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Overview:

BcCZO-II aims to understand how critical zone (CZ) architecture evolves over time, how it conditions hydrologic and biogeochemical response and ecosystem structure, and how it will respond to future changes in climate. Objectives are: 1) Document CZ evolution in the Colorado Front Range, where climate has been the major driver for the last 40 Myr; this entails determining rates of exhumation of the range and its adjacent basin, and documenting the structure of the CZ at key sites across the range. 2) Understand how weathering, transport, and biological processes shape the CZ (process to form). 3) Discover how CZ architecture governs the storage and flow of water, nutrients and sediments (form to function). 4) Explore CZ functional response to near-future changes in temperature and precipitation, and associated changes in ecosystem and fire regime. 5) Communicate findings through talks, papers, K-12 education, undergraduate classes and research, and simulations based on process models that capture CZ dynamics. Methods include: 1) monitoring weather and water in selected sites across the Boulder Creek watershed, 2) sampling rock, soil, vegetation, and water for physical, chemical, and genetic data, 3) collecting cores, geophysical data and outcrop descriptions of CZ structure, 4) constructing conceptual and numerical models to quantify CZ evolution in past climates, and present-day and future CZ functioning.

Intellectual Merit :

The central aim of BcCZO is to develop a deeper understanding of the structure, functioning, and evolution of the critical zone in a mountainous landscape. This understanding is required to answer fundamental questions in earth and environmental science, such as: How does rock turn to sediment? How do landscapes evolve? What controls hydrologic and biogeochemical fluxes and ecosystem services? The Colorado Front Range provides an ideal natural laboratory for exploring these questions, as the results from BcCZO-I have shown; it typifies mountainous landscapes of the American West that support large human populations. Mountain CZs have been shaped by a complex climatic history, leaving a long legacy. The juxtaposition of hard crystalline rock of the mountains against soft shale of the Plains, each with a different biota, forces acknowledgement of the roles of rock type and of both biogeomorphic and biogeochemical feedbacks in the evolution of the CZ.

The transformative nature of the program lies in its integrative and interdisciplinary approach. The BcCZO-II project brings together a diverse team of ecologists, hydrologists, geomorphologists and geochemists from CU, USGS, and Colorado School of Mines, knit by major threads that include snowmelt, subsurface flow, multiple roles of biota, emergence of long-term climate legacies, and numerical models that cross disciplinary boundaries. Weather and fire events have driven perturbations in water, sediment, and solute export from the mountains that are being monitored, and that stimulate modeling efforts that include projection into a warming climate. Research on snow, the geobiology of deep weathering, the roles of slope aspect, and the use of cosmogenic radionuclides connects BcCZO to other CZOs.

Broader Impacts :

Beyond training researchers in interdisciplinary science, the impact of BcCZO will be extended through five related activities:

1) Engagement of the CU Science Discovery program. CZ science will be delivered to secondary students and teachers in Colorado through a Field Course for Colorado Teachers, Mountain Research Experience for high school students, and traveling BcCZO School and Community programs. A graduate CZO Science Discovery Outreach Fellow will benefit from working with Science Discovery education professionals. 2) Engagement of underrepresented minority students in research. A REU program to be proposed will serve students recruited from three historically black universities and from CU. The BcCZO faculty, CZO REU Fellow and graduate students will provide a three-week course combining classroom and field research experiences. 3) Educational simulations. The BcCZSim Fellow will transform CZ models into interactive simulations, each tested by Science Discovery students and teachers, and contributed to the Science Education Resource Center(SERC). 4) Future-casting hydrologic and ecosystem states to 2050. This will contribute to water and environmental management policy. 5) Cross-CZO integration. Cyberseminar series, CZNetwork

workshops, joint modeling and field efforts, and the Drill-the-Ridge program will strengthen the CZ community.

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Boulder Creek Critical Zone Observatory-II: Evolution, Form, Function, and Future of the Critical Zone

1. Background and results from prior support

NSF0724960 Boulder Creek Critical Zone Observatory: Weathered profile development in a rocky environment and its influence on watershed hydrology and biogeochemistry. PI: **SP Anderson**, Co-PI: **RS Anderson**, **N Fierer**, **AF Sheehan**, and **GE Tucker**, Sr. Personnel: **D McKnight**, **A Blum**, **S Murphy**, N Caine, M Williams, C Wobus, M Leopold, J Voelkel, K Loague \$4,249,997. 9/1/07-8/31/12. *NSF1239281 Boulder Creek Critical Zone Observatory Renewal:* PI: **SP Anderson**, Co-PI: **RS Anderson**, **N Molotch**, **H Rajaram**, **GE Tucker**, Senior Personnel: **H Barnard**, **D McKnight**, **A Blum**, **S Murphy**, **N Fierer** \$1,000,000. 9/1/12-8/31/13.

Boulder Creek CZO (BcCZO) was established in 2007 as a natural laboratory to study how erosion and weathering together shape the architecture of the critical zone. The observatory takes advantage of the Colorado Front Range (Fig. 1) as a setting in which climate has unleashed glacial and fluvial downcutting at different times and in different segments of the Boulder Creek watershed. In this setting, the goals were to understand how weathering (both physical and chemical) and transport processes control the structure of the critical zone, and to explore the impact of critical zone structure on hydrological, geochemical and biological functions of the landscape. The project built upon decades of research and monitoring, primarily in the alpine-subalpine parts of the watershed (Niwot Long Term Ecological Research (LTER) site), and brought together a team of geomorphologists, microbial ecologists, geophysicists, hydrologists, and geochemists to accomplish this.



Fig. 1 Boulder Creek CZO LiDAR overlay on oblique view toward the west from High Plains to Front Range crest (Anderson SP et al., 2012a). Glacier extent at Last Glacial Maximum shown in headwaters. Boulder Canyon cuts into crystalline rock of the Front Range. Quaternary strath terraces record episodic fluvial incision of the High Plains.

Infrastructure

We recognized Boulder Creek as encompassing three distinct erosion regimes with differing critical zone architectures: glacially scoured headwaters, a low-relief, possibly steady-state landscape ("Rocky Mountain Surface," see Anderson et al., 2006), and fluvially rejuvenated hillslopes lining Boulder Canyon. We built or augmented infrastructure in each setting. The project extended Niwot LTER infrastructure in Green Lakes Valley with cosmogenic radionuclide (CRN) dating of glacial retreat (Dühnforth et al., 2011), installation of soil moisture and temperature sensors, and daily time-lapse photos of the basin since 2008. In the previously unstudied Gordon Gulch watershed

on the Rocky Mountain Surface, we established 2 stream gauges, 2 weather stations, 6 groundwater wells, snow sensors, soil moisture and temperature monitoring, lysimeters, and a program of weekly water sampling. In Betasso watershed, which represents fluvially rejuvenated slopes lining Boulder Canyon, we installed a 10-m meteorological tower, snow depth, soil moisture, temperature, and matric potential sensors, and we sample its ephemeral stream each week. Instrumentation is detailed in the Facilities and Equipment supplement. Bedrock coring to 124 m depth at the divide in Betasso in January 2013, will

yield data on water table dynamics and unambiguous imaging and samples of weathered rock in an area that has undergone baselevel lowering. Geophysical characterization in all three watersheds (Leopold et al., 2008; Befus et al., 2011; Clarke 2012) reveals depths to fresh rock in these different erosion regimes.

Significant findings and successes

1. Long-term evolution

Boulder Creek watershed brings into relief the strong legacy of past conditions in present landscapes, and the interconnections between different parts of landscapes (Anderson SP et al., 2012a). The region as a whole has undergone exhumation in the late Cenozoic (Wobus et al., 2010), but the timing and style varies. Quaternary glaciation of the headwaters (Ward et al., 2009; Dühnforth et al., 2011) carved Ushaped overdeepened valleys in the crystalline core of the Front Range, and deposited moraine complexes. Downstream, strath terraces on the Plains indicate exhumation as well, although offset in timing from the glacial headwaters: rivers occupied terrace surfaces during glacials and cut down during deep interglacials (Dühnforth et al., 2012). A simple interpretation is that variations in sediment supply from glaciers control downstream channel incision, yet channels without glacial headwaters are also incised and are lined with terraces (Anderson SP et al., 2012a). The incision of these non-glaciated watersheds could be due to variations in sediment supply from non-glaciated hillslopes that were subjected to periglacial conditions (Anderson RS et al., 2012) in the headwaters, or due to upstream migrating knickpoints from lowering of the glaciated master channel. The broad strath terraces of the High Plains are underpinned by easily eroded Mesozoic Pierre shale. Where downcutting rivers encounter the hard crystalline rock (e.g., Boulder Creek batholith) of the Front Range, incision is focused into narrow defiles such as Boulder Canyon (Anderson RS et al., 2006). Canyon cutting should affect groundwater fields, and sets off slow relaxation of adjoining bedrock slopes (Anderson SP et al., 2012a). Quaternary climates produced overall incision, but at different rates and times throughout the watershed. Bedrock slopes lining canvons are even now undergoing weathering and exhumation spawned by glacial climates.

2. Spatial variation in surface energy balance

The catchment energy balance influences both long-term landscape evolution, and short-term catchment hydrology and biogeochemistry. Water flux through hillslopes is tightly connected to local surface energy balance in this landscape where mean annual temperature is near 0°C, and hence snow and frost are important. The surface energy balance is manifested in the first order characteristic of the critical zone, its thickness. Shallow seismic refraction revealed a striking pattern of deeper weathering profiles on north-facing slopes (15.3 m) than south-facing slopes (12.9 m) in Gordon Gulch (Befus et al., 2011). Although forest composition varies with slope aspect, the direct influence of trees on the weathering front at these depths (>10 m) is small, because forests are Holocene phenomena at this elevation (ca. 2500m) (Minckley et al., 2012) while these weathering fronts reflect 10^5 - 10^6 yr of evolution (based on denudation at 20 m/Myr; Dethier and Lazarus, 2006). The strong difference in moisture and water delivery with slope aspect must influence weathering and erosion over the timescale of critical zone profile development (Anderson SP et al., 2009).

Considerable effort has gone into measuring and modeling snow in alpine terrain (e.g. Jepsen et al., 2012), but less attention has been paid to patchy, marginal snowpacks such as form over the Rocky Mountain surface and in Gordon Gulch (Anderson SP et al., 2009, 2012b). Although south-facing slopes are often bare in winter, catchment runoff is dominated by spring snowmelt. But the difference in snowmelt timing strongly influences water delivery to the weathering front. North-facing slopes receive less radiation, and are more shaded by a close-canopy lodgepole pine forest. The sustained melt of accumulated snow from these slopes in spring flushes water through the vadose zone (Hinckley et al., 2012). In contrast, intermittent melt events throughout the winter on sunny, ponderosa pine woodland south-facing slopes produce lower water fluxes through the vadose zone, and are more effective at deep wetting than is delivery of the same amount of water in one sustained pulse is more effective at al., 2011 and in review). We infer that aspect control on water fluxes translates into differences in chemical

weathering rates. Surface energy balance also controls thermal conditions. Our numerical models demonstrate that weathering and sediment transport by climate-controlled frost processes can reproduce the observed asymmetry in Gordon Gulch weathering depths (Anderson RS et al., 2012).

3. Short-term events

Wildfire is an example of a short-duration disturbance that disproportionately influences environmental processes in the critical zone. In September 2010, the Fourmile Canyon Fire burned 2600 ha of the Boulder Creek Watershed and profoundly altered hydrologic and geomorphic processes. In the year after the wildfire, the increase in discharge caused by snowmelt runoff and low-intensity rain and mixed snow-and-rain events was similar upstream and downstream of the burned area (Murphy et al., 2012). However, convective thunderstorms at high precipitation intensities produced short-term flash floods not typically observed in unburned watersheds. Discharge downstream of the burned area was 80fold greater than pre-storm discharge (compared to less than 50 percent increase upstream of the burned area). Consequently, the convective storms transported substantial amounts of sediment from burned hillslopes to Fourmile Creek and resulted in large increases in concentrations of DOC, nitrate, total suspended sediment, and sediment-associated metals downstream of the burned area (McCleskey et al., 2012; Murphy et al., 2012; Writer et al., 2012; Writer and Murphy, 2012). The July storms were typical of Colorado Front Range thunderstorms (storms of this size have a 20-50 percent chance of occurring each year), yet the stream's response to these storms provides clear evidence that burned watersheds are prone to flash floods that transport substantial amounts of sediment to downstream water bodies. These changes in hydrologic response are diagnostic of a shift in runoff generation processes from subsurface (pre-fire) to surface (post-fire) mechanisms (Ebel et al., 2012; Moody and Ebel, in review). The shift to predominantly infiltration-excess runoff generation substantially reduces the threshold precipitation intensity at which overland flow occurs. Much smaller increases in runoff were observed in the second year, despite similar rainfall intensities, possibly due to vegetation recovery. Aspect-driven differences in soil temperature/moisture regimes and soil-water retention were reduced after the wildfire (Ebel, 2012a.b. 2013), which may have important consequences for vegetation recovery and ecosystem resilience.

4. Biogeochemistry and microbial ecology

Environmental perturbations such as fire and climate change influence, and are influenced by, soil biogeochemistry and microbiology. Our research on edaphic controls revealed that hillslope position (Eilers, 2011) and depth in soil (Eilers et al., 2012) influence the composition of soil microbial communities, particularly the proportions of taxa associated with the quality and quantity of C inputs to soil (Eilers et al., 2010), and the dynamics of nitrate pools (Hinckley et al., in prep). Amazingly, we found that there is much greater microbial variability across the soil depth profile than is typically seen across biomes, with rare (and poorly understood) taxa dominating in the deeper soil depths. Fluorescence measurements show that plant-derived soil organic matter (SOM) increases with depth (Gabor et al., 2010). In saprolite, however, microbially derived SOM becomes dominant, potentially representing an ecological feedback that promotes weathering. Seasonal patterns in stream dissolved organic material (DOM) indicate that during high runoff DOM originates in the upper soil layers. However, the DOM quality observed in Boulder Creek and Gordon Gulch runoff does not match that of leachates from the upper soil horizons. Thus, rapid sorption and chemical fractionation, which has been demonstrated in stream sediments, may account for these differences at the landscape scale. Further, the high variability in DOM in Gordon Gulch may relate to changing flow paths, with the episodes of highly microbial DOM character corresponding to drainage from microbially dominated saprolite. These changes in stream DOM were found to be the main factors driving the high degree of temporal variability in stream bacterioplankton communities within this watershed (Portillo et al. 2012).

5. Human resources, productivity, and outreach

BcCZO has a staff of 4 professional research assistants, collaborated with or supported 6 post-docs and 17 graduate students, and involved 58 undergraduate students. We published 55 papers and produced 2 PhD, 9 MA and 18 undergraduate theses.

BcCZO partnered with the University of Colorado (CU) Science Discovery program to bring critical zone science to K-12 learners and teachers, reaching ~3,500 kids and 300 teachers. We created videos providing an overview of the CZ, and describing our scientific methods; these are used in Science Discovery and CU classes, and are accessible on our website. BcCZO also presented a program on wildfire, geology, soil, and water at Operation Water Festival, a program attended by about 1,000 fifth-grade students and teachers from Boulder Valley schools. In addition, we have provided three offerings of a CZ course at CU (two graduate, one undergraduate), and run two graduate seminars. Finally, BcCZO provided a venue for undergraduate research largely through the Keck program run through Williams College and through mentoring students in the NSF-funded UNAVCO Research Experience in Solid Earth Science for Students (RESESS), which has a mission to broaden participation in earth science.

Lessons learned

1) At the outset, we focused on erosion regimes within the Front Range as independent natural experiments to exploit. We now appreciate that each region is connected to and responds to changes in neighboring parts of the landscape (Anderson SP et al, 2012a). The High Plains record timing of incision of the watershed through terrace ages; we now recognize that the High Plains also provide an experiment to explore how different rock types (soft sediments vs. the hard crystalline rocks) exhume in response to changes in sediment and water flux. Moreover, the shale of the High Plains provides a connection to Shale Hills CZO. 2) We have learned to appreciate that the CZ has strong legacies of climate regimes in the past. Failure to acknowledge these legacies would lead to incorrect inference about the relevant processes and rates; lessons learned from the past will inform predictions of CZ response to future climate change. 3) We have refined our inquiry into critical zone architecture to focus on its interfaces: air-land (topography), mobile regolith-rock, and weathered-fresh rock. We realize the importance of key processes, such as snow hydrology and its interaction with vegetation, the role of biota in mobilizing regolith. 4) All CZOs recognize the need to improve understanding of incipient weathering at the bottom of weathered rock and the transformation of weathered rock to saprolite as it is slowly exhumed. 5) Not least, we have learned the importance of building a cohesive team of scientists willing to work together. The chemistry of interactions among team members is perhaps more important than productivity or effort of individuals. The magic of CZ research occurs during cross-talk among the researchers, which is best fostered by a cohesive team with a strong desire to meet regularly.

2. Scientific Justification for BcCZO-II: Critical zone evolution, form, function and future

Landscapes evolve through the actions of many thousands of rainstorms and snowmelt seasons and freezing nights and tree lifetimes, each rearranging mass or altering its chemistry in a small way. Understanding this evolution therefore involves understanding how individual weather events (rain, snow) are filtered through the landscape itself, how water or frost or biologic agents induce sediment motion or rock breakdown, and knowing how to appropriately sum these over time. Understanding these connections provides a framework from which to gauge how these systems respond to future climate (Fig. 2). BcCZO aims to understand how critical zone architecture, defined as the vertical arrangement of layers in the critical zone as well as three-dimensional topography of each layer, forms over time. To do so, we must understand processes that move material around or alter it chemically. Water is involved in almost every process that matters. As its flow through the critical zone is itself dependent on the architecture of the critical zone (the depth and permeability of regolith, the steepness and three dimensional organization of slopes, and the fabric of CZ ecosystems), the analysis of critical zone evolution, form, and function becomes iterative.

Our goals are to: 1) Document critical zone **evolution** in the Colorado Front Range, where climate has been the chief driver since the end of the Laramide orogeny about 40 Myr ago. This entails determining rates of incision and exhumation of the range and its adjacent basin, as well as describing the structure of the critical zone throughout the range. 2) Understand how individual processes shape the critical zone (**process to form**). Weathering processes and sediment transport processes together shape hillslopes and move weathering fronts into rock. 3) Discover how critical zone architecture influences the

storage and flow of water (**form to function**). The critical zone serves as a filter for water quantity and quality delivered to streams. 4) Explore critical zone functional response to **future** perturbations. As temperatures increase (especially summer), and the elevation of the rain-snow transition rises, and as fires or insect infestations change in frequency or intensity, we will require process models to explore the landscape's hydrologic, geomorphic, and biogeochemical response. Anticipated outcomes include models of processes at short timescales, and an integrated model of critical zone evolution, function and response to future climate to 2050. The team, described in the Management Plan, brings together expertise in geomorphology, hydrology, geobiology, ecology, and geophysics.



Fig. 2 Conceptual model of BcCZO, illustrating the long term **evolution** of the BC landscape, the processes responsible for generating the CZ **form** on a hillslope scale, which in turn governs the hydrologic and ecological **function** of the landscape. The CZ services delivered by the CZ will change in the **future** as climate changes.

Conceptual model

The critical zone is a three dimensional system, comprising surface topography and subsurface layers with their own three-dimensional shapes. At its simplest, however, the critical zone can be thought of in profile, with prominent interfaces (Fig. 3). The dynamics of these interfaces, which connect the processes to the form of the CZ, are controlled by material type (geologic legacy), water flux (hydrology), weathering (geochemistry, geobiology), and sediment transport (geomorphology).

It is no surprise that the evolution of the CZ reflects the rates of motion of the major interfaces that define it: the land surface, the base of mobile regolith, and the base of weathered rock. It is equally obvious that the hydrologic and ecological services provided by the CZ depend upon its architecture. The excitement and the challenge lie in the diversity of the processes involved in driving the long-term evolution of the CZ, and in rendering its services. Our effort is designed to address these linked intellectual tasks and yield models capable of forecasting future behavior of the CZ. To that end, in the next section we describe a program of research that builds on the following *key themes*: (1) Understanding the variations in space and time of fluxes of mass, water, energy, and nutrients. (2) Recognizing linkages

across disciplines and scales, from microbiota to trees and pores to watersheds. (3) Illuminating geomorphic feedbacks between the mountains (as source of water and sediment) and the adjacent plains (as baselevel for mountain drainage basins). (4) Documenting the legacy of the climatic and geologic past in shaping the present-day CZ and its behavior in the future.



Fig. 3 Conceptual diagram of critical zone architecture. We focus on three interfaces: 1) land surface (atmospheremobile regolith), 2) top of rock (mobile regolith-weathered rock), and 3) base of the critical zone (weathered rock-fresh rock). The water table (unsaturatedsaturated zone interface) crosses solid layers. and is more dynamic. Weathering and transport processes shape this architecture over time, deliver sediment to the adjacent streams, and govern the hydrologic and ecological services provided by the CZ.

3. Science Implementation Plan

This proposal is organized to focus on (1) the *interfaces and the intervening layers* one by one. Each entails a cross-disciplinary mix of processes, and therefore serves to demonstrate the cross-disciplinary nature of the CZ enterprise. We then discuss (2) the *integrative science*, including modeling, that grows out of the work on interfaces. The latter includes forecasts of hydrologic and geochemical behavior under potential future climate scenarios. Finally, we plan (3) *cross-CZO integrative activities*. For each interface we identify key research tasks, including field and modeling tasks that knit across timescales. Guiding questions include: How does the interface and associated layer evolve, and what sets the pace? What are the processes involved and what are the resulting fluxes in the modern landscape? What are the implications for the spatial patterns on hillslopes and to whole-landscape organization?

3.1 Science Implementation: Critical Zone Architecture and Processes

Interface and Zone 1: Land Surface and Mobile Regolith



It is on the land's surface that snow accumulates and melts, that trees grow and die and sometimes burn, that fauna dwell. The magnitudes of the swings in temperature and in moisture are greatest at and near this interface, at all timescales. The matter and energy passed to greater depths are preconditioned by their passage

across the land surface interface and through this mobile regolith. We support several intertwined activities, dealing with the water balance, the transport of mobile regolith, the involvement of biota in transport of water and sediment, and the role of disturbance events such as fire.

<u>Lumps and blocks: Patchiness in the landscape.</u> Hillslopes within the BcCZO are far from smooth. As illuminated in LiDAR imagery of the mountainous portion of the BcCZO (Fig. 1), all three target subcatchments are lumpy; they are dotted with outcrops that comprise anywhere from 10% (Betasso) to 60% (Green Lakes valley, GLV) of the landscape. The mobile regolith that covers the remainder of the landscape must be transported around these outcrops. This roughness is characteristic of mountainous landscapes, yet is seldom addressed head-on, and is certainly not addressed in any landscape evolution model, including our own. We wish to open this dark box. The lumps and outcrops reflect the blocky nature of the crystalline bedrock. Making progress on this aspect of the landscape will require addressing this blockiness in the field and in models, including characterization of the present outcrops and block sizes, the evolution of blocks, the origin of variations in block size, and the means by which blocks evolve in size both before entrainment and within mobile regolith. The patchiness of outcrops requires that we address the landscape in its full mapview. These outcrops introduce complexity in the landscape much like patchiness in other variables, generating "richness" in the topography; these will generate potentially

strong feedbacks with the distribution of snowpack, the thermal state of the landscape, and the hydrologic pathways by which snowmelt and rainfall pass through the landscape, and ultimately the distribution of biota in the landscape. The lumpiness of these landscapes provides us leverage in exploring the ecological and geomorphic process feedbacks at work here.

Hypothesis: The distribution and sizes of rock outcrops at the land surface reflects the larger unfractured blocks inherited from the tectonic fracture pattern. The alternative is that the outcrops are governed largely by pre-existing structural grain within the rock.

Tasks: i) Document fracture patterns in outcrops, in GLV (>50% exposure of bedrock), and in walls of Boulder Canyon. ii) Measure the detailed morphology of blocks as they weather out of their jointbounded niches (rounding their edges), constraining how their geometries evolve. iii) Generate models of fracture networks in 3D (e.g., Clemo and Smith, 1997) to assess the expected block size distribution in natural networks, against which our measured distributions may be held. iv) Develop models of rocky slope evolution that honor both the joint patterns and the evolution of blocks as they weather. Rounding of blocks drives evolution of torques on the blocks that ultimately allow toppling from bedrock niches.

<u>Transport of mobile regolith: The roles of biology.</u> Several processes conspire to transport mobile regolith downhill. Our challenge is to develop quantitative expressions for the efficiency of each possible transport mechanism with sufficient connection to climatic conditions to allow estimation of both past and future roles of each transport mechanism. As the temperatures in this landscape result in frost heave, we have developed transport rules that capture this effect as a function of the mean annual temperature (Anderson RS et al., 2012), and have developed and deployed sensors to capture the frequency and amplitude of heave events. But observations reveal that biological processes are also important in accomplishing soil transport. Acknowledging feedbacks between geomorphic and biological systems has been woefully inadequate in past geomorphic research (e.g., Zaitlin and Hayashi, 2012). The key biologic players in BcCZO at present are gophers and coniferous trees. Throughout western North America, gophers exert one of the strongest controls on successful conifer establishment (Ferguson 1999; Engeman and Witmer. 2000). However, gophers themselves are constrained to relatively deep, organic soils (Zaitlin and Hayashi, 2012), and by access to food, which is limited under mature forests (Anderson and



MacMahon, 1981). In many areas across the Rockies, this results in greater establishment of conifers on rocky slopes and outcrops, and persistence of grassy meadows on deeper soils. These ecological dynamics in turn create patterning in the geomorphic effects of gophers and trees: gophers move substantial amounts of fine-grain material (e.g., Butler and Butler, 2009; Gabet, 2000; Gabet et al., 2003; Yoo et al., 2005), increasing downslope

Fig. 4 Feedbacks in a geomorphically patchy landscape, between outcrops, trees, gophers, and mobile regolith production and transport.

movement of regolith, whereas tree roots both anchor sediments and break apart solid rock (e.g., Skeets and Barnard, 2011). This promotes preferential establishment of trees at the edges of rock outcrops, where the growth of roots helps to break up the rock mass there (Fig. 4). These ecological interactions, and their geomorphic results, are also strongly mediated by climate: on wetter N-facing slopes, trees have the upper hand and effectively exclude gophers, while in treeline or drier sites, the control of tree densities by

gophers appears to be strongest. Thus, while these patterns are self-reinforcing on the order of decades or centuries, climate change will predictably shift the abundances of these ecological players.

As much of a tree's volume is in its roots, the growth of roots in soil and in cracks in the underlying saprolite can both displace soil and enlarge existing cracks. We have taken preliminary steps to quantify the role of growth and decay of trees in transporting soil. The density of trees on S-facing slopes (ponderosa pine), the lifetimes of trees, and the displacements of soil by individual trees, result in relatively efficient downslope transport (Hoffmann and Anderson, in review).

Hypothesis: Gophers deter invasion of forests into meadows through herbivory; this promotes establishment of trees at the edges of rock outcrops, where root growth helps to break up the rock mass.

Tasks: i) Continue to document transport efficiency of trees by measuring root mounds and tree density. ii) Document the intensity of gopher activity and gopher-tree-soil thickness associations as a function of landscape position in all catchments, constraining dependence on both aspect and elevation. iii) Model tree and gopher populations on different slope aspects. We will employ reduced complexity, agent-based models of tree and gopher populations on both N- and S-facing slopes, constrained by measured species distributions, and the biology of germination probability on differing soil thickness, wetness, aspect and gopher herbivory. As described in integrative modeling (section 3.2), these biomodels will serve as layers that overlie the hillslope models, linking biological and geomorphic evolution.



Fig. 5 Snow hydrologic instrument cluster consists of co-located snow depth, soil moisture and temperature, sap flow, energy balance, and, in some instances, eddy covariance measurements. Snow depth sensors are stratified by proximity to trees (open areas, under-canopy, canopy-edge). This design has been implemented in the three current western CZOs.

individual trees (Fig 5), to ridgelines, to mountain ranges (Balk and Elder, 2000; Elder et al., 1998; Erxleben et al., 2002; Molotch et al., 2005; Winstral et al., 2002). We lack process models that reproduce these relationships. Such an advance would permit modeling of snowpacks in the past and under future

Surface Hydrology: Infiltration, runoff, and water balance. Water plays multiple roles in critical zone function and evolution. We seek to understand how precipitation is partitioned into ET, runoff, storage and infiltration, and how it varies with and is controlled by elevation, aspect, climate, vegetation, and soil/rock type. Understanding this variability in response is critical in predicting response to future change on human timescales and on past evolution. Our approach involves continuation and modest expansion of our hydrologic monitoring network, use of remote sensing to quantify the snow budget, and modeling of the interactions.

Snow in the BcCZO. The distribution and melt timing of snow dictates the spatial and temporal pattern of water inputs to the subsurface. Small-scale studies show that relationships between snow accumulation and terrain variables are nonlinear (Elder et al., 1998; Molotch et al., 2005). Statistical models highlight the roles of radiation, slope, aspect, elevation, vegetation, and wind redistribution on snow distribution at scales ranging from climate change scenarios. Snow studies within the BcCZO have strong potential for cross-CZO research through modeling output from similar instrumented data collection in varying terrain and climates. Snow interaction with trees necessitates tracking the fate of intercepted snow and ablation in the open versus under canopy. We know that trees have an interception limit, and therefore as total snowfall increases, the proportion intercepted decreases (Hedstrom and Pomeroy, 1998). Shedding of intercepted snow is more likely in warmer air, and therefore is expected to vary with altitude (Montesi et al., 2004). Climatology of the Front Range is such that lower elevations receive more snow in heavy spring storms, while higher elevations receive more snow in colder winter months. These and other considerations lead to an expectation of strong elevation gradients in the proportion of total snowfall intercepted by trees, and in the open versus under-canopy differences in snowmelt timing. We test two hypotheses with observations and models:

Hypotheses: Snow interception on trees is proportionally greater at higher elevation, and this generates an elevation gradient in differences between open versus sub-canopy snow accumulation (tree scale patchiness).

At higher elevation, where snowmelt occurs when solar elevations are greater, radiation plays a more significant role in melting snow. Conversely, at lower elevation we expect a reduced influence of solar radiation and more uniform snowmelt in open versus sub-canopy locations.

Tasks: i) Automatically monitor snow cover and related parameters (Fig. 5), stratified by canopy position, aspect, and elevation. ii) Manually measure snow depth and snow water equivalent along snow transect. iii) Model sub-canopy and open snow in different slope aspects and elevation.

To resolve differences in sub-canopy versus open snowpack states we will use SNOWPACK, a 1D finite element snow, vegetation, and soil model, run using Alpine3D, a spatially explicit extension of SNOWPACK (Lehning et al., 2006). The model emphasizes stratigraphic detail and fine-scale mass and energy exchange. This level of detail has great value in hydrological applications particularly in regard to ice layer formation, vapor exchange, grain size, and surface albedo, which are seldom explicitly modeled in land surface or hydrological models. SNOWPACK, by design, does not require calibration, and therefore can be used to simulate snow under different conditions, such as in future or in the past.

Forest Evapotranspiration (ET). The amount of biologically available water is arguably the central driver to both plant physiological and soil processes (Newman et al., 2006). Biologically available water is set by precipitation, runoff pathways, soil evaporation and water use by vegetation. Such knowledge is important for modeling the ecosystem consequences of changing climate, including both altered rainfall and modified atmospheric drivers of ecophysiological processes. ET is directly related to forested ecosystem gross primary production, and accurate prediction of carbon and water exchange relies on understanding the factors driving the rates and timing of forest transpiration and soil evaporation (Law et al. 2002, Williams et al. 2004). Thus, an understanding of the hydrologic potential of the landscape requires information on patterns of tree water use among species and at different landscape positions. Vegetation water use also strongly influences soil moisture profiles via direct uptake and hydraulic redistribution of soil water. During prolonged drought, some species will succumb to very low matric potentials in surface soils, while others may use deeper sources of water (Lee et al. 2005). The ability to use deep source water is largely dependent upon physiological characteristics, such as stem hydraulic conductivity, leaf area, stomatal conductance, and root distributions (Jackson et al. 2000). The extent to which deep water sources can be used by vegetation may also depend on the amount of biologically available water at a given position on the landscape and the soil physical properties.

Although it is increasingly clear that interaction between soil and vegetation controls water availability and flux, heterogeneous soil properties and plant physiological function are difficult to predict without extensive measurements. Soil properties are influenced by local climate and evolve over time. Soil pH or clay mineralogy, for instance, may record changes in mean temperature, moisture and vegetation. Currently, very little detailed spatial data exist for soil properties and plant physiological function beyond the hillslope scale, preventing our understanding of soil-plant-atmosphere coupling. As a result, few hydrologic models presently incorporate the detailed spatial soil properties.

Hypothesis: Slope structure and hydrology are first-order controls on stand-level evapotranspiration.

Tasks: i) Select trees that span the species and diameter distributions in plots. Measure tree transpiration rates directly using heat-pulse techniques. Install transpiration sensors at multiple depths within the xylem in order to characterize depth dependence of water flux. ii) Calculate the fractional contributions of transpiration and evaporation to the total water vapor fluxes from isotopic mass balance. iii) Partition soil water losses by quantifying changes in isotopic composition (Ferretti et al. 2003), using $\delta^2 H$ and $\delta^{18} O$ in plant and soil water, extracted by cryogenic vacuum distillation (Ehleringer et al. 2000).

<u>The role of fire.</u> The interesting suite of hydrologic, biogeochemical and geomorphic responses to the 2010 Fourmile Canyon fire were outlined on p. 3 above under "short-term events". The key features of post-fire conditions included a shift to predominantly infiltration-excess runoff generation. Subsequent high-intensity convective thunderstorms resulted in stream discharge downstream of the burned area that increased from less than one to 23 m³/s in less than 5 minutes, with a peak flow that was about three times greater than ever recorded on Fourmile Creek (Murphy et al., 2012), and generated order-of-magnitude increases in sediment loads and DOC, nitrate, and metal concentrations in streamflow. These observations lead us to ask: How long will it take for the hydrologic and geomorphologic response of this system to return to pre-fire conditions? While the post-fire response of water and sediment discharge may be short-lived, does the magnitude of the response make it a substantial driver of erosion in the Front Range? Other studies have suggested that common precipitation events in burned areas can lead to catastrophic erosion events that dominate the long-term sediment yield (Kirchner et al., 2001). Can this be observed in the long-term record of the Boulder Creek Critical Zone?

Hypothesis: The hydrologic, geomorphic, and nutrient responses at the watershed scale are substantial in the years immediately following a wildfire, but recover within 5 years.

As a corollary, one may entertain the hypothesis that *Front Range foothills erosion during the Holocene is dominated by episodic pulses from wildfire, with long term quiescent periods in between these disturbance events, dictated by the fire return interval.* In essence, this is an end-member scenario in which geomorphic activity is focused into rare extreme events.

Tasks: i) Continue to monitor water, sediment, and nutrients upstream, within, and downstream of burn area. ii) Model runoff during storm events in burned and unburned catchments, and couple runoff and sediment transport algorithms to calculate erosional response to the burn. This will inform landscape scale models in which post-fire and inter-fire geomorphic processes operate.

Interface 2: Base of mobile regolith and weathered rock/saprolite



The evolution of saprolite and its transformation to mobile regolith are seldom addressed in either conceptual or numerical models of landscape evolution. Yet the chemical, physical and biological processes that damage rock as it is transformed from fresh rock to mobile regolith both regulate the rate at which it

can be entrained, and govern the initial properties of the mobile regolith. In addition, it is increasingly recognized that the co-evolution of permeability in the saprolite and the geochemical alteration of the saprolite govern the hydrologic and ecological services rendered by this layer. We document rates using ¹⁰Be, characterize material properties of saprolite, and document its hydrology and associated geochemical alteration.

<u>Lowering rates.</u> We have documented 20-30 μ m/yr rates of lowering of the mobile regolith interface in Gordon Gulch (Foster et al., 2011; 2012; in review) using *in situ* ¹⁰Be from the top of the saprolite, and have developed the general theory for expected ¹⁰Be concentration field in an evolving landscape (Foster et al., in review). This effort has promoted discussion among CZOs about use of ¹⁰Be in CZ studies.

Hypothesis: Lowering rates will be slower in the warmer and drier Betasso catchment.

Tasks: i) Document *in situ* ¹⁰Be in rock at the top of the saprolite, and profiles in the mobile regolith, on a hillslope catena draping from forested rocky ridge through meadow. The mobile regolith profiles reveal vertical mixing depths, placing constraints on the dominant processes transporting mobile regolith.

<u>Rock fracture</u>. We have argued (Anderson RS et al., 2012) that damage of the rock while it resides in the saprolite layer preconditions it to entrainment at the mobile regolith interface. Damage includes physical, biological and chemical processes. While fresh crystalline rock in the Front Range was damaged

by Laramide tectonic processes (Molnar et al., 2007), our drilling of saprolite in both Gordon Gulch and Betasso has shown that the rock within the top several meters of the surface is considerably more fractured than the fresh rock below. Weibull (1951) and subsequent workers have argued that fracturing of rock becomes increasingly difficult as incipient flaws within the rock are exploited (Gumbel, 1958; Lobo-Guerrero and Vallejo, 2006; Todinov 2008, 2009; see Iverson (2012) as applied to glacial beds).

Hypothesis: The blocks that are ultimately entrained in the mobile regolith reflect the end-result of this fracture process and represent blocks that are very difficult to break.

Tasks: i) We will document fracture patterns in fresh rock as constraints on initial conditions for saprolite, using road outcrops, televiewer logs in our boreholes, and rock wall exposures in the GLV catchment. Given that the rate of lowering of the saprolite boundary is effectively an advection speed, we may deduce the rate and long-term average vertical pattern of rock cracking from the observed vertical profile of crack density (Anderson, RS et al., 2012). ii) We will document the size distribution of blocks at the base of mobile regolith, and characterize the flaw density of these blocks (for example using clast seismic velocity or tensile strength methods (Kelly, 2012)).

<u>Entrainment.</u> Several candidate mechanisms may entrain material into the mobile regolith layer, operating now and in the past: tree root prying, frost jacking. In general the fractures within the crystalline rock produce a tight jig-saw pattern of jagged-edged blocks that remain immobile unless physically disrupted by some energetic process. We know that depth to fresh rock is in general 4-8 m (Befus et al., 2011; Kelly, 2012). Damage is difficult to accomplish at these depths with frost-cracking processes, even when we allow glacial-interglacial cycles (Anderson, RS et al., 2012).

Hypothesis: Tree roots are important in generating near-surface cracking, and in entraining blocks form the mobile regolith interface.

Tasks: i) Document depth distributions of tree roots in soil pits, and in roadcuts carved into hillsides along roads that penetrate the Rocky Mountain Surface. These will augment previously documented rooting patterns of the major flora in this landscape (e.g. Berndt and Gibbons, 1958)

<u>Hydrology and chemical weathering of saprolite</u>. Saprolite—the most weathered, intact rock—is an important water reservoir (Graham et al., 2010), and is the source of material entrained in mobile regolith. Understanding its formation and behavior requires addressing the flux of water into the saprolite, and the factors that govern this flux. Saprolite may be a site of significant lateral redistribution of water. We also address the implications of water flux for silicate weathering kinetics, and sensitivity to climate.

Hypothesis: The structure of the saprolite zone—its mineralogy, bulk density, cohesion, porosity, and permeability—reflects a feedback between hydrology and chemical alteration.

Tasks: i) Continue monitoring moisture of both mobile regolith and saprolite (Gordon Gulch and Betasso), and water chemistry in streams, wells, springs, and lysimeters. ii) Develop 2D models of unsaturated-zone flow dynamics using VS2D (Lappala et al., 1987). iii) Implement numerical experiments on hillslope flow and weathering with the reactive-transport model PFLOTRAN, which combines saturated-unsaturated flow with reactive-transport capabilities (Hammond et al., 2007).

Data on rainfall, snowmelt, and soil hydrologic properties will provide model inputs, and moisture data will be used in calibration. The most intriguing finding from preliminary 1D and 2D modeling is that the saprolite water fluxes appear to be highly sensitive to the timing of water input: the contrast in snowmelt timing between the N- and S-facing slopes of Gordon Gulch leads to substantial differences in the volume and depth of water delivery to the saprolite (Hinckley et al., 2012; Langston et al., 2011; in review), potentially explaining the documented asymmetry in the depth of weathering (Befus et al., 2011). Adding reactive transport with PFLOTRAN will allow us to analyze the implications of vadose flow patterns for chemical weathering. A key goal is to quantify the influence of subsurface water partitioning (see below) on silicate weathering. For example, the upper saprolite is likely to see the greatest fluxes, but weathering patterns will also come from geochemical analysis of core and chips from drilling. Modeling of chemical weathering of granitic rocks will complement ongoing research in other CZOs (Riebe et al., 2004; Lebedeva et al., 2007, 2010; Brantley and Lebedeva, 2011), in which climates range from arid (Santa Catalina-Jemez) to wet tropical (Luquillo).

Interface 3: Deep Weathering Front



The bottom of weathered rock is the least accessible, most slowly evolving part of the CZ, yet processes occurring here set the stage for overlying CZ architecture, as material moves upward through the "reactor" (Anderson SP et al., 2007). Recent summaries have shown that the "chemically altered zone" is commonly 4-

8 m thick (e.g., Anderson SP et al., 2002; Dethier and Lazarus, 2006; Yoo and Mudd, 2008; West, 2012). In Gordon Gulch, we found a strong slope aspect control on weathering depth (Anderson SP et al., 2009; Befus et al., 2011), unique bacterial phyla in saprolite vs. upper soil horizons (Eilers et al., 2012), and redox-active dissolved organic matter in saprolite (Gabor et al., 2010). We expect deepest weathering to be found along pre-existing fractures (Molnar et al., 2007; Clarke and Burbank, 2011) that promote water circulation, affected by tree root depths (Schwinning, 2010, 2013), and driven by geobiology (Brantley et al. 2011b). We therefore focus on fractures, microbes, and environmental conditions throughout the weathered rock, and where we can access it, incipient weathering at the weathered-fresh rock interface.

Hypothesis: Microbial activity exerts a strong influence on the chemical alteration in weathered rock. Key controls on microbial activity and community composition at these interfaces include: water availability, supply of oxidants (such as oxygen and NO_3^-), and supplies of inorganic and organic carbon.

Tasks: i) Document rock character (fracture spacing, mineralogy, porosity, strength) in core from Betasso (drilled Jan. 2013), from cores planned in Gordon Gulch in this proposal ("Drill-the-Ridge"), and from rock walls in GLV and Boulder Canyon. ii) Analyze pore fluids from groundwater collected in wells and lysimeters to identify labile redox-active components and their cycling, including dissolved organic matter. iii) Apply "biopetrology" approaches to rocks recovered from fracture networks and zones of chemical alteration to elucidate links between chemical alteration of rocks and the activity of insitu microbial communities. iv) Analyze the phylogeny of bacterial and archaeal communities found in the interior of core samples using a high-throughput PCR-based approach.

These tasks will lead to a more dynamic conceptual model of deep weathering process by linking local environmental conditions, microbial communities, organic carbon pools, and microscale change seen during incipient alteration. As a cross-CZO activity, we will explore whether biological processes transition from domination by heterotrophic microorganisms near the surface to chemolithotrophs at depth (e.g. Buss et al., 2005, 2008), and the microbial role in mineral oxidation, dissolution and accumulation of carbon in the rock. A novel aspect of our proposed work will include determining whether redox-active dissolved organic matter (as detected in deep saprolite by Gabor & McKnight) is microbially-produced in-situ and mediates electron-transfer reactions that contribute to incipient mineral weathering. To resolve microscale redox-reactions in bedrock, we will use multiple-energy x-ray fluorescence microprobe and x-ray absorption spectroscopy to map changes in the oxidation state and speciation of Fe, Mn and S (Templeton et al., 2009; Mayhew et al., 2011; Mayhew et al., in review). Mapping and characterization of organic matter, and associated mineralogy, will be conducted using confocal scanning Raman microscopy (e.g. Menez et al., 2012) on samples carefully prepared without organic contamination in the new Raman microscope facility (see Facilities). The Raman spectrometer will be coupled to a confocal microscope that will permit the concurrent detection of microbial taxa through fluorescence in-situ hybridization (FISH) using probes selected or designed after high-throughput sequencing of extracted DNA. DOM concentration and fluorescence measurements, and voltammetry using solid-state Au/Hg amalgam microelectrodes, will be conducted on deep groundwaters and pore fluids, in order to identify labile redox-active components in the fluids (e.g. reduced Fe, Mn and sulfide and DOM rich in guinone moieties) (Cory and McKnight, 2005; Swanner et al., 2010).

We will analyze the bacterial and archaeal communities found in core samples using a highthroughput PCR-based approach (Fierer et al. 2012, Caporaso et al. 2012). Although our previous work focused on bacteria and archaea living in subsurface soil (e.g., Eilers et al., 2012), we will also analyze fungal communities, which have been shown to be important in weathering and metal-oxidation processes (Gadd 2007; Tang et al., 2012). Briefly, we extract microbial DNA from these samples, compositing multiple, replicate extractions from the deeper depths to obtain sufficient amounts of DNA. For the bacterial and archaeal community analyses, we will use barcoded primers that yield accurate phylogenetic and taxonomic information and exhibit few biases against any individual bacterial or archaeal taxa (Bates et al., 2011). The amplicons will then sequenced on the Illumina HiSeq or MiSeq platforms with data processed using QIIME (Caporaso et al. 2010) and additional data visualization techniques and geospatial analyses implemented in R. Fungal community analyses will be conducted in a similar manner, using a fungal-specific primer set (ITS1-F/ITS2) we have adapted for barcoded Illumina sequencing (McGuire et al., in press) that targets the ITS1 region and is universal for nearly all fungal taxa (Bellemain et al. 2010).

The microbial community data will be used to compare the relative abundances of specific taxa with depth and across the watershed to infer environmental conditions and the potential importance of specific weathering processes at the targeted interfaces. This use of microbes as 'bio-indicators' (Bradford and Fierer, 2012) holds promise as a complement the more detailed geochemical analyses described above.

3.2 Science Implementation: Integrative activities

1. Water table and subsurface water balance

The water table is a highly dynamic interface, exhibiting variations on event (hr-day), seasonal, interannual and greater time scales. Measuring the water table provides insights on hydrologic functioning of the CZ, which drives biogeochemical and ecological processes. Hydrometeorologic forcing, topography, and CZ architecture, such as fracture density in bedrock, control the water table elevation in mountainous and rocky watersheds. Key questions involving groundwater in both CZ functioning and evolution are:

i) How is the subsurface water balance partitioned between uptake by trees, lateral subsurface flow, and deep groundwater flow through fractured bedrock?

ii) What is the role of the water table in regulating the biogeochemical and ecosystem services provided by the CZ? How do these respond to changes in water table induced by climate change?iii) What constraints are imposed by the water table, subsurface flow, and water partitioning on



Fig. 7 Water system in crystalline rock of montane region. Mobile regolith overlies fracture variably saturated saprolite. Water system is perched on relatively impermeable rock several meters below land surface. The deep system is dominated by occasional fractures, most dry and a few wetted by connected fracture access to surface system. Dynamics of water delivery to stream is governed by lateral flow of perched system, in places intercepted by transpiration. Trees use water from different depths depending on water stress and their physiology. Water supply for domestic use to residents in the mountains is through deep fractures at 100-150 m depth.

geochemical (possibly microbial) reactions, and the processes that drive evolution of the interfaces that define the CZ architecture?

Subsurface water partitioning: Quantifying subsurface flow paths important for is constraining both CZ functioning and evolution, as water is an important driver of both biogeochemical and weathering processes. We observe a perched groundwater system in the shallow weathered zone of the study watersheds. This system receives inputs from snowmelt and rainfall, and is depleted by subsurface lateral flow, deep percolation through bedrock fractures and water uptake by tree roots (Fig. 7). The low permeability and fracture density in the bedrock likely restrict the hydrologically active portion of the landscape to the shallow weathered fracture zone. In Gordon Gulch, measurements indicate that the water table is above the top of fresh bedrock (Befus et al., 2011). The depths to water table and base of saprolite are approximately 5.7 m and 7 m, respectively, at a location on the S-facing slope, and 9.4 m and 15 m at a location on the N-facing slope. As noted above, variations in snowmelt patterns driven by aspect appear to cause these differences (Langston et al. 2011, in review). Deep drilling at Betasso in Jan 2013 revealed very dry conditions below the ~ 7 m thick highly fractured saprolite zone, until a water-bearing fracture was intersected at ~100m depth. The potentiometric head in the borehole stabilized at ~85 m. Thus, to different degrees at these sites, bedrock fractures may also drain the perched water table. Dissolved organic matter and water quality signatures in streamflow (Anderson SP et al., 2012b) point to deeper flow paths through the saprolite and fractures in the bedrock. The general features of the hydrologically active portions of the Betasso and Gordon Gulch watersheds resemble those described or hypothesized in previous studies of steep rocky catchments (e.g. Montgomery et al., 1997; Anderson SP et al., 1997; Wilson and Guan, 2004; Kosugi et al., 2006; Ebel et al., 2007; Salve et al., 2012).

Rigorous quantification of subsurface water partitioning in BcCZO catchments will require implementation of physics-based subsurface hydrologic models, extending the work of Hincklev et al. (2012) and Langston et al. (in review). Candidate models include InHM (VanderKwaak, 1999), PARFLOW (Kollett and Maxwell, 2006), PIHM (Qu and Duffy, 2007) and PFLOTRAN (Hammond et al., 2007), the last of which is also capable of simulating multi-component reactive transport in variably saturated flow. These hydrologic models should consistently incorporate (a) the differences in snowmelt inputs on the N- and S-facing slopes, (b) the differences in CZ architecture and associated hydraulic properties of the soil, saprolite and weathered bedrock zones, (c) the spatially variable fracture-dominated connectivity of deep bedrock, and (d) representations of plant water uptake, recognizing the significant (2-3m) depths to which tree roots may extend (Canadell et al., 1996; Berndt and Gibbons, 1958; Schwinning, 2010). The continuous water table, soil moisture, streamflow, and water chemistry data will be used as modeling targets to constrain the hydrologic models and property fields. Ability of the subsurface hydrologic models to capture the salient differences between the behavior of N- and S- facing slopes will also serve as an important modeling target. We will develop models to quantify the complex subsurface partitioning of water in the CZ of Gordon Gulch, which will also serve as a template for interpreting biogeochemical processes and weathering.

<u>Biogeochemical and Ecological CZ Services regulated by water fluxes:</u> The water table generally constrains the redox environment prevailing in the subsurface, with oxidizing conditions above the water table, and reducing conditions below it. This geochemical zonation has significant implications for the biogeochemical and ecological functioning of the CZ. For instance, it may be a factor responsible for the significant changes in microbial diversity observed with depth (Eilers et al., 2012). Hydrologic fluxes were identified as a key control on biogeochemical processes and microbial dynamics. Reactive transport models such as PFLOTRAN, described above, are promising tools for quantitatively addressing the role of hydrology in these contexts. Enhancing reactive transport models to include microbial dynamics and organic carbon will enhance their ability to quantify biogeochemical processes.

<u>Role of subsurface water fluxes on weathering reactions and the evolution of the CZ</u>: The redox gradients induced by the water table are also relevant to weathering reactions that influence CZ evolution (e.g. Ollier, 1988). A detailed understanding of the spatial distribution of weathering rates through regolith, saprolite and shallow bedrock zones requires multi-dimensional reactive transport modeling in the entire subsurface. These models will aid in testing alternative hypotheses on weathering rates across the entire CZ, including the role of biota (Brantley et al., 2011) in terms of tree roots and mycorrhizal networks, and microbial influence on weathering reactions. It is also important to recognize the blocky architecture of the saprolite and fractured bedrock in evaluating the nature of weathering rates. The transformation of fracture blocks into saprolite by the combined action of water, unloading and other near-surface processes, is another important research target.

While contemporary weathering rates may be quantified by coupling hydrologic models for presentday conditions to reactive transport models, such an exercise will not directly address the evolution of the CZ, which bears a strong legacy of the past. To address the processes that produced the CZ observed today within the Boulder Creek watershed, it is important to place the landscape in a paleoclimatic setting, and force hydrology and thermal processes with past climates. We will approach the behavior across glacial-interglacial time scales by employing "snapshots" of past climates, as the hydrology is slaved over relatively short time-scales to controls imposed by climate and thermal regime. For the Last Glacial Maximum (LGM), representing the glacial end-member climate, we will use archived results for the Colorado region from model runs reported in Liu et al. (2009) as we have in Duhnforth et al. (2012). We will implement robust coupled-process models that can quantify geomorphic, geochemical and biogeochemical process intensities associated with an "average annual hydrologic cycle" to assure capture of differences between seasons in the corresponding paleoclimates.

2. Landscape evolution models

We have discussed some interface-scale modeling tasks above. Modeling efforts at the hillslope to whole-landscape scale are described below. These address both the origins of specific landscape features over long timescales that illustrate couplings between elements of the CZ within our landscape (as advertised in Anderson SP et al., 2012a), and services provided by the CZ that involve crossing of one or more interfaces and layers whose study we have articulated above. We illustrate with two examples:

Modeling hillslopes. We have developed detailed 1-D hillslope models that operate over long timescales (Anderson RS et al., 2012). These are starting points for the next generation of models. In order to handle the outcrops and swales common in our montane landscapes, and the vertical architecture, we must expand models to 3D. Our hillslope models will operate at two timescales: annual to centuryscale, to capture the services rendered by the CZ, and 1ka-1Ma to capture long-term landscape evolution in the face of glacial-interglacial climate swings. On the short timescale, models will run on a prescribed hillslope topography and CZ architecture (layer thicknesses and properties). They must capture the essence of the interactions among these elements: snow, trees, rodents, reactive water transport, including microbiological mediation, and mobile regolith transport. Output from these models will include the flux of water, sediment and solute from the hillslope, and rates of modification of the mobile regolith and underlying saprolite. On the long timescale, models must also incorporate fracturing and weathering of blocks in the subsurface, entrainment of saprolite into mobile regolith, toppling of blocks from outcrops, and co-evolution of the ecological and geomorphic systems that allows exploration of self-organization of these landscape elements. For the hydrologic, ecologic and geomorphic components of these long-term models, will exploit the use of "snapshots" of the state of the system (described in hydrologic models below) at climatic end-members, such as present interglacial and LGM. Output from these long-term models is not only the evolving topographic form and architecture of the CZ (outcrop pattern, layer thicknesses and properties), but the expected temporal pattern of water and sediment discharge from the hillslope. These in turn inform models of the response of the fluvial system to modulations in sediment and water supply that we argue are important in the formation of the terraces that bound the Front Range.

<u>Modeling terrace formation on the High Plains</u>. Using the 2D landscape evolution model (LEM) CHILD (Tucker et al., 2001; Tucker and Hancock, 2012), we will answer the question: "What conditions are both necessary and sufficient for glacial-interglacial cycles to produce range-bounding flights of strath terraces?" Rivers crossing the High Plains appear to widen during glacial times, generating wide floodplains that are then abandoned during intense interglacial times. We have hypothesized (Duhnforth et al., 2012) that this behavior is driven by variations in sediment supply from the headwaters. But an alternative interpretation is that the abandonment of these broad surfaces is incited instead by the incision of a nearby "master" stream that serves as a local base level for the tributary "slave" stream. We will test the viability of alternative working hypotheses for terrace genesis, including oscillations in hillslope weathering and transport (Anderson RS et al., 2012), in hydrology (Pelletier, 2009; Wobus et al., 2010), and in glacial sediment supply (Hancock and Anderson, 2002). Master and slave tributaries will experience the same climatic swings, but the network geometry allows the master tributary to contain glaciers in its headwaters while the slave does not. A major challenge is explicit treatment of the widening

of the floodplain by backwearing of the bounding valley walls. By developing a method for modeling this process, we will overcome a significant barrier in the current generation of LEMs.

3. Future cast – BcCZO-2050

One of the greatest challenges facing the Earth Sciences community is prediction of the Earth's response to climate change in coming decades (NRC, 2012b). In the arid West in particular, the change will be manifested largely in delivery of water to the landscape and in melting of snow. As it is the quantity of water, the timing of its drainage from the mountains, and its chemical quality that matter to the citizenry occupying the Front Range corridor, it is important to predict these as best we can.

Much of the hydrologic, biogeochemical and ecological modeling machinery that we will develop is relevant to predicting the response of the landscape to plausible climate change scenarios. The now wellestablished very slow pace of landscape change argues that we may safely assume that the architecture of the CZ in this arid Rockies landscape will not change over decadal time-scales, and hence may be taken as static; the soil thicknesses, the distribution of rock outcrops, the permeability structure will remain unchanged. What will change are the hydrometeorological drivers, the air temperature, and those elements of the ecological and biogeochemical systems that respond quickly to these changes. Because ecology plays a role in both mechanically and chemically filtering the water as it moves through the landscape, the quality of the water delivered from the landscape will be altered. We will employ the strategy discussed above in which we target specific "snapshots" of the operation of the CZ in the past, but this time look forward a matter of decades, to 2050.

The first element in a framework for future-casting is the climatic forcing. Future hydrologic inputs in the mountainous regions of Colorado have been calculated using climate models run by NOAA and NCAR (Ray et al., 2008; Rasmussen et al., 2010), which result in forecasts of patterns of precipitation in a warming climate. These models suggest that the most important changes in precipitation and snowmelt patterns will be slightly greater winter precipitation, offset by faster snowmelt, and slightly reduced summer rainfall (e.g., Ikeda et al. 2010). While these models are valuable in establishing precipitation and temperature trends, their low resolution (4-km grids in highest resolution WRF models; Rasmussen et al., 2010; Ikeda et al., 2010) precludes representation of small-scale variations in radiative forcing (e.g., N- and S-facing slopes), or the elevation gradient that we know to be important across the BcCZO.

We will employ the hydro modeling methods outlined above, forced with archived WRF 4-km model runs to which we have access through collaboration with NOAA (D. Gochis, co-PI with N. Molotch on sustainability grant), but modified to incorporate fine-scale variations in radiative forcing, ecohydrology, and CZ architecture across the BcCZO to future-cast hydrologic changes resulting from climate change out to 2050. We will focus on these important issues:

• Is the hydrologic and biogeochemical functioning of the CZ made more resilient by the heterogeneity of the landscape at fine scales, or does the large-scale mean behavior predicted by low-resolution studies adequately represent regional behavior? The answer has potential implications for water management in this semi-arid region. To this end, we will compare calculated hydrographs from several points within the Boulder watershed with those calculated using the 4-km resolution land surface model (Ikeda et al., 2010 and archived model output available through NOAA-Molotch).

• How strong will the eco-hydrologic response be to climate change? We will employ physiologically consistent tree water uptake functions (Feddes and Raats, 2004; Skeets and Barnard, 2012) constrained by our monitoring of sap-flow and isotopic composition of tree water in a coupled modeling framework. We will compare model ET fields and hydrographs in which these feedbacks are either turned on or off. We expect biogeochemical process rates to change due to both increased atmospheric CO_2 and altered residence time of water in the landscape induced by a longer snow-free season.

• As summer temperatures increase over the Plains, we expect the intensity of summer thunderstorms to increase in the montane landscape. This raises the likelihood of lightning-induced fire, while the increased human population in the mountains raises the likelihood of human-induced fire. As the intensity of fires, and landscape recovery from fire depend upon the density of trees and the subsequent sequencing

of water delivery to the landscape (Ebel et al., 2012), we will explore expected response of the landscape to hypothetical fires in a 2050 climate with altered storm frequency and duration.

3.3 Science Implementation: CZO National cross-network activities

<u>CZ Network Cyberseminar Series</u>. All CZOs will work with CUAHSI, to run and advertise broadly six cyberseminars/yr, building upon the series run by CUAHSI in 2011-2012. In the next 5 years, we will highlight any work on CZ questions. In some cases, a cyberseminar may be scheduled as follow-up after one of the cross-network activities outlined below. All CZ topics will be included.

<u>CZ Network Research (CZNR) Workshops (\$15k/CZO)</u>. Each observatory will run one ~2.5-day CZNR Workshop on an interdisciplinary topic for ~12 scientists and students from in and outside of the CZO network. Each CZO host will provide travel allowances, housing, and meals. The intent is to stimulate intense work on discipline-crossing topic. The workshops will result in a proposal, synthesis paper, or integrative model. CZO data will be highlighted in the context of data from other sites. A likely topic for BcCZO hosted workshop is the deep critical zone, building on our coring and geophysical strategies, and interest in incipient weathering at the base of the critical zone.

Drill-the-Ridge (\$28k in BcCZO-II). Access to the bottom of weathered rock is difficult to gain but widely recognized as the CZ region we understand the least. Pilot coring projects have been run at all six original CZOs, and will be extended. The "Drill the Ridge" idea was proposed at the International Workshop on Design of Global Environmental Gradient Experiments using International CZO Networks (8-9 Nov 2011, Univ. of Delaware). The goal is to understand full CZ structure where 1D makes sense. Sampling rock and overburden, conducting downhole geophysics, and monitoring water level and temperature, will inform simple models. The preliminary data will inform proposals to core in more locations, with accompanying geophysical surveys, pump testing, and microbiological sampling. BcCZO cored to 124 m at the top of Betasso in January 2013, where the granodiorite bedrock is deeply weathered. and where we hypothesize CZ architecture will show evidence of the lowering of the water table when adjacent Boulder Canyon incision occurred (Anderson SP et al., 2012a). After drilling, water stood at 84 m depth. Downhole geophysics was completed by co-PI K. Singha. Our next objective is to core in Gordon Gulch, which is underlain by Paleozoic gneiss and is not impacted by canyon cutting. Wells in Gordon Gulch show that the water table is much higher (~10-15 m below surface) than at the divide in Betasso. A second target for coring is shale rock on the Plains, which would allow comparison of the weathering profile in shale developed under grasslands in a relatively arid climate with that at Shale Hills.

Joint Research Field Campaigns (\$15k/CZO). Each observatory will run a 5-day CZ Joint Research Field Campaign over the next five years. Each site will host one field campaign, similar in format but with different foci. The host will support travel and accommodation for a total of 12 students, postdocs or scientists from other CZOs in each campaign. The intent is to stimulate researchers to develop shared data, to work together across disciplines, and to introduce students to new sites and techniques. It is expected that results from each Campaign will become part of the CZO community data resources. If appropriate, the CZOs may use the CZ Network Research Workshops to develop focused questions for the field campaigns, or for the CZ Network Research Workshops. BcCZO will host in year 3 (2015-16) on a topic that fits with our internal integrative theme of the year.

<u>Cross-CZO modeling (\$10k/CZO).</u> Ongoing modeling activities at each CZO will be communicated and integrated across the network through a series of cross site visits. During those visits, modelers will be cross-fertilized in terms of conceptualizations and codes and will learn how to make best use of available data. To facilitate, each CZO is pledging \$10k for travel. As BcCZO is co-located with the CSDMS at INSTAAR, we anticipate hosting networking meetings that can take advantage of CSDMS staff to foster construction or translation of codes in open source format.

4. Outreach and Broader Impacts Implementation Plan

K-12 education: Science Discovery

From 2009-13, BcCZO partnered with CU Science Discovery to develop and deliver engaging handson science programs. These included classroom and field activities for underserved 5th grade students, week-long field science camps for middle school students ("Go With the Flow" and "Fire and Ice"), fullday CZ workshops ("Exploring Change in the Critical Zone") and interactive display stations for community outreach events. Materials are based on current CZ science focused on topics such as geology, hydrology, fire ecology and soil science. These programs directly impacted ~3,500 students (60% from underrepresented groups) and more than 300 teachers. BcCZO-II and Science Discovery will now capitalize on these resources and focus its efforts on providing secondary teachers and students with field experiences and connecting more students (grades 4-12) throughout Colorado to current CZ science through school presentations, workshops and community outreach programs, as follows:

<u>CZO Field Course for Colorado Teachers.</u> BcCZO researchers and Science Discovery staff will coordinate a 3-day professional development field course for 12 middle and high school science teachers from throughout Colorado. The goals of the field course are to: expose teachers from around the State to current CZ research; increase teachers' content knowledge of CZ-related topics; and provide teachers with curriculum, materials, field activities, and BcCZO data that they can use to make science stimulating and relevant for their students. During the field course, teachers will live and work at CU's Mountain Research Station, located at 9500 ft. in the Front Range of the Colorado Rockies, interacting with CZO scientists and experiencing field research first-hand. Science Discovery staff will integrate hands-on lab and field research activities with guest scientist presentations, field trips and teacher discussions.

<u>Mountain Research Experience for High School Students.</u> The Mountain Research Experience is designed to provide high school students with an authentic field research experience at CU's Mountain Research Station. Each summer, 12 students, selected through a competitive application process, will participate in a 5-day research course focused on BcCZO science. The goals of the high school field course are to: increase high school students' interest in and understanding of geological and ecological field research; heighten high school students' interest in conducting longer-term (year-long) field research projects in collaboration with CZO researchers and graduate students; and connect students to science professionals as role models. In days 1 and 2, students will participate in introductory field activities that will provide an overview of current CZO research. In days 3 and 4, they will work in teams on selected research projects, with each research team guided by a CZO faculty or student researcher. On the final day of the course, students will present their research findings to their classmates, CZO and Science Discovery staff, and other scientists at the field station. For students enrolled in a senior research class (e.g., Boulder Valley School District's Science Research Seminar course), the field course provides a springboard experience that can connect them to their senior research project.

<u>BcCZO School and Community Programs.</u> BcCZO and Science Discovery will continue to bring hands-on activities, already developed in the previous years of this grant, to schools around the State, with a target audience of underserved 4th-8th grade students and teachers, including those in rural areas. Science Discovery, with its extensive network of K-12 school partners throughout Colorado, will coordinate classroom programs and community outreach events. The *CZO Science Discovery Outreach Fellow*, a CZO graduate student funded primarily to do K-12 education outreach, will lead these hands-on activities, with additional support provided by Science Discovery staff. The goals of the School and Community Programs component are to: increase students' interest in and excitement for science and science-related professions; expose students and teachers to current CZ science; and provide underserved students, including those in rural areas, with undergraduate and graduate level scientist role models who can heighten their interest in science while countering stereotypes about scientists. Combined, these programs will reach more than 60 teachers and 1,200 students each year.

Undergraduate research education: Engaging underrepresented minorities

BcCZO research requires a combination of numerical modeling and field data collection, and is well suited to undergraduates due to the short-term sampling required to capture some processes of interest. We plan to support Dr. Val Sloan, former RESESS program director, to work with BcCZO faculty to write an REU supplement supporting a minority-focused undergraduate research and training program. Sloan will work with Kamini Singha (Colorado School of Mines), Suzanne Anderson, Anne Sheehan, Holly Barnard and others to plan the REU. We build on Sloan's experience with RESESS, and Singha's

four years of experience developing an REU at Penn State University with three Historically Black Universities (HBUs): Jackson State University, MS; Fort Valley State University, GA; and Elizabeth City State University, NC. We anticipate building a three-week intensive program that blends students from the three HBUs and students from CU. The goal is to combine classroom education with a field campaign, linked to the Theme of the Year, making partial differential equations come "alive" and promoting CZ Earth science as a career trajectory. Our BcCZO faculty cover hydrogeology, geophysics, ecohydrology, Quaternary geology, and geomorphology. Graduate students will help to mentor the undergraduate participants; one designated the CZO REU Fellow will hold greater planning responsibilities. There will be no "cookbook": students will formulate scientific hypotheses, with appropriate scaffolding and guidance, and determine how to test these hypotheses. Students will explore concepts associated with physics-based numerical modeling, including model generation (initial and boundary conditions, parameterization), and the implementation of discretized mathematics to describe diffusion processes. They will then make field measurements to test or parameterize their models. By involving students in research early in their potential careers as scientists and engineers, we will streamline their educational path, provide them with a toolbox for their future, and establish a community of friends and colleagues from other institutions who share similar scientific interests. The students' data and modeling will be published, insuring a positive feedback loop between research and education.

Education through models: The BcCZSim

Models can serve as outreach tools as well. These come in two types: simulations that create movies of dynamic systems such as snow, hydrology, or landscape evolution; and interactive simulations of dynamic systems. An example is found at http://phet.colorado.edu/en/simulation/glaciers, an interactive glacier simulation now downloadable in 27 languages. Each year, the BcCZSim Fellow, a postdoc or student, will be selected to take one or more of our models into the public realm as a simulation. The particular choice of model will be made through discussion among the modeling subgroup and the BcCZSim Fellow, and be tied to the Theme of the Year, potentially in collaboration with other CZOs. For the first year, construction of a 1D hillslope model is planned with sliders that govern the rate of mobile regolith entrainment, efficiency of hillslope transport rate, and rate of adjacent stream incision to explore their controls on hillslope form and response time. The target audience is broad, so that the simulation can be employed in K-12 and college classes alike; as such the BcCZSim Fellow will interact with Science Discovery to provide an immediate test-ground for the simulations. Our efforts will also be coordinated through the CSDMS EKT effort, with which we have close ties, and and contributed to the Educators portal at the NSF-supported Science Education Resource Center (SERC). Models we envision taking into the public realm include: • Hillslope evolution • River profile evolution • Snowmelt across a landscape • Response to fire • Boulder Creek hydrographs.

5. Engagement and Dissemination Plans

Engagement. BcCZO welcomes researchers who wish to use data, models, and infrastructure we develop. We have benefitted from activities of several visiting researchers: Brian Clarke and Doug Burbank (NSF 1227228, UC Santa Barbara) are currently conducting geophysical surveys to explore near surface fracture patterns (see letter of collaboration). Arnaud Temme (Wageningen Univ.) studied soils and hydrology in alpine and high elevation sites in 2012, and has students working on theses. NSF Earth Sciences Postdoctoral Fellows R. Barnes, E.-L. Hinckley, and A. Harpold chose BcCZO as a home for their projects. Will Ouimet (U. Connecticut) brought undergraduates and a graduate student to work on exhumation rates and slope evolution. Chris Mavris (Zurich, Swiss National Science Foundation postdoc) came to Boulder to conduct lab experiments on soils and soil organic matter. François Chabaux (Univ. Strasbourg, France) is working with SP Anderson on U-series analysis of weathering fronts. Others have approached us about working with us, but these are the projects that have borne fruit.

In coming years, we plan to increase traffic to BcCZO through active engagement, which we hope will stimulate incorporating BcCZO into proposals and use of BcCZO infrastructure. 1) Each fall, we will *advertise* via website and listservs to encourage researchers to use BcCZO. 2) BcCZO researchers

will visit other institutions along the Front Range corridor. This effort is predicated on the idea that local interactions are the most likely, and will actively seek interaction with others at the USGS and Colorado School of Mines, as well as Colorado State University, NCAR, and University of Wyoming. 3) We will *invite* a several local scientists to join our Annual Science meeting. We will encourage any who use BcCZO to participate in this meeting if their travels permit. 4) We will *host field trips*: BcCZO is hosting the Kirk Bryan fieldtrip "Critical zone evolution: Climate and exhumation" as part of the Geological Society of America meeting in October 2013.

Finally, we will aid all researchers who come to BcCZO with help in permitting, field logistics, and access to laboratory space. Our field/lab staff will help with sampling, field campaigns and monitoring.

<u>Dissemination</u>. BcCZO outcomes will be disseminated through presentations, journal publications, database publication, model publication, web access to educational materials, and placement of trainees. The first place for dissemination is in BcCZO Annual Science meetings and science planning meetings (see Management Plan), where latest findings are communicated among team members. The next level of dissemination is scientific meetings (e.g., AGU, ESA, Goldschmidt); we have budgeted student travel each year. Journal publications are the most formal dissemination; we have budgeted for page charges.

Data is available through the BcCZO website and by request. Generalizable models developed in BcCZO will be contributed to the Community Surface Dynamics Modeling System (CSDMS). The CSDMS provides a smooth mechanism for researchers in the international community to access and implement models. Our outreach activities produce educational materials that will be made available on our website, through CU's Science Discovery website, through CSDMS' EKT program, and through the Science Education Resource Center (SERC): http://serc.carleton.edu/index.html.

We view our undergraduate student, graduate student and post-doc alumni as our most important product. These individuals will have a lasting impact. By engaging them in interdisciplinary research and outreach as normal activities, we promote Earth science as a holistic discipline, with a clear sense of responsibility to communicate to the broader public our methods, findings and excitement about science.

7. Timeline

Fall semester	Spring semester	Summer	
Science planning meetings	High school field sch		
Select Theme Implement	Teacher PD	Ann	
Science Discovery workshops all year	Graduate seminar	REU	Mtg

<u>Yearly timeline</u>: In order to accomplish the integrative goals of CZO, each year BcCZO will select a science Theme of the Year, and goals for modeling, simulation, field, experimental, and/or data synthesis publications. Selection of the theme will occur over several science planning meetings at the beginning of Fall semester (late August), just after our Annual Meeting (early August). The theme does not supplant individual research efforts, but may motivate changes in individual priorities. The theme will also focus choice of processes or evolution targeted in the CZSim modules produced each year and the topic for the Spring graduate seminar. The process of selecting a research theme each year allows the team flexibility to respond to new developments and events over the five years of the project.

Possible *Themes of the Year*: influence of short-term events on processes and evolution (e.g., wildfire), slope aspect and surface energy balance control on CZ form and function, biogeomorphology, legacy of past climate on present CZ processes, forecasting future CZ processes under changing climate. We are likely to select the aspect question in Year 1, because we have data in need of synthesis and modeling, and because this has already been identified as a cross-CZO theme. *Project timeline*. Activities already planned in particular years:

Year 1: Write minority-focused REU proposal (July 2013 submission), headed by V. Sloan; Drill the

Ridge coring in Gordon Gulch; host GSA Kirk Bryan field trip (scheduled Oct. 30, 2013)

Year 2: Cross-CZO Research Workshop, tied to our Theme of the Year

Year 3: Cross-CZO Joint Field Campaign (student training event), tied to our Theme of the Year. Responsibilities of PIs in accomplishing these tasks are outlined in the Management Plan.

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Bold: BcCZO researchers *Work supported by BcCZO-I

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