

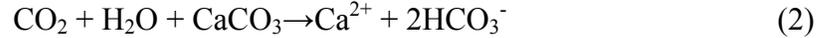
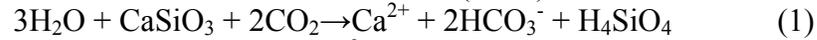
Using carbon isotopes to determine the sources and mass balance of CO₂ during shale weathering at Susquehanna Shale Hills Critical Zone Observatory

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Statement of Proposed Work: Coupled physical and biogeochemical processes transform bedrock into soils and provide inorganic nutrients to terrestrial ecosystems. These mineral weathering reactions consume CO₂, exerting important controls on global carbon cycles and climate change over geological timescales. Silicate mineral dissolution particularly, as a negative feedback, dictates atmospheric CO₂ concentrations (rxn 1). Thus it is critical to determine the silicate dissolution rate and the associated CO₂ uptake. However, in bedrock that contains both silicate and carbonate minerals, the amount of CO₂ that is consumed during silicate dissolution is hard to quantify due to the large amount of carbon that is released into water during dissolution of the more soluble and reactive carbonate minerals (rxn 2).



Shales, especially black shales, store the majority of fossil organic carbon, with 1 wt.% of organic content on average but reaching up to 40-50% (Copard et al., 2007). Although most of the ancient organic matter is relatively refractory, it is altered slowly at Earth's surface, through combustion, oxidation, hydrolysis and microbial consumption, referred to as biogeochemical weathering (rxn 3; e.g., Clayton and Swetland, 1978; Littke et al., 1991; Petsch et al., 2000; Jaffe et al., 2002). Thus, the formation and alteration of organic matter are important in the balance of atmospheric CO₂ and O₂ levels on global scales (Petsch et al., 2000, 2005; Sageman et al., 2003).



Organic matter in shales may be a critical source of nutrients and food. For example, a case study showed the majority of nitrogen in trees was derived from N-rich shales in nutrient-limited ecosystems of Northern California (Morford et al., 2011). In soils, micro-organisms are concentrated at the surface where food is abundant; a higher abundance of micro-organisms is commonly observed in the deep ground near the fossil organic matter sources (e.g., Petsch et al., 2005; Rumpel and Kogel-Knabner et al., 2011). The depletion of organic carbon in shales is accompanied by opening of pores (Kennedy et al., 2002; Fischer and Gaupp, 2005). Indeed, loss of even 1% of organic matter by mass (with low bulk density) will produce significant porosity in these shales. These pores make weathered shale easily accessible to oxygenated fluids, accelerating further weathering reactions (Fischer and Gaupp, 2005).

In summary, shale weathering is closely related to carbon cycles: uptake of CO₂ during mineral dissolution and release of CO₂ by oxidation of ancient organic matter. Given the ubiquitous distribution of shale on the continental land surface, it is critical to investigate the shale C budget: both CO₂ acquisition during mineral weathering and CO₂ release during decomposition of ancient organic matter. I propose to quantitatively determine C mass balance in the SSHO watershed using stable carbon isotopes, by identifying major carbon reservoirs and quantifying turnover rates of different carbon pathways. The NSF funded Susquehanna/Shale Hills critical zone observatory (SSHO) in Pennsylvania is a perfect natural laboratory for such an investigation, where soils are developed on Rose Hill shale.

In previous work, we observed that silicate dissolution dominates at shallow depths, while ankerite (Fe-rich carbonate) dissolution begins below 20 meters below ground surface (Jin et al., 2010). Indeed, evolution of water chemistry has been investigated along the water flowpaths, and data shows soil water cations from shallow soils are predominantly contributed by clay dissolution while carbonate dissolution signals are only observed in the ground water as evidenced by elevated dissolved Mg and Ca concentrations (Jin et al., 2011; Brantley et al., 2012). Furthermore, soil water [DOC] and soil organic carbon (SOC) storage have been linked

closely to landscape features (Andrews et al., 2011). High-resolution data by Andrews et al. (2011) captures the hot spots and hot moments of organic carbon, suggesting that SSHO is an active catchment where organic carbon decomposes quickly. However the sources of soil respired CO₂ is unknown, probably with contribution of ancient and modern carbon.

I plan to study C concentrations and isotopic compositions ($\delta^{13}\text{C}$) of different reservoirs in the Shale Hills catchment, including organic matter in the soils and Rose Hill bedrock, carbonate minerals, CO₂ in the soil gas, and dissolved inorganic carbon (DIC) and DOC in the natural waters (soil water, ground water and stream). The goals are: 1) to evaluate the degradation of organic matter in controlling seasonal variations of soil CO₂ concentrations; 2) to determine the relative contribution of silicate and carbonate dissolution to overall stream DIC; 3) to identify the sources of stream DIC: soil CO₂, atmospheric CO₂ and/or carbonate C; and 4) to quantify the CO₂ budget over the whole watershed by determining the mineral weathering rates and organic matter decomposition rates. This case study will help understand C fractionation in the surface and subsurface and develop C isotopes as an environmental tracer. More importantly, it will allow us to evaluate the roles of shale in global CO₂ cycles. Specifically, I will collaborate with Drs. Susan Brantley, Jason Kaye, and Elizabeth Hasenmuller at Penn State to:

- (1) Collect soil gas samples at different depths at three sites along a planar hillslope (ridge top, mid-slope and valley floor). Gas samples will be collected twice through existing soil gas samplers and injected into pre-evacuated vials, one during the growing season (May 2013), and the other during the winter (February 2013).
- (2) Sample two complete soil profiles, for soil C concentrations as well as C isotopic compositions.
- (3) Request archived Rose Hill bedrock, saprock (DC1 and DC2 cores) and soil samples (SPRT and NPRT sites), and investigate the C isotopic compositions and concentrations of ancient organic matter during its decomposition, and those of ankerite.
- (4) Collect soil water samples at different depths at the same hillslope as the soil gas samples, ground water at several locations within the catchment, and first order stream water in the Shale Hills catchment, and analyze dissolved inorganic carbon concentrations and C isotope compositions.

Analytical work will be performed primarily at the University of Texas at El Paso (UTEP), with two undergraduate assistants, including soil and rock organic carbon concentrations, soil [CO₂], and natural water DIC and DOC. UTEP does not have the facility for stable carbon isotope analysis, so the carbon isotope ratios will be measured in the Stable Isotope Laboratory at the University of Arizona. I expect the data collection will be complete by the end of summer 2013.

Proposed SSHO Interactions: This project is complementary to the existing NSF-funded Susquehanna Shale Hills critical zone observatory and its satellite sites, where existing data and current understanding on gray shale of Silurian Rose Hills Formation provide a solid foundation for our new investigation. This work targets on C, and fits well the overall theme of the SSHO, quantitative prediction of Critical Zone creation and structure, focusing on pathways and rates of water, solutes, and sediments. This proposed scientific work links tightly to one of the key questions SSHO group aims to answer: **what processes control fluxes of carbon and reactive gases at different landscape positions?**

I expect at least one conference abstract and one peer-reviewed publication from this seed grant, with collaborators at Penn State as co-authors. We will follow strictly the EAR data policy (http://www.nsf.gov/geo/ear/EAR_data_policy_204.pdf) to publish our dataset, no later than two years from acquisition/analysis. Data and metadata collected for this project will ultimately be made available to the public through the Critical Zone database. I will also make the unpublished data, including geochemical data and images openly available, through creating a web-based data file on PI-Jin's research websites and the international Critical Zone Exploration Network (www.czen.org). Announcements of new publications and datasets will be made in a timely manner to inform the research community through the CZEN mail list.

This project will piggyback on the Susquehanna Shale Hills critical zone observatory. First, we will request subsamples of parent rocks and soils archived by SSHO groups. Furthermore, we will use the infrastructures in the field, including lysimeters, soil gas samplers, and ISCO automatic samplers for groundwater/stream collection, as well as metadata collected by different instrumentations and sensors in the field (e.g., soil temperature, depth to water table, etc). Physical samples will be permanently catalogued and archived in PI Jin's research lab at the University of Texas at El Paso after the completion of the project. Samples will become available to any qualified investigator upon requests.

This project includes the training of two undergraduate students and development of the academic career for PI Jin as a female junior faculty at UTEP, a research-intensive doctoral university with a Hispanic majority student population. Collaboration between UTEP and Penn State will attract participation of Hispanic and female graduate and undergraduate students in environmental research, help them develop necessary skills for studies in critical zone processes, water quality and climate change, expose them to cutting-edge sciences, and prepare them for future career opportunities in the Environmental Sciences. This research will be used as case studies in the classes and seminars taught by Jin at UTEP. In addition, the project will be collaborative with Penn State Elizabeth Hasenmuller who will be fully involved in the project coordination.

The summer field school offered by Shale Hills CZO provides an excellent opportunity to support general environmental education and bring public awareness of critical zone sustainability. I will encourage participation of undergraduate students from UTEP in this learning experience, through their involvement in this project.

Anticipated results and outcome

The examination of inorganic and organic carbon concentrations and stable isotope ratios of various carbon reservoirs along the hydrologic flow path from surface soils enriched in organic matter but leached of carbonate minerals, into underlying bedrock containing abundant carbonate minerals. The dramatic change in carbon biogeochemistry over soil and weathered rock of increasing depth illustrates the strong interactions of silicate and carbonate minerals with biogenic CO₂ generated predominantly in overlying organic soils, as well as decomposition of "old" organic matter at depth from the underlying bedrock. I request funding through this Penn State NSF seed grant to collect preliminary data to help develop isotopic tools to understand transformation and transport processes that involve inorganic and organic C. This will serve as a basis for pursuing future NSF funding, to utilize C isotopic signatures and understand C cycles in the terrestrial ecosystems under different climate, vegetation, and lithology.