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Abstract
A transect of sites has been established in North America and England as part of the Critical Zone Exploration Network (CZEN) to investigate the rates of soil formation across a climate gradient. Sites reported here are all underlain by an organic-poor, iron-rich Silurian-age shale, providing a constant parent material lithology from which soil is forming. This climosequence includes relatively cold and wet sites in Wales, New York and Pennsylvania, with temperature increasing to the south in Virginia, Tennessee and Alabama. Puerto Rico provides a warm/wet end member for the transect, although this site does not lie on the same shale formation as the Appalachian Mountain sites. Geochemical, mineralogical, and cosmogenic isotope analyses are being completed similarly at all sites to allow direct comparisons and eventual modelling of the weathering processes. Preliminary results from Wales, Pennsylvania and Virginia show soils become more sodium-depleted and the depth to bedrock is significantly deeper at the wet/warm site in Virginia. The fraction of Na lost relative to parent material composition at each site varies linearly as a function of mean annual temperature. Overall, results from the transect will promote a better understanding of how climate changes and human activities impact soil formation rates.

Key Words
Soil, climate, weathering, feldspar

Introduction
Terrestrial life is wholly dependent on the properties and processes within the critical zone, which encompasses the top of the tree canopy to aquifers beneath the earth's surface (Brantley et al., 2007). As a central constituent of this zone, soil serves as an interface for gas and water exchange and plays a major role in nutrient cycling that supports ecosystems (Amundson et al. 2007). However, the rate at which soil forms in the critical zone is not well understood. In working to address this question, numerous researchers have looked at how soils or watersheds differ in form and function across environmental gradients. These studies have included the quantification of physical erosion, pedogenic development, and geochemical fluxes as a function of climate and parent material (i.e. Rinaido et al. 1995; Chadwick et al. 1990; White and Blum 1995; White et al. 1999; Rasmussen et al. 2007; Jin et al. 2010). While these studies have included both field and laboratory measurements of chemical and physical weathering rates, they have generally not included sedimentary rocks such as shales. Additionally, literature synthesis studies, such as that by Bockheim (1980), have used previously published data to investigate the influence of gradients on soil properties, but not all data were collected in the same manner, complicating interpretation. There is a need, therefore, to understand weathering rates at a larger scale and to integrate geomorphology, pedology and geochemistry to interpret complex soil systems. A Critical Zone Exploration Network (CZEN), in which sites and scientists are linked across environmental gradients, is being developed to investigate rates of soil formation. In much the same vein, the CZEN outlined here will test the hypothesis that shale weathering rates vary predictably as a function of climate. The conceptual framework of the CZEN sites is not unlike the soil formation model proposed by Jenny (1941) in which the type of soil formed at any given location varies as a function of climate, organisms, relief, parent material and time. The approach of studying large-scale environmental gradients has already been successfully employed in investigating the dissolution of feldspar in loess parent material along the Mississippi River in the United States (Williams et al., 2010).

Methods
Site selection
The climosequence is defined by the following seven sites: Wales, New York, Pennsylvania, Virginia, Tennessee, Alabama and Puerto Rico (Fig. 1). Wales provides a cold/wet end member of the transect and

Puerto Rico represents a warm/wet end member. Sites, with the exception of Puerto Rico, which is located on a chemically similar, but younger, shale, are located on shale of the Rose Hill Formation (equivalent to the Red Rock Formation in AL and the Gwestyn Shale Group in Wales). The Rose Hill Formation is Silurian in age, Fe-rich, and organic-poor. The Pennsylvania site is the Susquehanna Shale Hills (SSHO) Critical Zone Observatory and is the location of a coordinated geomorphological, geochemical, hydrological, and soil science study. Analyses from two sites that lie within the Observatory are reported here (WRT, SPRT, Jin et al., 2010). In addition, analysis of a third site that lies on the Rose Hill Shale within a few kilometres of the observatory is also reported because it developed on strata of the Rose Hill Shale that are closer in composition to the other sites along the transect. A comparison of those sites is used to estimate local heterogeneity.

To identify sites, GIS was used to isolate similar locations with respect to lithology, aspect, topography and land use. After locating potential sites, field work at each site confirmed similarities. Furthermore, all sites were located along ridgetop topographic positions so that they could be interpreted as "1-D" profiles (Jin et al. 2010). In a "1-D" profile, after accounting for evapotraspiration losses, water generally moves vertically to bedrock, at which point lateral flow may occur; this simple model facilitates comparison across sites (Brantley and White, 2009). Also, stratigraphy was considered to ensure similar sampling locations within the shale unit. Finally, attempts were made to minimize the contributions from glacial till and colluvium as much as possible. Variables which varied unavoidably among sites included vegetation and erosion rate. An implicit hypothesis underlying our study is therefore that the effects of these variables on rates of soil formation are minor compared to climate.
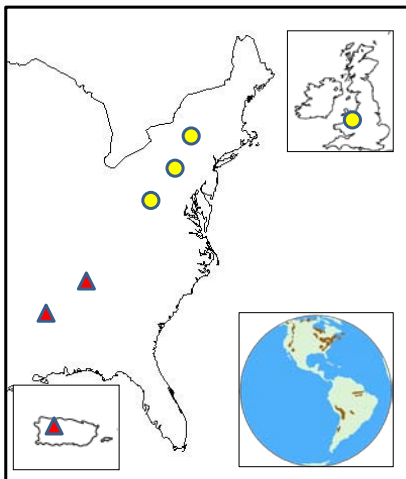

Figure 1. Sampling locations on the climosequence. Circles represent sites already sampled while triangles represent future sampling sites. Lower left inset shows Puerto Rico, upper inset shows Wales (Plynlimon watershed, Neal et al., 2001) and inset globe shows distribution of Silurian-age shales in the western hemisphere.

Soil sampling and chemistry
Soils at each site were sampled by depth (10 cm increments) using a 5 cm diameter auger. Bedrock depth was defined as depth of augering refusal. Bulk soil chemistry was measured on bulk soil samples after grinding with a mortar and pestle to pass through a 100 mesh sieve (150 µm). A Li metaborate digestion followed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the abundances of major elemental oxides. To quantify the relative mass of elements lost from the parent rock, the mass transfer coefficient $\tau_{Ti,Na}$ was calculated. When this value is less than zero, the element has been depleted relative to unweathered bedrock; when this value is greater than zero, the element has been enriched relative to bedrock (Brimhall and Dietrich, 1987; Anderson et al., 2002). For these calculations, titanium was used as the immobile element and parent was defined as the average of multiple bedrock samples at each location. Average shale composition at the Wales site was obtained from published data, rock samples were collected from an exposed outcrop in VA, and in PA, average composition of a drillcore at SSHO and an outcrop of Rose Hill shale nearby was used as parent. Error was calculated by propagating the analytical error and the error due to heterogeneity of parent compositions.

Results
Presented here are results from Wales, Pennsylvania (PA) and Virginia (VA) soils. Depth to bedrock

increases along the gradient from Wales to Virginia as mean annual temperature increases from 7 °C to 13 °C. Depth to bedrock is 35 cm in Wales, 75 cm in Pennsylvania and 100 cm in Virginia. Sodium, which is inferred from detailed mineralogy at the PA site to be present only as feldspar (Jin et al., 2010), shows incompletely developed depletion profiles (Brantley and White, 2009) that vary in extent of depletion across the three sites (Fig. 2). In Wales, approximately 20% depletion of Na is observed at land surface, whereas almost 50% depletion relative to parent composition is observed in PA and VA at the surface. Furthermore, the bottommost samples for Pennsylvania and Virginia do not return to the average parent composition for those sites, suggesting that the depth to unweathered rock is significantly deeper than the bottom of the augered profile. This observation contrasts with depletion at Wales, where the bottommost sample is indistinguishable from the parent composition. Na depletion was only significant in the uppermost sample of the Wales soil.
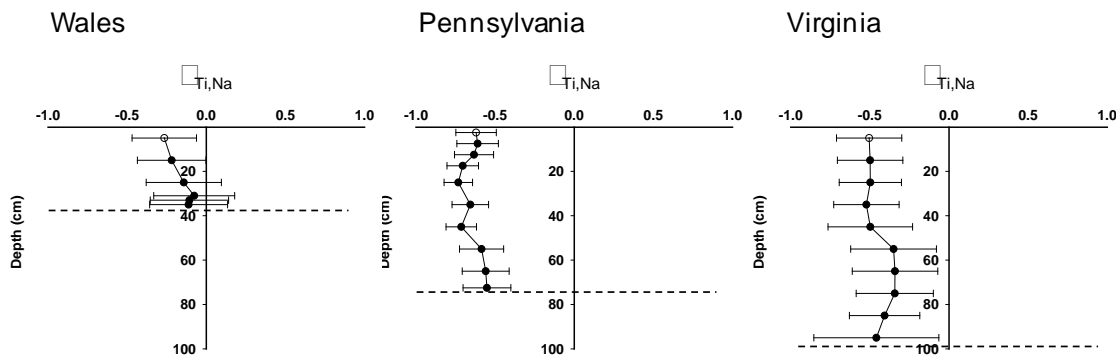

Figure 2. τ values for Na as a function of depth in Wales, Pennsylvania (several kilometers from the SSHO site) and Virginia. Dotted lines represent depth to bedrock, defined as the depth to refusal, at each site.

The fraction (f) of Na depleted relative to average parent composition was calculated based on the following expression (Williams et al., 2010):

$$f = \frac{\sum \tau^k_{Ti,Na} (z_k - z_{k-1})}{z_n} \tag{1}$$

Here $\tau^k_{Ti,Na}$ is the mass transfer coefficient calculated for a sample from depth k in the profile, $(z_k - z_{k-1})$ is the depth interval over which the sample was collected, and z_n is the depth to refusal for augering. Na depletion along the gradient varies as a function of both mean annual temperature (MAT) and mean annual precipitation (MAP). The fraction of Na depleted from the entire augered profile increases linearly with MAT, from only 20% Na lost at the coldest site in Wales to almost 50% at the warmest site in VA. Analysis of three different profiles in Pennsylvania suggests a range in the fractional Na depletion from 20 to 50%. In contrast, the fraction of Na lost as a function of MAP increases from PA to VA but decreases in Wales. While the site in Wales receives 1.6 to 2.5 times more precipitation than VA or PA, the fact that soils are the least depleted in Na in Wales may be indicative of the strong role of temperature in controlling weathering of feldspar (Williams et al., 2010). Alternately, the small depletion from Wales shale may be related to the fact that this site was glaciated within the last 15 kya. Future efforts will be made to include the rate of erosion or the exposure age of soils in our analysis. We are also calculating the values of the chemical depletion factor (CDF) based on the following equation (Riebe et al., 2004) for comparison along the gradient:

$$CDF = \left(1 - \frac{[Ti]_{rock}}{[Ti]_{soil}}\right) \tag{2}$$

Where $[Ti]_{rock}$ and $[Ti]_{soil}$ are the concentrations of an immobile element, in this example, Ti, in the rock and soil, respectively. CDF can also be calculated from τ by including all major elements:

$$CDF = -\frac{\sum_j \tau_{i,j} C_{j,p}}{\sum_j C_{j,p}} \tag{3}$$

Here, $\tau_{i,j}$ is the average τ value for a mobile element, j, relative to an immobile element, i and $C_{j,p}$ is the concentration of the mobile element j in the parent, p. CDF calculated with these equations increases with MAT for the soils sampled here.

Conclusion and Implications

Data from this large-scale climosequence suggests soil chemistry and depth to bedrock vary with changes in temperature and precipitation. Na, largely present as Na feldspar, has been depleted in all profiles examined thus far, with a greater fraction of Na depletion (*f*) relative to bedrock at the warmest site. In the coldest, wettest site, only 20% of Na has been weathered over the entire soil profile while the warmer, wet VA site has lost 44% of the original Na in parent calculated over the entire soil profile. Na depletion varies monotonically with temperature but not with precipitation. The climosequence approach to addressing the question of shale weathering rates shows potential for quantifying weathering processes in soils underlain by the same lithology. The approach outlined here will also be used to investigate other environmental variables. For example, lithologic contrasts will be analysed between the organic-poor shale reported here and another site located on organic-rich Marcellus shale, in PA. Also, land use contrasts can be compared in Wales, where two catchments, roughly identical in size and lithology, are managed as grassland and forest – these sites can therefore provide insight on the effects of land use on shale weathering. Finally, this climosequence could eventually be extended to an equator-to-pole gradient study of Silurian-age shale soils extending from West Africa to Spain, Wales, Norway and Svalbard.

References

Amundson R, Richter DD, Humphreys GS, Jobbagy EG, and Gaillardet J (2007) Coupling between biota and earth materials in the critical zone. *Elements* **3**, 327-332.

Anderson, SP, Dietrich WE, Brimhall GH (2002) Weathering profiles, mass-balance analysis, and rates of solute loss: Linkages between weathering and erosion in a small, steep catchment. *GSA Bulletin* **114**, 1143-1158.

Bockheim JG (1980) Solution and use of chronofunctions in studying soil development. *Geoderma* **24**, 71-85.

Brantley SL, Goldhaber MB, and Ragnarsdottir KV (2007) Crossing disciplines and scales to understand the critical zone. *Elements* **3**, 307–314.

Brantley SL and White AF (2009) Approaches to modelling weathered regolith. In 'Reviews in Mineralogy and Geochemistry: Thermodynamics and Kinetics of Water-Rock Interaction.' (Eds. EH Oelkers and J Schott.) Vol. **70**, pp. 435-484 (Mineraological Society of America and Geochemical Society).

Brimhall, GH and Dietrich WE (1987) Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results on weathering and pedogenesis. *Geochimica et Cosmochimica Acta* **51**, 567-587.

Chadwick OA, Brimhall GH, and Hendricks DM (1990) From a black to a gray box – a mass balance interpretation of pedogenesis. *Geomorphology* **3**, 369-390.

Jenny, H. (1941) Factors of soil formation. (McGraw Hill: NY).

Jin L, Ravella R, Ketchum B, Heaney P, and Brantley SL (2010) Mineral weathering and elemental transport during hillslope evolution at the Susquehanna Shale Hills Critical Zone Observatory. *Geochimica et Cosmochimica Acta* In review.

Neal, C., Reynolds B., Neal M., Pugh B., Hill L., and Wickham H. (2001) Long-term changes in the water quality of rainfall, cloud water and stream water for moorland, forested and clear-felled catchments at Plynlimon, mid-Wales. *Hydrology and Earth System Sciences* **5**, 459-476.

Rasmussen C, Matsuyama N, Dahlgren RA, Southard RJ and Brauer N (2007) Soil genesis and mineral transformation across an environmental gradient on andesitic lahar. *Soil Science Society of America Journal* **71**, 225-237.

Riebe, CS, Kirchner JW, and Finkel RC (2004) Erosional and climatic effects on long-term chemical weathering rates in granitic landscapes spanning diverse climate regimes. *ESPL* **224**, 547-562.

Rinaido A, Dietrich WE, Rigon R, Vogel GK, and Rodriguez-Iturbe I (1995) Geomorphological signatures of varying climate. *Nature* **374**, 632-635.

White AF and Blum AE (1995) Effects of climate on chemical weathering in watersheds. *Geochimica et Cosmochimica Acta* **59**, 1729-1747.

White AF, Blum AE, Bullen TD, Vivit DV, Schulz M, and Fitzpatrick J (1999) The effect of temperature on experimental and natural chemical weathering rates of granitoid rocks. *Geochimica et Cosmochimica Acta* **63**, 3277-3291.

Williams JZ, Bandstra JZ, Pollard D, and Brantley SL (2010) The temperature dependence of feldspar dissolution determined using a coupled weathering-climate model for Holocene-aged loess soils. *Geoderma* **156**, 11-19.