH₄ budget occupied by gas hydrates remains poorly understood.

• Unambiguous identification of abiogenic vs. other sources and integration into geological context:

Conventional application of stable ¹³C isotope composition of abiogenic methane in Earth's deep crust and mantle has been shown to be non-diagnostic of either source or mechanism of HC production. This remains a fundamental challenge in identifying any abiogenic component in crustal accumulations of hydrocarbon trapped in conventional reservoirs in Earth's crust, such as the global resource of "isotopically light dry gas" found in giant gas fields such as Urengoy, Siberia. Recent instrument advances and technique combinations in isotope geochemistry show promise in resolving some of the ambiguities. One key area lies in the integration of noble gas isotope geochemistry with stable isotopes. This combination geochemistry has the potential to more accurately type-source the fluids and gases involved in Earth's Carbon cycle. 'Isotopologues' (molecules having the same atomic mass but variable combinations of rare isotopes, e.g. ¹³C¹⁶O¹⁸O) and 'Isotopomers' (molecules with intra-molecular isotope fractionation) are key developing techniques which have huge potential for identifying biogenic vs. abiogenic sources and the respective chemical reaction pathways.

• Conditions (temperature, pressure, and chemical routes) of light hydrocarbon (<C6) formation:

The light hydrocarbon gases contain the highest ratio of hydrogen to carbon of any hydrocarbon molecules. The chemical pathways to hydrocarbon gas formation require high relative abundance of hydrogen. The hydrogen may be sourced either within the carbonaceous material that is cracking to form gases, as partial pressure of H₂ from microbial or inorganic synthesis, or as an H₂-bearing reactant, such as water. Understanding gas formation processes requires understanding both the carbon source and the H₂ source. Rates of gas formation may be limited by availability of either component.

HC gases can be generated microbially, by thermal and possibly catalytic bond breaking reactions in larger hydrogen-bearing carbonaceous materials, by reduction of CO₂, CO, and other oxidized carbon-bearing substances with hydrogen, and by reactions of graphite or diamond with water. Identification of the processes that contribute to the composition of gases within natural accumulations at scales from giant, commercial fields to nano-scale defects in minerals requires documentation of the characteristics of the endmember compositional ranges (molecular and isotopic) generated by each process. The challenge is to clearly identify these

endmembers to form the basis for mixing models that will allow quantification of different gas sources within any type of gas occurrence.

• Unknown pathways of HC production in the ‘spent’ kerogen to graphite stage:

Transformation of sedimentary organic matter (kerogen) to crystalline graphite in metamorphic rocks or diamond in ultra-high pressure metamorphic rocks involves release of heteroatomic molecules (N, O, S bearing carbon-hydrogen structures) and hydrocarbons from the molecular structure as it reorganizes into a crystalline form of carbon. At the earliest stages of metamorphism the carbonaceous residue is described as partially graphitized and chemically the material contains about 20 atom % H although the H content may be as high as 50 atom % within greenschist facies metamorphic rocks. The final stages of reorganization into graphite or diamond with loss of the remaining H are not well documented. We do not know the highest temperatures at which measureable amounts of H remain in the graphitic structure, nor do we know the isotopic composition of this reservoir of H in metamorphic rocks. We do know that during high-grade (amphibolite facies and higher) metamorphism reduced carbon is mobile and can occur in mineral assemblages as “fluid deposited graphite”. However, little is known about the chemical purity of this inorganically precipitated carbon. The challenge is defining the characteristics of graphitic material that is the residue of sedimentary organic matter that distinguish it chemically and isotopically (including hydrogen isotopic composition) from graphitic material that has formed from an inorganic reaction between fluids and minerals. This distinction has implications for gas resources and for evidence of the earliest biosphere on Earth or life on other planets.

• Very high P-T reaction routes and phase equilibria of hydrocarbons in the mantle (up to 10’s of GPa and 1000’s of K) - experiments, theory and simulation, and field studies:

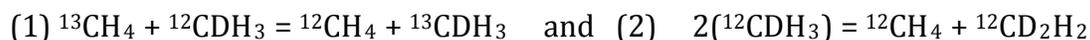
Chemical reactions leading to the formation of methane under conditions typical of the deep crust or mantle are poorly defined. Under pressures of several GPa or above, chemical bonds are substantially weakened as ionic interactions become favored over covalent interactions. Exotic phases of molecular materials, such as superionic water, have been discovered in diamond anvil cell experiments and predicted through ab initio simulations. Reactions of simple fluids with minerals can produce methane, but these processes are not well understood. Further work encompassing high pressure experiment, ab initio simulations, thermochemical modeling, and chemical kinetic modeling is required to better understand the mechanisms of methane formation. Some of the theoretical advances required are described in Theme 2 in this document. Extreme P-T conditions also occur during comet and meteorite impacts. The role of such impacts in delivering carbon-containing materials and/or pre-biotic materials to the earth during its formation requires further study.

• **Nontraditional identification and quantification of source, mixing and transport processes of aqueous and HC fluids:**

The use of carbon, hydrogen, oxygen, nitrogen and sulfur isotopes and their application to understanding hydrocarbon and related fluid source are well documented. We identify here three promising 'non traditional' techniques that have significant potential.

1. Isotopologues

It is increasingly apparent that D/H and $^{13}\text{C}/^{12}\text{C}$ are not sufficient to distinguish biogenic from abiogenic CH_4 . A significant advance in this regard will be the ability to measure the relative abundances of rare isotopologues of methane gas. The term "rare isotopologue" refers to molecules composed of more than one rare isotope. Their usefulness lies in the fact that their distribution involves intra-phase or intra-molecular isotope signals that can be measured without reference to any other species. The relative abundances of rare isotopologues can be used to trace temperature of formation as a consequence of intramolecular exchange reactions. Two reactions can be written that characterize the intra-molecular distribution of carbon and hydrogen isotopes in CH_4 .



The rare isotopologues $^{13}\text{CDH}_3$ and $^{12}\text{CD}_2\text{H}_2$ in reactions (1) and (2) are stabilized by the reduction in vibrational frequencies associated with the presence of two adjacent heavy isotopes relative to the purely stochastic distribution of isotopic species. For many gases, including CH_4 , this exceptional stability is on the order of several or even tens of parts per thousand (per mil, ‰) at temperatures corresponding to Earth's surface. Preliminary calculations show the trajectories in plots of the relative abundances of $^{13}\text{CDH}_3$ and $^{12}\text{CD}_2\text{H}_2$ imparted by diffusion in air, aerobic methanotrophy, and oxidation by OH radicals produce diagnostic covariations of these species. Experiments conducted on labeled gases and on gases equilibrated at high temperatures show that rare isotopologs of CO_2 does not re-equilibrate isotopically at temperatures less than 200°C during sample collection, transport, and purification. Key applications and challenges using isotopologues are:

1. An improved understanding of the origin and reaction history of methane.
2. Theoretical studies to determine the magnitude of kinetic vs. equilibrium fractionations and effect of T on isotopologues in the higher HC's.
3. Experimental confirmation and calibration of theoretical predictions.
4. Examination and determination of the reaction mechanisms responsible in key HC systems to address the question of biogenic vs. abiogenic processes.
5. Design and construction of a gas-source mass spectrometer capable of making these measurements is in the initial stages.

2. Isotopomers

Isotopomers are molecules where carbon isotopes can occupy different sites within the molecule. For example, propane (C_3H_8) has carbons in two different sites at the

center and end of the molecule. Theoretical calculations suggest that $\delta^{13}\text{C}$ values of the two carbon sites differ significantly at equilibrium. Such intra-molecular isotopic fractionation can provide a key insight into the sources and mechanisms of propane and other HC's and, like isotopologues, is ground-breaking technology.

3. Noble Gases

Other key isotopic techniques include the measurement of noble gases (He, Ne, Ar Kr and Xe). This suite of inert gases have an isotopic compositions that enable fluids from the mantle, crust and atmosphere (dissolved in groundwater) to be resolved and quantified in any fluids (gas, water, oil). The differential solubility and diffusive properties of the noble gases enable fluid process such as kinetic fractionation and phase interaction to be identified and quantitatively modelled. Accumulation of radiogenic noble gases can, for example, provide age information on the fluid system of interest. The concentration of atmosphere-derived noble gases can quantify groundwater interaction with a system. ^3He is a direct indicator of magmatic fluid involvement and is often linked to mantle carbon flux. Because the noble gases are chemically inert they provide a critical physical framework (fluid source, physical process) for interpretation of composition and stable isotopes. This stable isotope/noble gas combination was recently used to effect to significantly advance our understanding of the subsurface behaviour of CO_2 in geological sequestration analogues. Improvements in noble gas mass spectrometry (multi-collector technology) in only the last few years have improved the precision of isotopic determinations by over an order of magnitude. This opens the door for quantification of process and fluid source resolution in hydrocarbon origin studies at level not possible before.

Priority Research Directions:

Pilot Projects

It is abundantly apparent that our current understanding of thermogenic and biogenic natural gas generation and transport cannot and does not explain the chemical and isotopic composition of some major gas reservoirs. Amongst these is the super-giant Urengoy gas field in western Siberia and recently reported fields in the Songliao Basin, China. Both natural gas systems are in proximity to geological terrain favorable to either abiogenic hydrocarbon production routes or direct mantle fluid input and have been proposed as a possible source of the anomalous gas field compositions. Access to sample these fields and to geological and production information in the next 1-3 years are essential for any study and probably cannot be achieved without the help of the DCO and the Sloan Foundation. With these sample suites, application of existing stable and noble gas techniques will have an immediate science impact. Isotopologue and high-precision noble gas MS technology, within three years, will use this sample resource to develop novel analytical techniques and clarify the origin and processes that have operated on these key gas fields. Both modeling and laboratory experiments under controlled

conditions are essential to place any field results into context. Existing expertise and facilities in both areas are well placed to make significant and rapid progress if sufficiently integrated through the DCO initiative.

The extent of the source and physical chemical processes generating these anomalous end member systems needs to be put into a global context. This could be through the compilation of an extensive data base that both enables similar systems to be identified and allows the potential contribution of these anomalous gas types to gas fields dominated by more conventional hydrocarbon sources to be determined.

Decadal Goals

Building on successful completion of the pilot projects identified above, decadal Priority Research Directions are aimed at making transformational advances in our knowledge on biogenic vs. abiogenic hydrocarbons in nature, including the geologic past. Key research directions with high return include:

- Development of novel analytical techniques: Chemical and isotopic (compound-specific, clumped, and intra-molecular isotopes) compositions of hydrocarbons and associated fluids (noble gases and others) potentially provide the best information on their origins and transport from the deep Earth. Some of the best hydrocarbon samples from the deep Earth, including fluid inclusions from mantle-derived rocks, are available only in minute amounts. Therefore, breakthroughs in analytical techniques for high-sensitivity/high-precision chemical and isotopic compositions of hydrocarbons and associated fluids are required (e.g., advanced MS, NMR).
- Experimental and theoretical study of reactions, kinetics, and pathways of HC-mineral system under deep Earth conditions: Key parameters in reaction kinetics and equilibrium, and transport mechanisms of hydrocarbons in the presence of various mineral assemblages should be mapped out under deep Earth conditions (up to 10's of GPa and 1000's of K). This goal requires a synergistic combination of theory, simulation, laboratory experiments, and transport modeling. The development of theory and experimental database on isotopic distributions for clumped and intra-molecular isotopes and noble gases is equally important.
- Establish unambiguous criteria for identifying abiogenic HC's: Techniques developed and knowledge acquired from the above two research directions may provide the basis for establishing criteria for identifying abiogenic HC's in nature. However, even with the most advanced techniques and approaches from this decadal study it is essential that any chemical and isotopic signatures of hydrocarbons and associated fluids should be considered within the context of overall geological and geochemical information of a given hydrocarbon reservoir. Select large gas fields of

probable abiogenic origins (e.g., gas field in western Siberia) should be studied in detail to test the utility and validity of abiogenic signatures.

- Establish global importance of flux, mass, and distribution of abiogenic HC's: To achieve one of the ultimate and overarching goals, several synergistic approaches can be taken, including (a) compilation of all available chemical and isotopic data of major gas-oil fields from across the world and, (b) testing and validating abiogenic criteria for select major gas-oil fields and to classify the contribution to them from abiogenic sources.

2. Physics and Chemistry of Deep Carbon

The behavior of carbon-bearing materials ultimately arises from microscopic and atomic scale processes. In order to understand carbon in the Earth, we must understand the thermodynamics of carbon materials, fluids, and molecules and the kinetics of their reactions. In addition, we considered the importance of new carbon-based materials, which could be a very important societal spinoff of the DCO.

“Physics and chemistry of deep carbon” is the natural third theme group after “Reservoirs and Fluxes” and “Deep Life”. There was consensus around considering the conditions at which CO₂ becomes supercritical a natural boundary between “shallow” and “deep” Earth (i.e. P=7 MPa, typical in shallow hydrocarbon reservoir depths of a few 100 m).

Theme group 2's structured innovation exercise at the workshop generated a range of PRDs with both theory/simulation and/or experimentation/instrumentation components. The innovation proposals naturally fell into the following eight partially overlapping PRD categories:

1. Thermodynamics of Carbon-bearing systems:

A large integrated experimental-theoretical effort is needed to compile reliable thermodynamic data for the (C, H, O, salt) system and the solubility of carbon dissolved as a trace constituent in other phases under the conditions of the deep earth. The former are needed to address goals outlined in Theme 1 (Abiogenic vs biogenic carbon) and the goals in Theme 3 (Impact of deep carbon science on surface and near surface processes) in this document. Both types of data are needed to address needs of the Reservoirs and Fluxes directorate. It remains to be seen whether a set of parametric equations can suffice to describe the equation of state (EOS)¹ data compiled from experiments and simulations at the conditions of P, T and X (composition) relevant to the deep Earth. This program is at least comparable

¹ Equation of state (EOS) used throughout the text refers to the free energy formulation $G(T,P,X)$ from which all thermodynamic properties can be obtained (species and solvent activities, phase coexistence of low and high density phases and composition, enthalpy, etc.).

in scope to, and may even exceed in effort, the decade-long EOS program conducted at the U.S. National Laboratories and NEA targeting nuclear fusion (H, He) and nuclear fission (actinides). It could potentially (re)use existing facilities, staff resources and processes.

A suite of novel probes is needed for studying the EOS of the high P - T carbon phases. Carbon K-edge spectroscopy is a powerful tool for understanding carbon bonding and chemistry, but is largely limited to being a surface probe due to the low carbon K-edge energy. X-ray scattering (XRS) has widened the reach of x-ray absorption spectroscopy (XAS) on low- Z samples, which has been limited to the soft x-ray range, to systems and sample conditions where the penetration capability of a hard x-ray probe is essential. In addition it has opened up the possibility to measure spectra that are symmetry forbidden in XAS. Use of XRS for high P - T carbon systems has been limited due to the diminutive XRS cross-section, in many systems very long scanning times are required to obtain a high quality spectrum. Moreover, advances in neutron probes can provide extremely useful and complementary structural information to synchrotron-radiation probes. The most critical improvement is therefore a combination of improved instrument efficiency (solid angle), focusing optics, and brighter sources. This would have an enormous impact on high-pressure carbon-specific spectroscopy. Nanodiffraction would enable structural study of submicron single crystals in multiphase assemblages and nanoXCT would enable studies of texture and density measurements on amorphous phases. Solubility of trace carbon in other phases (silicates, oxides) at high pressures and temperatures can be investigated with techniques such as high-mass resolution SIMS and nanoSIMS.

As an aside, EOS studies must, at least in part, be based on, and consistent with, the “real rock” record. It matters not how “accurate” or “precise” the experimental data or theoretical predictions are. If these results disagree with what we see in real rocks we must re-consider the assumptions and/or conditions used in the experiments or modeling. It is essential that the scientists involved in this effort interact with others who work closely with natural samples to assure that appropriate conditions and assumptions are invoked and that the end results are consistent with the rock record.

2. Dynamics of chemical deep carbon processes: Kinetics

Our understanding of the dynamics and reaction kinetics for deep carbon processes is even more incomplete than for thermodynamics. The rate limiting steps and the relevant transition states are mostly unknown. Identifying and characterizing carbon transformation reactions in the dynamic regime is an enormous challenge to theory and experiment, fundamental for studying deep carbon processes in the planet and thus crucial for the goals of the Reservoirs and Fluxes directorate. It also provides guidance for improving kinetics for synthesizing new materials. Experimental characterization requires developing high P - T capabilities for time-resolved probes which couple with the relevant time scales. For processes with

longer time scales (e.g. diffusion), fast detectors and streak cameras can collect synchrotron x-ray diffraction measurements on millisecond and nanosecond timescales. On the ultrafast side, typical e.g. for molecular dynamics (MD), chemical reactions and phase transitions in solids can be studied at sub-picosecond times; this requires femtosecond probes to study the time evolution of atomic and molecular structure. Laser sources in the infrared, visible, and ultraviolet can produce ultrashort pulses for studying the dynamics of valence electrons in atoms, molecules, and solids. Developments in time-resolved X-ray diffraction with sub-picosecond time resolution — as afforded by the Linac Coherent Light Source (LCLS), and next-generation coherent hard x-ray and synchrotron-radiation sources — have potential for characterization of rapidly changing structures and providing insights of the temporal evolution of physical and chemical processes on the atomic scale.

The new dynamic platforms require technical developments for adaptation to deep carbon science. There is ongoing development of fast in-situ diagnostics necessary to measure material properties within the short duration of dynamic experiments, including Raman spectroscopy, x-ray (many techniques), NMR, radiography (e.g., inclusions, phase separation), resistivity, conductivity, temperature, visible to infrared spectroscopy. Usually, these techniques have been developed for a specific application and are not easily extended into other areas of phase space. Technique development is necessary to ensure that measurements reach the accuracy required for model development and comparison to observations. New techniques will need to be developed to study chemical reactions under dynamic compression and to overcome the challenge of working with reactive materials. For example, can dynamic experiments be designed to obtain the desired data before the material reacts with the confining cell?

Theoretical methods to predict chemical kinetic processes are not as well developed as those for equation of state properties. The fundamental challenge is to effectively sample rare events in situations where the mechanism of the event is not known a priori. The expected emergence of highly available peta- and exa-scale computing in the next decade makes it possible to combine replica methods and other advanced sampling methods with quantum calculation of barrier heights and pathways. Combined advances in computational methods and hardware should lead to the reliable prediction of reactions in complex environments during the next decade.

3. Geobiochemistry:

The material in this category aligns closely with the Deep Life Directorate. Whereas Deep Life will focus on the biological aspects, this effort will focus on the chemistry and physics that results from Deep Life. How does life interact with its environment, by changing the chemistry of fluids, by catalyzing reactions and mineral growth, and by generating or destroying porosity.

A large part of the research in geobiology in the last decade has centered on the production and processing of nanoparticles produced via biochemical pathways. The structure of a nanoscale material may not resemble the structure of the bulk (different bond patterns, etc.). To find a global minimum structure (as might be present in the natural system) requires a search over configuration space. As the number of degrees of freedom grows the problem becomes intractable. The electrons in these materials are often highly correlated and their correct description might require higher level electronic structure calculations and in some cases new theory.

A good target for present-day simulation tools is the interaction of complex biologically produced molecules (e.g., siderophores, molecules that chelate transition metal ions) with mineral surfaces and the effects of these interactions on enhanced mineral dissolution. New simulation tools that can efficiently find reaction pathways in these systems need to be developed. A related area is computational studies of electron transport from exocellular oxidation/reduction reactions across membrane proteins. Studies in this area are also now possible because of recent experimental progress.

An area important to the understanding of life processes that has not received much attention is the simulation of bioenzyme reaction mechanisms and their effect on the carbon cycle (e.g., RNA self replication in prebiotic systems effects of mineral surfaces, the exoenzymes involved respiration based on iron minerals, etc). There has been impressive progress at the microbiological level (discovering what is happening) but much less progress on the chemical mechanism (why and how these reaction work, e.g., the atomic level biochemical mechanisms). First principles methods have been used in such applications in pharmaceutical drug design research. Similar concepts and calculations can be applied to the analysis of complex biogeochemical processes in extreme environments. The deeper understanding of the enzyme mechanisms obtained should improve the understanding of the chemistry utilized by living systems in extreme conditions of temperature, pressure and under anaerobic conditions. The better understanding of key enzyme reaction would support the development of biomimetic pathways in enhanced energy recovery strategies (e.g., the better understanding of the mechanism of carbonic anhydrase should lead to more efficient CO₂ sequestration strategies). A major road block to the application of simulation methods to geobiological problems at the enzyme mechanism level is characterization of these systems at the atomic level (e.g., there are no X-ray structures of important enzymes). These are disordered systems that are easily changed on manipulation. *In situ* studies provide indirect information. Experimental studies that attempt to provide detailed atomic level information about important enzyme pathways should be a target of DCO EEC support.

4. Structure, solubility, speciation and properties of carbon-bearing fluids:

Quantification of the properties of carbon-bearing aqueous fluids and their interactions with minerals in the deep crust and mantle is of fundamental importance for understanding the speciation and behavior of carbon in the Deep Carbon Cycle and thus crucial information for the Reservoirs and Fluxes (RF) directorate. This information is also important for the efforts of theme 1 (above) and theme 3 (below) as described elsewhere in this document. Remarkably little is known about the physical chemistry of carbon in salt water in equilibrium with minerals at pressures of the deep crust and mantle. This is a major knowledge gap closely related also to thermodynamics and kinetics (sections 1 and 2 above). With the advent of new experimental and theoretical approaches it will be possible for the first time to address this challenge. Novel diamond cell techniques can be developed in combination with synchrotron XRF, XAFS and X-ray microtomography and Raman spectroscopy that will enable measurement of the solubilities of minerals and quantification of aqueous C-bearing species.

New fundamental theoretical and computational molecular-level methods need to be developed to help identify the species observed or inferred experimentally. All of these results can then be incorporated in revised equations of state for the standard state properties of aqueous and carbonic species and to constrain the non-ideality of mixing. This will enable the prediction of the standard free energies of hundreds of aqueous C-bearing species over a huge range of pressures and temperatures. In turn, this enables quantitative chemical mass transfer calculations of the fate of C during fluid-rock interactions in the deep crust and mantle.

Starting with water itself, we need experimental measurements and theoretical calculations of the fundamental properties of water, water-CO₂, and water-CH₄ mixtures, including in the presence of salt. Specifically the dielectric constant and the dissociation constant of water at pressures greater than 5.0 kbars and at elevated temperatures are needed. Integration of the results of the above with equations of state for aqueous ions would provide leverage of the already existing massive computational capability for aqueous ions below 5 kbars into the elevated pressure regime. The Gibbs free energies of hundreds of aqueous species at high pressures and temperatures could be generated.

Theoretical and experimental studies of the potential role of metastability in mineral-water-hydrocarbon systems at elevated temperatures and pressures must be undertaken. Methane (like other hydrocarbons) is not thermodynamically stable but merely metastable over a large range of P, T conditions where it is observed or inferred to exist. It is unknown how high in temperature and pressure this metastability and/or kinetically inhibited stability persists, and what the impact of the metastability phenomenon is on deep Earth composition and on deep Earth material properties. Incorporation of the results obtained above for water into the databases of chemical mass transfer codes would enable quantitative modelling of mineral-water interactions at high T and P. Specifically, the role of the oxygen

fugacity f_{O_2} (or hydrogen fugacity f_{H_2}) in such systems in influencing the relative metastabilities of different C-bearing species could be addressed.

Experimental studies need to be carried out to investigate the metastability of hydrocarbons and the kinetics of methane formation. These investigations could be integrated with the types of theoretical calculations described above. For example, the kinetics of transformation of species such as methanol into methane at elevated T and P need to be carried out. Reactions such as this will help to determine the boundaries of a high P, T metastability field for organic species. Novel higher-pressure hydrothermal diamond anvil cells are needed for this. Theoretical studies could be initiated immediately to 1000 C and 5 kbar to investigate the consequences of such metastability. Incorporation of the results obtained above for water into the databases of chemical mass transfer codes would enable quantitative modelling of mineral-water interactions in high TP experiments. Specifically, the role of f_{O_2} (or f_{H_2}) in such systems in influencing the relative metastabilities of different C-bearing species could be addressed.

Results from such studies will impact other areas of deep carbon science such as quantification of fluid-rock interactions involving movement of carbon between deep reservoirs, modeling of abiotic hydrocarbon formation and modeling of shallow and deep carbon sequestration

5. Mineral-fluid interaction under extreme conditions: Surface, colloid, and interface science:

Understanding and controlling interfacial processes for carbonates and other C-bearing minerals and colloids, particularly at high pressures typical of Earth's interior, is crucial for a range of energy related and environmental applications. The role of mineral surfaces in catalyzing hydrocarbon formation at high T and P is only just beginning to be investigated. C-bearing minerals such as calcite, graphite, and magnesite interact with H_2O - CO_2 -hydrocarbon fluids during extraction of fossil fuels from deep oil reservoir or from high-P clathrate deposits during geothermal energy production, at subsurface nuclear waste sites (deep boreholes), and most importantly during the geologic sequestration of CO_2 (Carbon Capture and Sequestration — CCS). In addition, interfacial interactions involving C species in the crust and mantle are relevant for Earth processes such as the conductivity of the lower crust, the wetting behavior and extraction of carbonatite magmas in the upper mantle, and possibly for core-lower mantle interactions. Despite the importance of colloid and interfacial processes involving C-bearing species and C-rich fluids, little experimental attention has been paid to solid/fluid interface structure, composition, and dynamics (kinetics) at high P-T because relevant experimental techniques used at ambient conditions (synchrotron X-ray reflectometry, AFM, XPS, SFG) are difficult or as yet impossible to implement at high P and T conditions. In addition, theoretical models of the mineral-water interface under these conditions have yet to be developed.

Specific knowledge gaps related to interfaces at high-P include:

- I. speciation, nature of bonding, the nature and role of the electric double layer, and complexation of both C-species and other cations and anions at solid C-based and silicate interfaces and in interfacial fluids as a function of P-T-X ;
- II. understanding whether properties at confined interfaces (buried interfaces) are identical to those at free fluid/solid interfaces;
- III. determining (and ultimately controlling) surface free energies of C-phase/fluid interactions in the crust and mantle as a function of P-T-X and stress state;
- IV. determining how C-phase colloids vary in their physical and transport properties as a function of P-T-X and
- V. understanding how the presence of a silicate rock surface impacts pathways (“catalysis”) and product distribution of chemical reactions between fluid components.

In order to adequately address these problems, integrated theoretical and experimental approaches are required. Focusing on experimental aspects of the problem, improvements must be made in both experimental apparatus (pressure cells) and to in-situ and ex-situ diagnostic tools. Cells need to be developed that allow robust spectroscopic and reflectometry-based interrogation of free mineral/fluid interfaces at P ranging from 10 MPa (“deep”, i.e. above the P of the critical point of CO₂) to upper mantle conditions (10s of GPa). Lower P cells can potentially be constructed of aluminum or titanium with sapphire windows, higher P cells must probably be improved-design hydrothermal diamond-anvil cells (perhaps with novel coatings to minimize cell/fluid reactions). Improvements to existing tools (e.g. Raman, SFG, neutron, x-ray sources) should allow higher-fidelity interrogation of novel pressure cells. Ex-situ diagnostics (e.g. nanoSIMS) may be complementary for interrogating solid interfaces, but cannot be used for interface fluids. To study buried interfaces, next generation synchrotron sources that provide coherent hard x-rays are needed to penetrate polycrystalline materials and image those interfaces. Such hard-x-ray coherent sources may also provide adequate brilliance and sufficiently short pulse lengths to begin to provide real-time information on interfacial dynamics. Ultimately, researchers need to be able to evaluate interface processes (e.g. kink growth, element incorporation) that occur on nanosecond to microsecond timescales. These data must then be incorporated into theoretical molecular models (DFT, molecular dynamics) of interface processes.

Ultimately, understanding fluid/mineral interfaces at a fundamental level opens up the possibility of manipulating surface structures and free energies and therefore controlling reaction driving forces and kinetics during fluid-rock interactions.

6. Advances in theoretical and computational methods, instrumentation, and advanced precisions diagnostics:

Major advances in theoretical and computational methods, as well as next-generation developments in instrumentation and precision diagnostics are needed to implement the DCO physics and chemistry science.

A. Improving theoretical formalisms and high-performance simulation capabilities for carbon and its compounds under deep Earth conditions:

The interior of the Earth below the shallow crust is currently inaccessible to direct *in-situ* experimentation. Valuable insights can be gained from indirect experiments such as seismology and from samples retrieved by drilling the crust and — in the future — upper mantle. The overwhelming majority of “impossible” *in-situ* experiments, however, must be replaced by theoretical and computational studies combined with idealized laboratory experiments where feasible. The role of modeling and simulation is therefore as crucial for DCO as is, e.g., lattice gauge theory and simulation for high-energy particle physics. A thorough focused review of available techniques is needed targeting both structure, (meta)stability and dynamics (finite-temperature properties) of carbon compounds and carbon-bearing mixtures, in all relevant domains of P, T, space and time (for size and time-dependent phenomena) from the crust to the core. Which techniques are providing fit-for-purpose precision in which (P, T) range, for which elements and composition ranges? Determining and tabulating ranges of applicability together with the expected error bars is a necessary first step to developing improvements to existing techniques. Computational methods and approaches that require minimal or no fitting to experimental data (aka. “*ab initio*” or “first principles” methods, AI or FP) play an especially important role in the study of carbon materials at deep Earth conditions because such data do not exist or are indirectly derived and/or not reliable. Computational approaches in broad current use include AI methods like coupled cluster (CC), second order Moller-Plesset (MP2) or Quantum Monte Carlo (QMC) based on wave-functions, Density Functional Theory (DFT) using different approximations for exchange-correlation functionals, and molecular dynamics (MD) and Monte Carlo with parameterized interaction potentials. DCO progress will therefore critically depend on utilizing these methods to the extent possible and on “bridging the scale gap”, i.e. finding ways to upscale such atomistic models for studying systems larger than a few nanometers over simulation times longer than a few nanoseconds (current state-of-the-art).

AI computational approaches are particularly valuable because of their lack of reliance on experimental parameters. Among these, density functional theory (DFT) has emerged as a compelling theoretical framework for studying both high pressure and high temperature materials for relatively large number of atoms (a few thousands). The main limitation in predictive power lies in the quality of the exchange-correlation functional employed. Wave-function based methods (CC, MP2 and QMC) can be taken to high precision, but due to the great computational expense are restricted to a relatively small number of atoms (<100). Empirical

model potentials, on the other hand, can be used to simulate the dynamics of billions of atoms, but the interaction potentials have a limited range of validity. Validating the methods under extreme conditions of P and T by comparing with experiments or more exact theoretical methods remains a major challenge.

Material improvements are required across the entire range of methods for modeling macroscopic materials and processes from the atomistic perspective:

- I. Achieving accurate enough AI calculations for “large” systems (thousands of atoms). This can be addressed by improved exchange-correlation functionals in DFT, including hybrid methodology, e.g. using electron exact exchange.
- II. Achieving accurate computations at high temperatures where electronic excitations are present. The validity of finite-temperature DFT with the commonly used exchange-correlation functionals needs to be assessed. Improvements can be introduced by employing beyond-DFT methods such as GW, quantum Monte Carlo (QMC) and hybrid functionals. The former two provide only static corrections (no forces) while the last is in, principle, an *ad hoc* method. Therefore, a combination of various techniques may be required to solve specific problems.
- III. Acquire the capability to do more accurate (to better total energy accuracy than 0.01 eV/atom) AI calculations for a very limited number of atoms (below 100). The forceful development of quantum Monte Carlo (QMC) methods for the study of carbon in the earth's interior will be of particular utility here. The growth in computational power over the past decades and the massive parallelism of modern high performance computing architectures make this a good time to advance the use of QMC beyond low Z elements. The projector augmented wave approach, e.g., is a method of treating the core electrons in density functional theory calculations and its extension to QMC would be of great utility.
- IV. Develop dynamical mean field theory (DMFT) approaches where DFT fails to predict the stability of strongly correlated materials.
- V. Acquire the ability to treat the dynamics of 1000s to billions of atoms, at varying degrees of sophistication in interatomic interaction, at high pressure and temperature. Such simulations are necessary to calculate the free energy of liquids or perhaps more importantly to calculate chemical rates. An important recent development in this regard is the Gaussian Approximation Potentials (GAP). These new empirical potential fields focus on the local environment of the atoms by a projection scheme instead of the traditional bond distances and bond angles. On the other end of the spectrum, new methods such as metadynamics, accelerated dynamics, milestoning and the finite temperature string method are efforts to improve the efficiency of MD sampling of phase space and of the calculation of rare events

(chemical reactions). Finally, the available portfolio of methods to extract useful information from dynamical simulations must be improved (e.g. viscosities, measurable spectra, diffusivities, reaction rates etc.)

Computational efforts are an integrated part of modern science, progress in this PRD category will therefore support several PRDs in the other DCO themes and directorates. Simulations of high fidelity not only steer experiments and reduce the volume of experimental data required, but can provide information that is otherwise impossible to obtain due to cost, complexity, or hazards. Success in reaching several of the research goals outlined in this report relies upon high-fidelity modeling of the common elements of the Earth's crust and mantle: H, C, O, Si, Al, Mg, and Fe. Within the next decade, we need to be able to routinely, accurately, and rapidly perform a predictive analysis for a selected thermophysical property, for a particular combination of minerals and solvents..

B. Experimental methods, instrumentation, and advanced precision diagnostics:

There are significant technical needs to model the processes that led to the present-day broad distribution of carbon and to interpret samples collected from the deep Earth. Realistic numerical models of large-scale processes such as impact events, magma-ocean freezing, and mantle convection require knowledge of physical and thermodynamic properties over extremely large areas of phase space. Specifically, equations of state are needed over large pressure, temperature, and composition ranges. Because all of the major processes are dynamic, the kinetics and rheology of the whole system (not only the carbon-bearing phases) must be known.

Furthermore, the models to describe EOS, kinetics, and rheology must be fast and accurate enough to make the problems computationally tractable. Specific needs include:

- A coordinated experimental and theoretical effort to acquire physical and thermodynamic properties data over broad ranges of P-T-composition space for both carbon-bearing materials and their host rocks and fluids.
- The development of tractable numerical models to implement the complex data (MELTS is a good analog, as are previously developed reaction path models such as EQ6 or PhreeqC for mineral-water systems at crustal pressures and temperatures). Theoretical developments are necessary to provide appropriate phenomenologies that can accurately describe behavior over a large range of PTX. This needs continuous feedback with the modeling of the dynamic processes and observations to determine whether or not the models are accurate enough to be able to address the guiding science questions..

7. The broad distribution of carbon within Earth:

The emphasis here is to extend the focus in the Reservoirs and Fluxes directorate science from data collection to the development of comprehensive models of individual materials for use in models of dynamic processes.

The present-day distribution of carbon throughout Earth (core, mantle, and surface) is a result of processes active during planetary accretion and the subsequent thermal and chemical evolution of Earth. During Earth's formation, volatiles were incorporated by accreting planetesimals. Initially, the growth of small planetesimals did not involve significant heating; toward the end stages of planet formation, all impact events led to significant melting of the mantle and the generation of (possibly multiple) magma oceans. The solubility of carbon and other volatiles in the magma ocean and the depth of the magma ocean determine how much carbon remains within the mantle and how much is outgassed to the atmosphere as the magma ocean cools. Based on noble gas data, convection has devolatilized a limited portion of the mantle over 4.5 Gyr. Hence, the initial incorporation of carbon and other volatiles is a critical component to understanding the origin and distribution of carbon in the Earth today.

The following open science questions and technical needs also address Question 6 from the Reservoirs and Fluxes group "What is the ultimate origin of Earth's carbon?"

- How much carbon was removed from the mantle during the end stages of planet formation? How deep were the magma oceans and what was the magnitude of devolatilization? (potential pilot project; can be addressed in 3 year time frame)
- Which processes were most important for the present-day distribution of carbon between the core, mantle, and surface? (e.g., primary accretion, the last impact event, initial rapid cooling/vigorous convection stage, long-term sluggish convection; can be addressed in the 10 year time frame)
- How have processes controlling the distribution of carbon within the Earth changed over geologic timescales

There are significant technical needs to model the processes that led to the present-day broad distribution of carbon and to interpret samples collected from the deep Earth. Realistic numerical models of large-scale processes such as impact events, magma-ocean freezing, and mantle convection require knowledge of physical and thermodynamic properties over extremely large areas of phase space. Specifically, equations of state (EOS, see above) are needed over large pressure, temperature, and composition ranges. Because all of the major processes are dynamic, the kinetics and rheology of the whole system (not only the carbon-bearing phases) must be known.

Furthermore, the models to describe EOS, kinetics, and rheology must be fast and accurate enough to make the problems computationally tractable. Specific needs include:

- A coordinated experimental effort to acquire physical and thermodynamic properties data in broad ranges of P-T-composition space for both carbon-bearing materials and their host rocks and fluids. The development of tractable numerical models to capture the complex data (MELTS is a good analog). Theoretical developments are necessary to provide appropriate phenomenologies that can accurately describe behavior over a large range of PTX. This needs continuous feedback with the modeling of the dynamic processes and observations to determine whether or not the models are accurate enough to be able to address the guiding science questions.
- Appropriate scale observations to compare and test the results of numerical simulations of the broad distribution of carbon in the Earth.

Overcoming these technical needs can lead to a great leap forward in the understanding of the initial state of the Earth. The capability for modeling giant impacts has just reached the point where the question of devolatilization at the end stages of planet formation can be addressed. The accuracy is primarily limited by the available equations of state and, to a lesser extent, rheological properties. Models of the freezing of magma oceans, which have advanced in recent years to address outgassing and distribution of phases within a planetary mantle, are also limited by basic thermodynamic information on the constituents. A critical period that warrants more attention is the early state of the Earth after freezing the magma ocean to study the devolatilization during the first overturn of the mantle. In addition, mantle convection models critically need more realistic rheologies and equations of state.

Understanding the anthropogenic impact on climate requires both detailed understanding of short-term surface perturbations as well as long-term cycling of carbon in the planet. Fundamental improvements in the ability to model the major dynamic processes in the Earth (particularly mantle convection) will lead to more accurate predictions of long-term anthropogenic impacts.

8. New carbon materials:

Carbon-based materials, ranging from diamond to fullerenes and carbon fibers are potentially revolutionizing fields ranging from electronics and optics to armor. This has been emphasized by awarding the 2010 Nobel Prize in Physics to Geim and Novoselov for their graphene experiments. DCO research can have a profound impact on this area of “new carbon materials” that could be pursued as part of the DCO mission. Are there forms of C-materials that could be found under pressure that would perform more useful functions? Can pressure be used to facilitate organic reactions to make pharmaceuticals cheaper or to make new useful

molecules? The experimental and theoretical methods developed under the DCO can be used to greatly expand this area. Accurate micro and nanoanalysis and accurate prediction are needed. Study of nanoparticles (as colloids or on surfaces) under pressure is a particular challenge, as is the study of organic chemistry under pressure. Considering the wealth of forms for pure carbon (graphite, diamond, graphene, carbon nanotubes, glassy carbon, nanocrystalline diamond, diamondoids, amorphous carbon), there is enormous potential for exciting discoveries. Adding in all the oxidized and reduced types of carbon there is a vast playground for finding new structures and novel bonding. For example, CO₂ has a very complicated phase diagram, forming a number of extended solids at high pressure and variable temperature. The existence of these structures is a useful constraint for theory and computations and may provide guidance for designing novel materials based on carbon structures. Results may also impact research on carbon sequestration.

Scientific objectives and potential research projects derived from Priority Research Directions (PRDs):

- Determination of the solubility of carbonate minerals and diamond in aqueous fluids speciation to 100 kbars and 1,000 C and silicate melts using theory and experiment: Study of the kinetics of mineral dissolution and precipitation is also important.
- Investigation of fundamental properties of water and water/carbon phase fluids above 10 kbars: The dielectric constant, dissociation constant, and viscosities of the fluids are needed to model the geophysical fluids, their speciation, and their reactions with rocks and minerals.
- Speciation in carbonated aqueous fluids: This includes much of organic chemistry under pressure.
- Quantitative investigations of the quantity of carbon removed from the mantle during the end stages of planet formation.
- Determination of how deep were the magma oceans and what was the magnitude of devolatilization
- Investigations of dynamic compression of CO₂-H₂O fluids at different strain rates to obtain phase boundaries, equations of state, kinetics, and conductivity: These studies will help us to understand planetary devolatilization processes, and the carbon content of the Earth.
- Establishment of integrated experimental and theoretical studies of methane metastability as functions of pressure and temperature.

- Determination of the conditions under which hydrocarbons will form when the formation of methane is kinetically inhibited.
- Development of novel spectroscopic studies in the diamond anvil cell of the properties of water and dissolved C-species at mineral-water interfaces at high pressures and temperatures. Establishing how the nature of the electric double-layer changes with pressure and temperature.
- Acquisition of experimental data on carbon-bearing aqueous systems at crustal PTX conditions. We propose a combined experimental and analytical study to determine the PVTX properties of H₂O-CO₂-CH₄ fluids, possibly including dissolved NaCl, over the range 25-700°C and up to 500 MPa. Extensive data for this mixed volatile system currently do not exist. Such a study will be accomplished by combining synthetic fluid inclusion and hydrothermal diamond anvil cell techniques with recently developed Raman spectroscopic techniques to determine the compositions of coexisting phases *in situ*. Specifically, the properties of carbon-bearing fluids in the vicinity of the H₂O critical point and in the region of anomalous PTX behavior (\approx 200-300°C and 100-200 MPa) will be determined. These data are critical to the development of realistic equations of state owing to the rapid and unusual change in PTX behavior in this PT range. These data will feed into studies that are developing equations of state to predict properties of H₂O-CO₂-CH₄ fluids at crustal PTX conditions. These data are also critical to understand the role and distribution of carbon-bearing phases in the earth because the ability of fluids to flow and to transport mass and energy is dependent on the PVTX properties. As such, earth scientists studying these processes will benefit from the proposed activity and it will lead to more realistic models of earth processes involving carbon-bearing fluids, including volcanism, ore-forming processes, hydrocarbon generation and migration, and carbon capture and storage technologies.
- Comprehensive investigations of the equation of state (EOS) of carbon-bearing aqueous systems at crustal and mantle pressure-temperature-composition conditions using theory and experiment: Data for this mixed volatile system currently do not exist at pressures greater than 1.5 GPa. Experiments would include synthetic fluid inclusion and hydrothermal diamond anvil cell techniques combined with recently developed Raman spectroscopic techniques to determine the compositions of coexisting phases *in situ*. Theory will include first-principles molecular dynamics and development of potentials for classical atomistic simulations. Particularly important

are the properties of carbon-bearing fluids in the vicinity of the critical line, from which emanates a region of anomalous behavior. These data are critical to the development of realistic equations of state owing to the rapid and unusual change in PTX behavior in this PT range. These data will feed into studies that are developing equations of state to predict properties of H₂O-CO₂-CH₄ fluids. These data are also critical to understand the role and distribution of carbon-bearing phases in the earth because the ability of fluids to flow and to transport mass and energy is dependent on the PVTX properties. As such, earth scientists studying these processes will benefit from the proposed activity and it will lead to more realistic models of earth processes involving carbon-bearing fluids, including volcanism, ore-forming processes, hydrocarbon generation and migration, and carbon capture and storage technologies.

- Determination of the phase-diagram of iron-carbon mixtures under mantle and core conditions. Quantitative knowledge of the phase diagram in the region 100 GPa to 400 GPa and between room temperature and 5000 K, including solid-solid phase transitions and melt line under several hundred GPa pressure. Such a project would combine theoretical work and dynamic compression experiments (isentropic compression from pre-heated samples, perhaps even pure liquid iron).
- Support for deep life microbiological studies by performing theoretical and experimental investigations of electron transfer mechanism and other fundamental biochemical processes under high P-T conditions.
- Investigations of the kinetics of reactions in carbonated aqueous fluids: Reaction rates are crucial, since many compounds may be metastable or not form due to kinetics. For example, under many conditions methane is the stable molecule, but instead hydrocarbons form due to kinetic inhibition of methane formation. What catalysts promote methane formation and breakdown of hydrocarbons, and how efficiently?
- Determination of the phase-diagram of iron-carbon mixtures under mantle and core conditions: Such a project would combine theoretical work, static, and dynamic compression experiments.
- Experimental studies of the solubility of carbon in a magma ocean of upper mantle composition (how much goes into the atmosphere/surface vs. mantle) and in iron (+X) melts under mantle

pressures (how much goes into the core). The goal is to understand how carbon is distributed initially in the early hot planet.

- Numerical studies of the mixing between the projectile, mantle, and core during the end stages of accretion in order to determine the initial distribution of carbon being added by the projectile and the thermal state of the planet. The thermal state of the planet, specifically the distribution of melt, is necessary to constrain the solubility studies to understand the pathways for carbon to be sequestered into the core and mantle.
- Establishment of a large-scale project on high-pressure thermochemistry of carbon: This would entail a unique method for collecting needed experimental (and possibly theoretical) data. An Office of Thermochemistry of Carbon would be started run by a scientist who is empowered to develop a database and program for thermochemistry of carbon containing systems. He or she would have a budget to put out contracts for particular missing data, and hire an investigator to do experiments (or possibly theory) to obtain data, which the office would then incorporate into the self-consistent database. This database and program would systematize all pressure data on thermochemical properties of carbon materials and fluids. As a first step, phase diagrams for major rock-forming minerals drawing upon existing experimental data and theoretical techniques should be developed (e.g., this project could be done without attaining new data or as a pre-cursor step to identifying the phase spaces that need new data.) Such phase diagrams (tabulated or analytical) are needed for calculations of planetary accretion (impact events) and understanding past and present reservoirs and fluxes.
- Formation and resourcing of a very-large-scale deep carbon computing facility: With the move towards cloud computing, high-bandwidth networking and virtual collaborations, existing (most prominently NSF and DOE, but also emerging commercial) facilities could be leveraged to provide the near exascale compute resources needed for DCO. Work on the following subjects could begin immediately, and substantial results could be delivered in a relatively short timeframe:
 - Form a High-Performance Computing DCO Science team to co-design the infrastructure and coordinate all related efforts.
 - Develop and implement the administrative and collaboration infrastructure needed for scientists from multiple distant locations to conduct joint compute projects (e.g. administrative agreements between DCO, Sloan, DOE, NSF, industry and

others, collaborative work environments, data management and distribution etc.) on multiple heterogeneous and distributed HPC facilities.

- Develop new and adapt existing application software to run effectively on the multi-processor, multi-core architectures that are expected to provide the bulk of future growth in high-performance computing. There has been significant progress in implementing molecular dynamics (MD) methods on these new and emerging computer architectures. Implementation of existing fast Fourier transform and local basis AI codes on these machines is not straightforward. Present codes usually do not scale past 1000 processors, and the methods and codes that scale well and perform best on 100000 processors and beyond may not be the ones dominating the field today. The computer science community needs to be involved to tackle these challenging problems. Conversely, it needs to be investigated how existing, currently over-demanding and under-utilized but easy to parallelize applications can be implemented on emerging scaleable computer architectures.

3. Impact of Deep Carbon Science on Surface & Near Surface Processes

The regulation of atmospheric carbon dioxide over geological time involved the balance between weathering and associated sedimentation, plate subduction and volcanism. Within this framework, certain processes contributing to changes at the Earth's surface were long lived, operating on the time scale of millions of years. Conversely, other processes influencing the surface or near surface operated on the time scale of days to thousands of years, including biological activity in the form of photosynthesis and respiration. In addition to the atmosphere and oceans as major carbon sources and sinks at the surface, other major carbon reservoirs include sedimentary rocks, particularly carbonates, dead terrestrial and marine organic matter, and carbon in the terrestrial and marine biosphere. These reservoirs supplied the carbon to the subduction zones that recycled the carbon into the mantle or crust. The amount and rate of carbon delivered to the deep earth was governed by a number of interrelated processes: weathering rates and associated sedimentation within accretionary wedges at plate boundaries, exposed area of the continents being weathered and the spreading rates of lithospheric plates.

A number of key aspects of this “conveyor belt” process are still poorly constrained: (a) processes controlling the rate and extent of weathering, (b) the stability and redistribution of carbon compounds at the surface, (c) contribution of non-volcanic carbon sources to the surface or near-surface carbon budget, (d) the form, amount

and rate of carbon delivered to different types of sediment sequences associated with different types of subduction zone geometries, (e) the processing of carbon-bearing sediments in different subduction zones, and (f) how to properly assess, synthesize, and model data sets of varying completeness and quality obtained from different carbon surface and near-surface reservoirs.

Contribution of deep carbon to the rock record through geologic time.

Global carbon cycle models suggest that release of gases from the solid Earth has been a primary control of paleoatmospheric CO₂ (to a lesser extent CH₄) contents and through the greenhouse effect, of global paleotemperatures. Because these models utilize simplified and indirect assumptions about CO₂ degassing, improved quantification is warranted. The *Reservoirs and Fluxes* Directorate identified measurements of the contribution from present-day volcanic degassing as a critical need, which in turn can provide a baseline for modeling the global carbon cycle and provides insight into the potential budgets of CO₂ from paleodegassing. Because the flux of CO₂ from subaerial volcanics is lower than estimates of global consumption of atmospheric CO₂ by subaerial silicate weathering, other CO₂ sources are required to balance the global carbon cycle. If we exclude direct emissions from the craters or flanks of volcanoes, there are still a number of poorly constrained sources of CO₂ (and CH₄) that could have potentially contributed to the paleo-carbon budget and may still be contributing today. High heat flow regimes located primarily at plate boundaries could contribute additional CO₂ necessary to balance the global carbon cycle. Processes such as oxidation of CH₄ generated from serpentinization of ultramafics and from thermocatalysis of organic matter could provide, albeit unquantified, source of CO₂ to the atmosphere. Magmatic degassing was probably a major contributor to global warming in the past particularly during the Cretaceous. Metamorphic CO₂ degassed from regimes of shallow, pluton-related low-pressure regional systems, may have contributed significantly to global warming proposed for the Cretaceous and Paleocene/Eocene. Global warming initiated in the Jurassic may have resulted from CO₂ degassing associated with continental rifting of Pangea. Increased global temperatures during the Cretaceous have also been linked to CO₂ degassing from flood basalts, and subsequent rapid release of large quantities of CH₄ by decomposition of gas hydrates (clathrates).

In the more distant geologic past (Phanerozoic and older), there is even more uncertainty about how the carbon cycle worked, its link to global climate and the cycles of tectonic supercontinent construction and dispersal. Some models suggest that the Earth started out with a CO₂ atmosphere that was derived from degassing of the mantle after a giant impact. Others suggest that CO₂ was added late to the Earth's surface. In either case, it is required that most of the CO₂ be transferred to the mantle. Judging from available estimates, roughly 99% of the modern Earth's carbon is stored in the mantle and core, and most of the rest is stored in near-surface carbonates. Only about 0.0002% of the Earth's carbon is in the atmosphere. The regulation of atmospheric CO₂ on geologic timescales is accomplished by a

complex set of processes, but a key aspect of the Earth's evolution is the apparent capability to return carbon from the surface environment to the deep Earth via subduction zones.

Knowledge gaps exist in two key areas: a) rates and variability of non-volcanic deep carbon output, chiefly CO₂ and CH₄, to the atmosphere and b) the nature (types, distribution and magnitude) of carbon storage change over long periods of geologic time. In concert with activities promoted by the *Reservoirs and Flux Directorate*, there is a need over the next 1-3 years to develop remote and real-time monitoring systems for present-day CO₂ and CH₄ derived from non-volcanic sources of deep carbon such as major fault zones, subaerial and ocean hydrothermal vent systems, and thermocatalytic processing of organic matter. This effort would involve deployment of a real-time sensor network at ground level (terrestrial and ocean based) and with satellites in addition to direct sampling at key locations to provide validation of remote measurements.

A detailed inventory of carbon contents and mode of preservation are needed for a wide variety of geologic terrains, most notably igneous and metamorphic provinces. As part of this inventory special focus can be made on exhumed subducted materials such as found in the Oman ophiolite complex. A concerted effort is needed to assess previous work and examine global ophiolite mantle outcrops to investigate processing and partitioning of carbon in subduction zones. During metamorphism, and perhaps especially in subduction zones, carbon may be released back to the atmosphere as CO₂ as a result of decarbonation reactions. Assessments are needed to estimate how much is released which is dependent on how much is subducted, and how carbonate-rich the rocks are that are being metamorphosed. One method involves coupling estimates of average fluid fluxes during metamorphism or magma emplacement with the estimated CO₂ contents of the exsolving fluids. A second considers the total volume of carbonate rocks consumed via processing at elevated temperatures and pressures. Both approaches require assumptions regarding the efficacy of expulsion of deeply generated CO₂ at or near the Earth's surface. These field-based studies should be complemented by bench-scale experiments that interrogate the rates and mechanisms of volatile release from key rock types exposed to a variety of P-T-X reaction paths that emulate magma emplacement/decompression and sediments experiencing metamorphic conditions.

Processes controlling the fate of deep carbon in the surface and near-surface regimes.

In general terms, the cycling of carbon between surface and deep reservoirs is understood on long time scales, but short-term societal influences are not well constrained and the details of specific biogeochemical processes require further investigation. The *Reservoir and Fluxes Directorate* white-paper well describes a number of key technical challenges and proposed studies on carbon cycling and exchange, but additional DCO studies in shallow sedimentary systems would fill key gaps. For example, sedimentary hydrate deposits found in ocean floor sediments

are a potential source of clean hydrocarbons, and large-scale destabilization of this dynamic methane reservoir (as well as permafrost occurrences) due to global warming is thought to be adding a further burden of green-house gas to the atmosphere. Despite their importance, remarkably little is known about clathrate hydrate systems in the areas of:

1. the sources,
2. fundamental thermodynamics of mixed phases;
3. rates and mechanisms of formation and decomposition;
4. high- P & low- T phase equilibria;
5. effects of salinities and sediment types; and
6. acoustic and rheologic properties of clathrates.

Knowledge gaps in these areas make it difficult to predict the occurrence and distribution of hydrate deposits. A fundamental understanding of the structures of clathrate forming liquids/ice-liquid interface is currently lacking despite the importance of characterizing both the precursors and post-decomposition structures as hydrocarbons are taken up and released by water/ice.

Similar knowledge deficiencies plague our understanding of carbonate mineral formation and destruction. Carbonate mineral formation is critical to removing and storing carbon in both the shallow Earth (soils, sediment), and the deep Earth. Whether and how carbonates form, and their rates and mechanisms of precipitation and dissolution, all affect how the climate system works over geologic timescales. At present, neither the equilibrium thermochemistry nor the kinetics of mineral reactions involving carbonates and silicates are well understood across pressure-temperature space at the high CO_2 loading rates expected during processing of organic-rich sediments or carbonates in subduction zones. Fundamental questions include whether carbon can be subducted to the mantle, and how the carbonate minerals record isotopic and chemical indicators of their environment of formation.

In addition to better quantification of carbon in sediments in subduction zones, similar work on sedimentary deposits of volumetric significance, such as deep sea fans, would enable more accurate determinations of carbon fluxes out of the surficial environment. The major submarine fans are expected to be the most significant carbon reservoirs because the rapid sedimentation tends to bury and preserve organic carbon reaching the ocean, while distal seafloor settings have low sedimentation rates and lower preservation potential. There is good evidence that indicates that over geologic time the rates of sediment delivery have changed, controlled by changing tectonic and climatic triggers. What is unknown is whether modern sediments now entering the ocean are typical of the flux over longer periods of time and how much organic carbon has been locked up in these repositories. Better assessments of the rates and mechanism of carbon preservation in sediments are required to better predict environmental and anthropogenic influences on carbon burial. These fans have the potential to lock up carbon over periods of 10^7 – 10^8 yr, while their ocean basin remains open. Some of these carbon-

bearing sediments may be uplifted, eroded and reworked as the basins in which the fans have been deposited are subducted, deformed and incorporated into mountain belts. These same fans are susceptible to destruction by subduction over long periods of time. Indeed some fans, such the Bengal Fan, are deposited in basins already being fed into trench systems.

An integrated multidisciplinary effort (in the bio-, geo-, and chemical sciences) is needed to develop holistic, robust, and accurate methods for predicting the formation and destruction of hydrate and carbonate deposits in a wide-range of near surface environments. The relative inputs of deep abiogenic, bacterial, and thermogenic methane in hydrates are not known, either locally or globally, and new isotopic tools (e.g. Tandem MS) would be extremely valuable in this regard. Advanced analytical and computational tools will lead to improved understanding of mineral properties and interfacial behavior. However, there are still limitations on experimental approaches to growing minerals under sufficiently well controlled conditions. A revolutionary advance is needed in experimental methods aimed at quantifying mechanisms and rates of formation and destruction of key carbon-bearing phases such as clathrates and carbonates under controlled conditions, coupled with use of advanced characterization techniques and computational approaches to probe interactions from the pore to molecular scale. Neutron diffraction and tomography coupled with innovative loading/flow-through systems are idea tools to investigate the poorly understood physical and structural properties of clathrate hydrates and carbonates in situ under simultaneous P and T conditions. For example, a new tri-axial core-flood loading apparatus at the Los Alamos Neutron Science Center (LANSCE) allows integrated experiments of neutron diffraction and tomography, thermal calorimetry, mechanical deformation, and ultrasonic interferometry under identical P-T conditions on the same sample. One excellent example of the former is the Bengal Fan associated with the Himalayan orogeny.

Further carbon analysis of IODP drill cores from subduction zones, proposed in the *Reservoir and Fluxes* white-paper should be expanded to include samples from other significant sedimentary environments. Scientific drilling of the major submarine fans has to date only penetrated short distances, typically 100's of metres, into stratigraphies that can exceed 15–20 km. A concerted effort is needed to analyze carbon in existing cores from sedimentary fans to quantify their carbon storage. Sediment fans associated with either existing trench systems or accretionary plate boundaries would be targeted as the first set of representative sediment systems to be probed with deeper drilling.

A longer range decadal goal will be to utilize advanced drilling and coring technologies to provide a more complete characterization and reconstruction of how the flux of terrestrial organic carbon into sediment fans has varied over long periods of geologic time.

Development of fully coupled numerical models that quantify the processing of deep carbon during sedimentary cycling.

Knowledge gained in all four DCO Directorates will provide a unique opportunity to reassess in far more quantitative terms the impact of deep carbon on the global carbon cycle. The overarching goal will be to analyze the stability of the surface and near-surface carbon cycle and its dynamical response to perturbations both from present-day stimuli as well as those that have influenced the paleo-record. Additionally, modeling of surface and near-surface processes must be linked to distribution, migration and release of carbon from the deep earth. Transformative understanding of the carbon cycle and the role of deep carbon will depend on our ability to characterize and describe it in terms of complex structures and their reorganization — i.e. interrogation of “dissipative structures.” In particular we need to quantify the consequences of both positive and negative feedback processes on carbon distributions among key reservoirs such as the atmosphere, oceans, continental waters (e.g. rivers, lakes) and the crust. An assessment of carbon reservoirs and fluxes among these in the surface and near-surface regime must complement similar evaluations of deep carbon and its return to the earth’s interior via subduction. Updating and refining existing concepts such as treating cycles as “global kinetic” analogues of complex chemical reactions can take full advantage of new data and advanced computing capabilities.

Three key modeling challenges are identified: (a) Synthesize carbon cycles data for surface and near-surface reservoirs such as terrestrial and marine clathrates and continental-derived carbon, (b) Develop models that assess surface and near-surface carbon cycling systems across varied spatial and temporal scale, and (c) Utilize high performance computing resources to build increasingly more robust models.

Simulation, numerical modeling and data synthesis are essential and difficult components in addressing the challenges of deep carbon impact on surface processes. Even if one has sufficient data a simplified model is often over determined and so the problem is ill-posed. In the present case it is clear that one does not have sufficient data. Thus in the data fitting forward problem there are many equally "good" solutions from the point of view of the fit alone but most of the models are not suitable in reality because they are not compatible with the physics, chemistry or geology. Thus the inverse problem is usually both over- and underdetermined and has to be regularized. In addition, in an attempt to determine the most appropriate model, both some form of model reduction/structure exploitation and data assimilation has to be incorporated. Each mathematical component is reasonably well understood on its own but to be successful these techniques have to be well integrated with what we understand about the application. Furthermore the large variation of spatial and temporal scales, the noise and uncertainty levels, incomplete nature of the data, not to mention their stochastic nature, exacerbates the difficulties considerably. Ultimately it is important that

some kind of verification is carried out, perhaps initially via surrogate models and or data but eventually via field and experimental investigation. To succeed one needs state-of-the-art data acquisition, model optimization and numerical linear algebra algorithms and a high performance computing environment integrated with as much domain knowledge as possible. For example, in the context of reactive transport modeling and simulation of multiscale systems over long horizons, hybrid models and novel architectures are needed for multi-phase flow and transport over different time and length scales and to simulate the transition from molecular statistical dynamics at the mineral surface to the equations of Navier-Stokes fluid flow at the pore scale. Another challenge in multiscale systems is the propagation of errors and uncertainty. Algorithms need to be incorporated to link models on different scales, including innovative upscaling and closure methods that take into account errors and uncertainty propagation across the different models. Such new pore-scale models (e.g. hybrid Lattice-Boltzmann models) can be used, for example, to design and evaluate experiments in high-pressure microfluidics systems. The representation of non-aqueous based chemistry is a scientific challenge that is critical for safe, long-term storage of CO₂ and other greenhouse gases in geologic reservoirs. To better understand this challenge, new chemical models are being developed using molecular dynamics to simulate the chemistry of mixed greenhouse gases when variations exist in the primary solvating fluid.

Simulation of geologic sequestration at the kilometer scale requires the coupling of physical, chemical, mechanical, and thermal processes (e.g. multiphase flow, mineral precipitation/dissolution, geomechanical deformation, and heat transfer) within modern subsurface simulators. The strong interactions and feedback between processes and the diverse timescales motivate pursuing fully-coupled solution schemes within models employed to improve solver convergence and reduce numerical error. The size and complexity of these models often necessitates the use of high performance computing, yet most simulators today do not leverage the computing power of modern supercomputers effectively, if at all. One of the key challenges regarding the effective application of high performance computing within subsurface science is the lack of scalable solvers at large processor core counts. An effort is needed to synthesize data/knowledge and develop models for formation and distribution of hydrate and carbonate deposits.

Impact of deep carbon science on society.

Climate and Environment: Deep carbon science will have a profound impact on our understanding of the global carbon cycle, and will lead to new tools and models for predicting the influence of natural and man-made processes on the environment. Integration of DCO studies with results of carbon-related surface sciences (e.g. climate modeling, oceanography, environmental studies) will be a strong enabler for the development of comprehensive numerical models of carbon cycling processes over multiple lengths and time scales. Specifically, estimation of more reliable deep-carbon flux rates to the atmosphere (via remote/continuous sensing) will reduce

uncertainties in climate modeling. Along these same lines, a better understanding of the carbon and nutrient links between the deep and surface biospheres could lead to new insights on the input and removal of greenhouse gases to/from the atmosphere.

Results from the DCO program will find applications in geo-based engineering systems, enabling effective and sustainable solutions for carbon capture and sequestration (CCS), enhanced geothermal systems, and possibly even safe nuclear waste disposal. Fundamental understanding of how carbon is processed and fixed in the subsurface (both biologically and abiologically) is expected to facilitate breakthroughs in novel CCS strategies. Key challenges include geochemical and biogeochemical complexity and dynamics in subsurface reservoirs, the numerical simulation of these multi-scale systems over long times, and understanding the efficacy of geologic storage through integrated characterization, modeling, and monitoring of geologic systems. Thermodynamic data for the CO₂-rich/H₂O system at high temperatures and pressures, in the presence of natural mineral assemblages, will find immediate use in some CCS systems (e.g. hybrid CCS and geothermal). A fundamental understanding of fluid-mineral interactions under supercritical conditions for CO₂ is critically needed.

Other climate-related spin-offs from the DCO program also are likely. For example, high-resolution tools for remote and continuous sensing of CO₂ and CH₄ fluxes from low-flux volcanic systems could be applied to quantify flux rates from anthropogenic sources, thus enabling better treaty and legal (carbon credit) validation. Better understanding of deep microbial systems for petroleum biodegradation may find application for oil spill remediation. It is also possible that continuous/remote chemical sensor data from volcanoes could lead to reliable predictions of natural hazards, such as eruptions and earthquakes.

Energy and Technology: Transformational technology innovation will be required to deliver the DCO program, and many tools and methodologies will find other uses in energy, natural resources, and other industries. In addition to the chemical sensor and bio-technology opportunities mentioned above, breakthroughs in sampling rocks and fluids at extreme conditions, novel materials, ultra-deep drilling, and advanced numerical modeling and verification systems will be more broadly applicable.

The energy industry in particular will be a prime beneficiary of the DCO program, in terms of sustainable exploration and production of hydrocarbons, improved CCS technologies, as well as other energy related spin-offs. Deep Life work aimed at characterizing the metabolic potential of the deep microbial biosphere could lead to novel methods for using natural microbial assemblages for enhancing oil recovery from reservoirs and upgrading heavy oil in-situ. Development of advanced analytical instruments (such as the proposed tandem MS instrument for detailed isotopic analysis) will provide powerful new tools for enhanced geochemical

characterization of petroleum systems. Experimentation and thermodynamic modeling of hydrocarbons and aqueous fluids at high temperature and pressures will result in fundamental phase behavior, partitioning, and solubility data that can be applied to novel subsurface upgrading processes and deep reservoir fluid characterization. Ultra-high T/P experimentation will result in advanced instrumentation, analytical methods, and materials may find applications in refining, drilling, and fluid sample and data acquisition. Proposed deep drilling to the deep crust or upper mantle will result in new technology for better/safer drilling to deep, but less ambitious, targets.

The origin and significance of abiogenic hydrocarbons from igneous and/or metamorphic sources is a controversial topic. Generally speaking, the oil and gas industry does not consider this type of source to be volumetrically significant in known oil and gas reservoirs of commercial value. Key problems which negatively impact the viability of the abiogenic theory are low concentrations per unit volume of rock, problematic migration/accumulation mechanisms (particularly the required focusing of low concentration fluxes), and questionable stability under certain redox and temperature conditions. In addition, there is strong geochemical and geologic evidence that nearly all commercial oil and gas accumulations are derived from a biogenic source (i.e. kerogen contained in fine-grained sedimentary rocks). Despite the above facts, abiogenic gaseous hydrocarbons of deep crustal or mantle origin could be significant in some geologic settings, such as accretionary prisms associated with subduction zones. DCO work on abiogenic hydrocarbons will help understand the habitat of this potential additional source of natural gas.

Priority Research Directions:

Pilot Projects

There is a need for a global survey of present-day non-volcanic sources of CO₂ and other carbon-bearing volatiles from all possible lithologic terrains but particularly igneous and metamorphic terrains. This real-time monitoring activity would complement one proposed by the Reservoir and Fluxes Directorate for volcanic sources. This survey should also include an assessment of exhumed subducted rocks such as ophiolites, but not exclude certain exhumed crustal rocks consisting of 'eroded upper plate material' associated with steep trench slopes.

We need to determine the form, stability and reactivity of major surface and near-surface carbon compounds (e.g. clathrates and particularly carbonates) that contribute to the sediment sequences that participate in the subduction process. Recently implemented novel analytical and computational tools can be used to characterize these materials. Further we need to understand the rates and preservation mechanisms of carbon entering ocean sediments that may be the source for carbon into subduction zones. A detailed accounting is also needed to quantify the carbon budgets of different types of sediments, what factors control

their formation and how they evolve through time. New drilling activities at key locations may be required to augment existing data sets.

Decadal Goals

Long range goals for the assessment and quantification of deep carbon impacts on surface and near-surface carbon will be closely linked to developments in advanced monitoring, drilling and coring, analytical, experimental and computational methodologies. There will be a clear need to deploy smart sensor technologies as they are developed and refined for both surface monitoring but also down hole. Borehole sensors that cannot only detect carbon and its total concentration but also determine speciation and perhaps even isotopic composition would revolutionize how we assess the subsurface.

Given the variety and extent of modern-day ocean sediment deposits that host carbon, particularly sediment fans, we envision a long-term drilling effort to probe these occurrences at greater depths. This would be a world-wide effort taking advantage of the IODP program. We need to expand this effort to also include paleo-sedimentary sequences that act as representative proxies of modern day systems to better understand the temporal and spatial evolution of carbon-bearing materials.

In concert with the effort to detail the characteristics of carbon materials in natural sediments through geologic time will be an effort to expand the near-term effort addressed in the pilot projects to quantify the form, stability and reactivity of key carbon compounds like clathrates and carbonates at conditions of pressure-temperature relevant to the surface and near-surface. This effort would complement studies identified in the Physics and Chemistry of Carbon Directorate and take full advantage of new in situ experimental and analytical methods anticipated in the near term such as special environmental cells and new beam lines at synchrotron and neutron facilities.

An important long-term goal will be to develop the computational architecture for modeling the carbon cycle that incorporates a variety of data types. Advanced algorithms which take advantage of new high performance platforms will be needed to link different spatial and temporal scales that couple physical, chemical, mechanical and thermal processes. The long-range grand challenge will be to extend the pore-scale to kilometer assessments down to include behavior of carbon-bearing systems at the molecular level.

APPENDIX

Energy, Environment and Climate Workshop

Shell Bellaire Technology Center

July 21-22, 2010

Houston, TX

Agenda

8:00 AM Registration at main Shell reception desk 3737 Bellaire Blvd., assemble in meeting room 2156; breakfast, agenda handout

8:30 AM Introduction: On-site safety, logistics, purpose of workshop, expected deliverables, agenda review

9:00 AM Connie Bertka, *Introduction Deep Carbon Observatory - DCO*

Plenary Session 1

9:30 AM Taras Bryndzia (DCO founders committee, Shell), *The origin of biogenic vs. abiogenic hydrocarbons – Shell's perspective*

10:00 AM Bob Buruss (USGS), *Geochemical issues at the intersection of deep carbon concepts and hydrocarbon resources*

10:30 AM Break, refreshments

11:00 AM Dave White (Schlumberger), *Deeper & More Difficult Carbon: Challenges, Opportunities and Technology in the O&G Industry*

11:30 AM Wendy Mao (Stanford), *Synchrotron x-ray probes for deep carbon*

12:00 PM Don DePaolo (LBNL): *Understanding and managing the Earth's carbon cycles: Deep planetary processes to geologic sequestration*

Break-out Session — Refinement of Priority Research Directions (PRDs)

11:00 AM

Theme 1: Abiogenic vs. biogenic hydrocarbons Room 1154
(facilitators/scribes: Horita, Ballentine)

Theme 2: Physics and chemistry of deep carbon (DC) Room 2156
(facilitators/scribes: Hickmott, Cohen, Sverjensky, Mattson)

Theme 3: Impact of DC science on surface & near surface Room 2244
(facilitators/scribes: Bonneville, Clift, Cole)

1:30 PM Theme 1: Report on PRDs Room 2156

2:00 PM Theme 2: Report on PRDs Room 2156

2:30 PM Theme 3: Report on PRDs Room 2156

3:00 PM General discussion / Next steps / Action items Room 2156

4:00 PM Adjourn

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