Deep carbon cycle through five reactions

Jie Li[1], Simon A. T. Redfern[2,3], Donato Giovannelli[4,5,6]

1: University of Michigan, Department of Earth and Environmental Sciences, 1100 N. University Ave, Ann Arbor, MI, 48109, USA

2: Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

3: Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China

4: National Research Council of Italy, Institute of Marine Science CNR-ISMAR, la.go Fiera della Pesca, Ancona, Italy

5: Rutgers University, Department of Marine and Coastal Science, 71 Dudley Rd., New Brunswick, NJ, USA

6: Earth-Life Science Institute, 2-12-1-IE-1 Ookayama, Tokyo, Japan

Abstract

What are the key reactions driving the global carbon cycle in Earth, the only known habitable planet in the solar system? And how do chemical reactions govern the transformation and movement of carbon? The special collection “Earth in five reactions - A deep carbon perspective” features review articles synthesizing knowledge and findings on the role of carbon-related reactions in Earth's dynamics and evolution. These integrative studies identify gaps in our current understanding and establish new frontiers to motivate and guide future research in deep carbon science. The collection also includes original experimental and theoretical investigations

of carbon-bearing phases and the impact of chemical and polymorphic reactions on Earth's deep carbon cycle.

Background

The Earth in Five Reactions (E5R) project was conceived in the fall of 2015 at the University of Rhode Island, USA, where the Deep Carbon Observatory (DCO) held a synthesis-planning meeting. DCO is a ten-year project supported by the Alfred P. Sloan Foundation with the overarching goal of understanding the quantities, movements, forms, and origins of Earth's deep carbon. Members of the international DCO Science Network are addressing this goal through investigations focused on four distinct and interconnected thematic disciplines – Deep Life (DL), Deep Energy (DE), Reservoirs and Fluxes (RF), and Extreme Physics and Chemistry (EPC). Since its launch in 2009, the DCO has initiated and supported scientific campaigns to investigate deep carbon, leading to numerous findings reported in more than 800 scholarly publications to date, and created an international network of more than 1000 deep carbon scientists (www.deepcarbon.net).

"Serpentinization is the most important reaction in the universe!" This bold statement made by a workshop participant provoked Jie Li, an EPC representative who had studied chemical and polymorphic reactions for decades but thought little about serpentinization, to challenge the assertion. Li argued that redox and melting reactions dictate global-scale differentiation and therefore are far more important than serpentinization. This fundamental question about the key drivers in deep carbon science sparked a lively and spirited debate and revealed a general lack of consensus. Jesse Ausubel, the Sloan Foundation's primary liaison to the DCO, watched this exchange and asked "How about Earth in five reactions?"

The idea emerged as a promising framework for synthesis: Chemical reactions are widespread and play important roles in Earth's carbon cycle. Viewing Earth processes through the lens of reactions would highlight the chemical aspect of DCO science and could stimulate dialogues across disciplines. Like math and music, chemical reactions are the same in the United States, China, Italy or, France. The concept works internationally, even if people understand little or no English, and therefore could be widely reported or easily translated.

Why five? The number was inspired by the familiar "five types of chemical reactions" in high-school chemistry textbooks. Mathematicians and physicists have had success with celebrating “Five Equations that Changed the World”. We considered selecting five reactions in each DCO community, in addition to the five that encompass all communities. However, for the idea to work effectively, we chose to limit the number to five, much like the number of medals in each Olympic sport is limited to three. In reality, "Five” is not a magic or required number as the outcome, rather a gimmick to stimulate the DCO community to build its shared experiences. It was exciting to find out what the outcome would be!

The E5R project aimed to identify the five most important reactions governing the transformation and movement of carbon in Earth, and then use these reactions as the central themes for synthesizing and disseminating the findings of the Deep Carbon Observatory. This thematic structure also provides a new and integrative perspective for understanding and advancing deep carbon science as a new, multi-disciplinary scientific discipline.

Selecting the top five carbon-related reactions

We began by polling the DCO community to introduce the “Earth in Five Reactions” initiative and seek input on the five most important carbon-related reactions on Earth. We launched a survey just before the Third DCO International Science meeting in St. Andrews, Scotland in the spring of 2017. The poll was distributed at the meeting and through newsletters of relevant organizations, providing the opportunity for all members of the DCO science network and others to weigh in. By the end of year, we received 120 submissions with dozens of proposed reactions. Representatives from all four DCO communities and researchers at various academic levels ranging from emeritus professors to undergraduate students completed the survey. More than half of the respondents not only answered the multiple-choice questions but provided additional comments. We also received about twenty very detailed answers with elaborate essays, illustrations, and references.

The first survey question is: What criteria should be used for selecting a handful of reactions out of myriad chemical processes involving carbon in different host phases, variable valence states, under a wide range of pressure and temperature conditions, and over a vast span of spatial and temporal scales? A reaction may be considered important because it is essential to sustaining life on Earth (e.g., photosynthesis that converts carbon dioxide and water into sugar and releases oxygen). A top–ranking reaction may involve a component that is minor in quantity but is of special economic and geological interest (e.g., diamond formation). Proposed as a potential solution to the global warming problem, carbonation of mantle peridotite may be viewed as potentially important. On a more fundamental level, crystallization of Earth's molten core to concentrate carbon in the solid inner sphere could stand out because it may bear on the driving power of the Earth's magnetic field. If all carbon at Earth's surface was initially dissolved in the mantle, as previously hypothesized. then the transformation of diamond to graphite could be an important reaction. Without this polymorphic transition, the activation energy barrier to reacting diamond with anything may be so great as to lock up a large fraction of carbon in the form of diamond. Some critical reactions may have stretched over an extended time scale (e.g., inner core formation) whereas others may be widespread spatially and occur under broad ranges of pressure and temperature (for example, redox reactions in solids and liquids). Unique reactions that can be used as indicators, tracers, or diagnostic tools for carbon cycling are other possible targets of interest.

The distribution of responses to the criteria question was not particularly clear cut, with prevalence, timing, location, nature and impact all having an approximately similar number of votes. The narrative comments were revealing as well, ranging from one individual stating that most significant was "importance in terms of the fluxes of carbon they process and their impacts on the habitable planet" to another who felt criteria should be based on how the reactions "change the oxidation state of carbon—reduced, neutral, oxidized, with the product of the reaction having very different transport properties". Most telling was a third commenter, who stated "I feel very strongly about this", which was reassuring given the effort that the team had put in to enabling the whole exercise. A further provocative response suggested that "one way is to ask what if the Earth could be made again, but with only five reactions, which five involving carbon would make it look most like it does today?" Clearly there are many routes to discussing the "importance" or interest in any particular reaction, or indeed what is meant by reaction – whether the term should be restricted to chemical reactions or whether process or physical reactions might also be included.

Survey respondents were then asked to pick their favorite reactions. Given the outcomes of the suggested criteria, the outcomes of the reactions viewed most important were not particularly surprising. The importance of photosynthesis to the development of life on Earth, and the importance of life to the respondents, is an understandable priority. Other reactions mentioned at this stage include precipitation of calcite and dolomite in the sea followed by mineralization to form limestone and dolomite (to sequester CO_2), silicate weathering to carbonate, asthenosphere melting (to allow plate tectonics), dissolution of CO_2 gas into water, respiration (reverse photosynthesis, to generate sugars), redox reactions of CO to C or CO_2, redox melting, the Sabatier reaction (the passage from inorganic to organic geochemistry), the burning of fossil fuels, and the polymerization increase in C-bearing minerals inside the deep Earth.

On the basis of the polling responses, we defined five broad categories of reactions for further consideration, including serpentinization, respiration/photosynthesis, degassing/decarbonation, extreme carbon sequestration, and diamond formation. These reactions encompass the four DCO communities and represent a diversity of reactants/products, pressure (P), temperature (T), and catalyst conditions, and reaction mechanism, energetics, and kinetics. Their importance may vary with depth as well as time in Earth's history.

In March 2018 we convened a two-day workshop to select the top five carbon-related reactions on Earth and develop a plan for sharing advances in deep carbon science with the scientific community and broader audiences using the E5R framework. The workshop was held at the Carnegie Institution for Science in Washington DC, USA. About 50 participants from seven countries on three continents represented the DCO community. The group was selected to reflect the totality of the DCO in terms of interests and scientific expertise, and achieved balance in terms of academic level, gender, and geographic distribution. Education and media experts, along with several members of DCO's Executive Committee, Secretariat, and SG2019, rounded out the attendees.

The participants were charged with choosing five discrete chemical reactions from among hundreds that make Earth the only known habitable planet. They began by considering the survey results and pondered what carbon-related reactions make Earth unique. The workshop provided a trans-disciplinary forum for researchers to review the state of current knowledge and to identify the critical mechanisms and processes governing the movements of carbon through Earth. The group discussed the role of the deep carbon cycle in plate tectonics and the geodynamo, the development of an oxygen-rich atmosphere, how microbial life has persisted throughout Earth's history giving rise to a diverse biosphere, various ways water has influenced Earth's evolution, and the origin of diamonds. All attendees presented their perspectives and shared their ideas on how we could use chemical reactions as a framework to understand and advance deep carbon science. With keynote speakers, short-talk presenters, and panelists primed to argue for or against their chosen reactions, debates were passionate and sometimes intellectually divisive. By the middle of day two, however, the group converged on a set of reactions central to defining Earth.

Five reactions were selected through anonymous voting. Prior to voting, participants agreed that a pair of forward and reverse reactions counted as one reaction, and that similar and closely related reactions would be grouped into a reaction class. With this understanding in mind, eight reaction classes made to the ballot (Table 1). Hydrogenation, carboxylation, carbonation, carbon dioxide dissolution, and hydration emerged as winners.

Understanding deep carbon cycle through key reactions

The quest to identify the five most important reactions in deep carbon science has demonstrated that chemical reactions can provide a unique and effective framework for synthesizing deep carbon research. Looking at a particular reaction such as serpentinization has stimulated dialogue across DCO communities, leading to a deeper appreciation of its role in

Earth's volatile cycles. Mafic and ultramafic rocks react with water to form serpentinite. The geological process of serpentinization significantly affects the reservoirs and fluxes of carbon at subduction zones. In the presence of iron, serpentinization may produce hydrogen and form methane, thus profoundly influencing deep life on Earth, and maybe even life's origins. Chemical reactions also can be used as "threads" to connect disparate findings into coherent and meaningful pictures. For example, redox reactions are prevalent in geological and biological processes and often involve carbon-bearing species with variable valence state. They are of interest to all communities within DCO: Redox reactions have been found to influence volcanism, diamond formation, the abiogenic production of hydrocarbons and are central to life's metabolism. By comparing the mechanisms, conditions and energetics of these reactions and studying how they vary spatially and through geological time, we may gain insights into the connections among the deep carbon cycle, the "great oxidation event", and the origins of life on Earth.

At the workshop, the top five reactions received comparable numbers of votes, suggesting that the richness of DCO findings cannot be straightforwardly captured by a small number of reactions and that there is a healthy diversity of equally important processes. The three deep Earth reactions, including two diamond-forming reactions, did not make the final five. These deep Earth reactions are undoubtedly important because at least 90% of Earth's carbon is likely stored in the deep mantle and core. The voting results thus suggest a lack of awareness and appreciation for this deep carbon, even among DCO researchers. It implies that understanding extreme carbon remains at the frontier of future research and will require more effort to bring public awareness.

Following discussion of the E5R survey and selection of reactions, a group of scientists was motivated to review and integrate recent findings through the lens of the selected reactions. This special issue will feature articles using the selected reactions to integrate DCO science findings and illuminate the forms and flows of carbon in Earth. The collection as a whole provides a big picture view of DCO discoveries in the preceding decade, what its four Science Communities have learned about the role of carbon in planetary function, and how the identified five reactions play an integral role in carbon storage and pathways in Earth. The collection will also include additional contributions of original research on other carbon-related polymorphic and chemical reactions.

The E5R synthesis project distilled the planet's essence into a set of key carbon-related reactions that make Earth special and then used the reactions to encapsulate much of deep carbon science. It has led to new insights to motivate and guide future research. We hope that the special collection will help establish new frontiers for scientific exploration and investigation to address the fundamental question of Earth's habitability.

ACKNOWLEDGMENTS

The "Earth in five reactions" project is supported by the Alfred Sloan Foundation through grant G-2016-7157 to the University of Michigan. The principal investigators of the project are Jie Li and Simon Redfern. The project received guidance from the Synthesis Group (a.k.a. SG2019) Chair Marie Edmonds and crucial support from SG2019 manager Darlene Trew Crist, Katie Pratt, and Josh Wood, survey respondents, and workshop participants. The authors thank Keith Putirka and Rachel Russell for supporting the special collection.

TABLE 1. The eight reaction classes on the ballot

Reaction class	**Representative Reactions**
Hydrogenation dehydrogenation	$FeO + H_2O = H_2 + Fe_2O_3$
Carboxylation decarboxylation	$6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$
Carbonation decarbonation	$CaSiO_3 + CO_2 = CaCO_3 + SiO_2$
Carbon dioxide dissolution outgassing	$CO_2(aq) = CO_2(g)$
Hydration dehydration	$2Mg_2SiO_4 + 3H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$
Redox freezing melting	$MgCO_3 + 2Fe = 3(Fe_{2/3}Mg_{1/3})O + C$
Metal silicate partitioning	$C(alloy) + 2FeO(silicate) = CO_2(silicate) + 2Fe(alloy)$
Fe-C solidification melting	$FeC_x(l) = FeC_y(l) + Fe_7C_3$, where $y<x$

FIGURE 1 E5R logo (left) and special collection theme figure (right) showing where the reactions likely occur during Earth's deep carbon cycle.