Coupled Modeling of Hydrologic and Geochemical Fluxes for Prediction of Solid Phase Evolution in the B2 Hillslope Experiment

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Abstract

A reactive transport geochemical modeling study was conducted to help predict the mineral transformations occurring over a ten year time-scale that are expected to impact soil hydraulic properties in the Biosphere 2 (B2) synthetic hillslope experiment. The modeling sought to predict the rate and extent of weathering of a granular basalt (selected for hillslope construction) as a function of climatic drivers, and to assess the feedback effects of such weathering processes on the hydraulic properties of the hillslope. Flow vectors were imported from HYDRUS into a reactive transport code, CrunchFlow07, which was then used to model mineral weathering coupled to reactive solute transport. Associated particle size evolution was translated into changes in saturated hydraulic conductivity using Rosetta software. We found that flow characteristics, including velocity and saturation, strongly influenced the predicted extent of incongruent mineral weathering and neo-phase precipitation on the hillslope. Results were also highly sensitive to specific surface areas of the soil media, consistent with surface reaction controls on dissolution. Effects of fluid flow on weathering resulted in significant differences in the prediction of soil particle size distributions, which in turn are predicted to feedback to affect hillslope hydraulic conductivities.

Introduction

- Artificial hillslopes (30 m long and 15 m wide, zero-order basin shape with a 10 degree overall slope, 1-m uniform soil depth) are under construction at Biosphere 2.
- The goal of the hillslope experiment is development of understanding how climatic, geologic and biologic factors are influencing movement of water.
- The objective of this study was to explore the impacts of initial particle size (specific surface area of primary minerals) and climatic regime (translated to flow rate and saturation degree) on mineral weathering and assess the impact of chemical weathering on the time and space evolution of hydraulic conductivity.

Methods

Material

- A black basaltic cinder material, obtained from the CEMEX Corp. Flagstaff, AZ
- Total elemental composition by lithium metaborate/tetraborate fusion followed by ICP-MS: 47.8% SiO_2, 16.3% Al_2O_3, 11.6% Fe_2O_3, 0.19% MnO, 8.12% MgO, 9.84% CaO, 2.93% Na_2O, 0.77% K_2O, 1.69% TiO_2, 0.62% P_2O_5, and 0.01% S.
- Elemental composition of individual minerals (Table 1) by microprobe analysis (Cameca SX50 electron microprobe, Gennevillier, France).
- Mass fractions of the minerals (Table 1) calculated using ModAn (Paktunc, 2001).
- Composition confirmed by Quantitative X-ray diffraction analysis (XRD) and
- Image analysis (ArcView GIS 3.2) of element distribution maps obtained by microprobe .
- Particle size by a Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer: 77.7% sand, 21.0% silt and 1.23% clay (loamy sand)
- Surface area by N_2 adsorption: 3.2 $m^2\ g^{-1}$

Table 1. Mineral composition and literature-derived equilibrium constants, *log*K_{SO} (25 °C) and dissolution rates (k_m) for primary mineral components of basaltic material and projected secondary minerals.

Mineral	Composition	Vol.	log K_{SO}	log k_m
		%	(25 °C)	moles $m^{-2}\ s^{-1}$
Primary				
				-11.6
Labradorite (feldspar)	$Ca_{0.64}Mg_{0.01}Fe_{0.04}Na_{0.35}K_{0.01}Al_{1.63}Si_{2.34}O_8$	35.87	18.20	-12.99
Diopside (pyroxene)	$Ca_{0.86}Mn_{0.01}Mg_{0.77}Na_{0.03}Ti_{0.05}Al_{0.25}Fe_{0.26}Si_{1.81}O_6$	6.53	20.38	-10.2
Forsterite (olivine)	$Mg_{1.47}Ca_{0.01}Mn_{0.01}Fe_{.0.52}Si_{0.99}O_4$	11.94	25.34	-10.4
Basaltic glass	$Ca_{0.36}Mg_{0.22}Na_{0.16}K_{0.09}Mn_{0.01}Fe_{0.49}Al_{0.58}Ti_{0.11}(HPO_4)_{0.05}Si_{1.87}O_{5.89}$	45.67	17.61	-11.06
Secondary				
$Fe(OH)_2$	$Fe(OH)_2$		13.90	-7.9
Kaolinite	$Al_2Si_20_5(0H)_4$		8.55	-12.89
Smectite	$(Ca_{0.02}, Na_{0.15}, K_{0.2})(Al\ Mg_{0.9}\ Fe_{0.29})_2Si_{3.75}\ Al_{0.25}O_{10}(OH)_2$		11.04	-12.5
Gibbsite	$Al(OH)_3$		7.76	-11.66
Pyrolusite	$Mn^{(IV)}O_2$		-17.64	-11
Goethite	$Fe^{3+}O(OH)$		0.5345	-10

HYDRUS-3D was used to simulate steady-state flow conditions for 2 climate regimes

- Lucky Hills Climate: the Lucky Hills watershed, AZ (0.0026 m h^{-1} rainfall over 56 days per year).
- Sky Island Climate: the simulated semi-arid Sky Island forest climate (0.0041 m h^{-1} rainfall over 74 days per year).

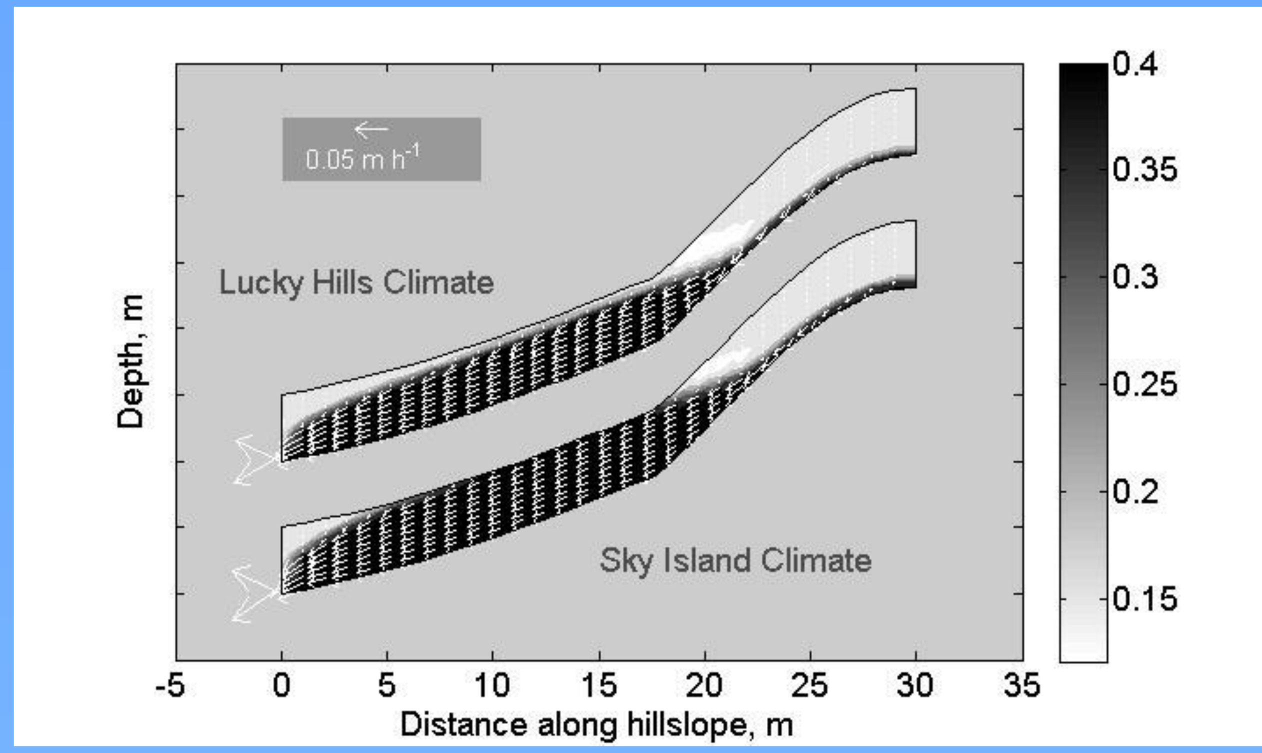


Figure 1. Water velocity (white arrows) and content (shading) profiles in the hillslope cross-section at the channel for the two simulated climates. Volumetric water content of 0.41 corresponds to saturated conditions. Y-axis tick mark spacings equal 1 m.

CrunchFlow2007 was then used to model mineral weathering coupled to reactive solute transport (Steefel, 2008) .

- The code CrunchFlow2007 solves the multicomponent reactive transport equation given by

$$\frac{\partial(\phi C_i)}{\partial t} = \nabla\cdot(\phi D_i \nabla C_i) - \nabla\cdot(\phi \mathbf{u} C_i) - \sum_{r=1}^{Nr} \nu_{ir} R_r - \sum_{m=1}^{N_m} \nu_{im} R_m$$

where φ is the porosity, C is the concentration of the i^{th} primary species, D is the molecular diffusion coefficient in porous media, **u** is the velocity vector, and R_r and R_m are the homogeneous (aqueous phase) and heterogeneous (mineral) reaction rates respectively.

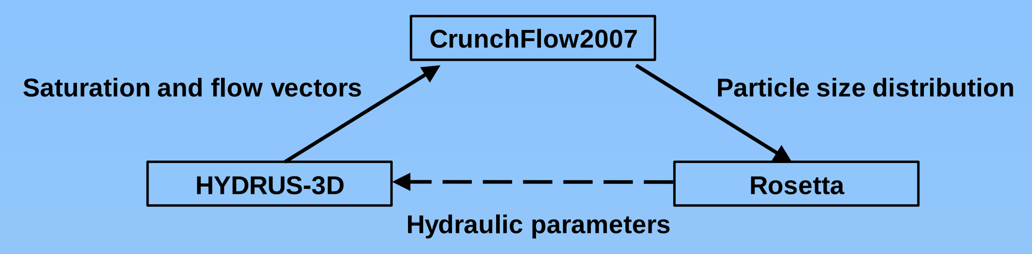
- Mineral dissolution rates in CrunchFlow2007 are described using:

$$R = A_m k_m \exp\left[\frac{-E_a}{RT}\right]\prod a_i^n \left[1-\exp(m_2 g^{m_3})\right]^{m_1} \qquad g = \frac{\Delta G_r}{RT} = \ln\left[\frac{Q}{K_{SO}}\right]$$

where R is dissolution rate in mol $m^{-3}\ s^{-1}$, A_m is mineral bulk surface area, $m^2\ m^{-3}$, k_m is the dissolution intrinsic rate constant in units of mol $m^{-2}\ s^{-1}$, E_a is the activation energy (kJ mol^{-1}), Q is the ion activity product for the mineral-water reaction, K_{SO} is the corresponding solubility product constant, and $\prod a_i^n$ is a product representing the inhibition or catalysis of the reaction by various ions in solution raised to the power n. Rate dependence on reaction affinity, g, (or Gibbs energy) is defined by the parameters m_1, m_2, and m_3 following relationships observed by Burch et al. (1993) and Hellmann and Tisserand (2006).

- Dissolution rate constants (k_m) were obtained from the literature for the minerals measured in the basalt
- Simulation duration 1000 days

Rosetta was used to estimate hydraulic parameters from soil texture evolution (Schaap et al., 2001). Saturated hydraulic conductivity (K_{sat}) is presented because it was most sensitive to changes in particle size.



Results

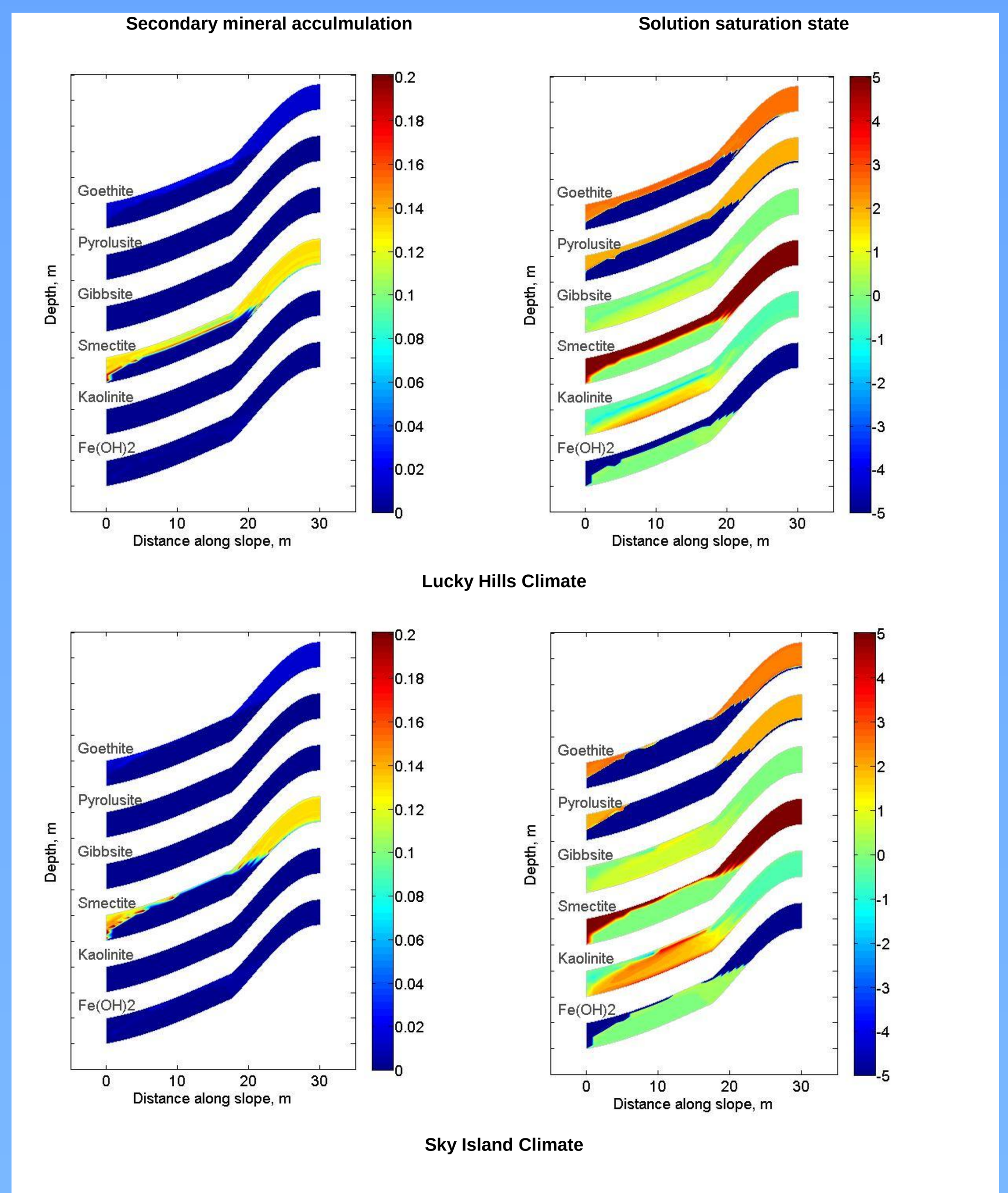


Figure 2. Volumetric (fraction of the solid) accumulation of secondary minerals (left) and relative saturation state of solutions, log (Q/K_{SO}), (right) for the Lucky Hills (top) and Sky Island (bottom) climate regimes after 1000 days of simulation. Y-axis tick mark spacings equal 1 m.

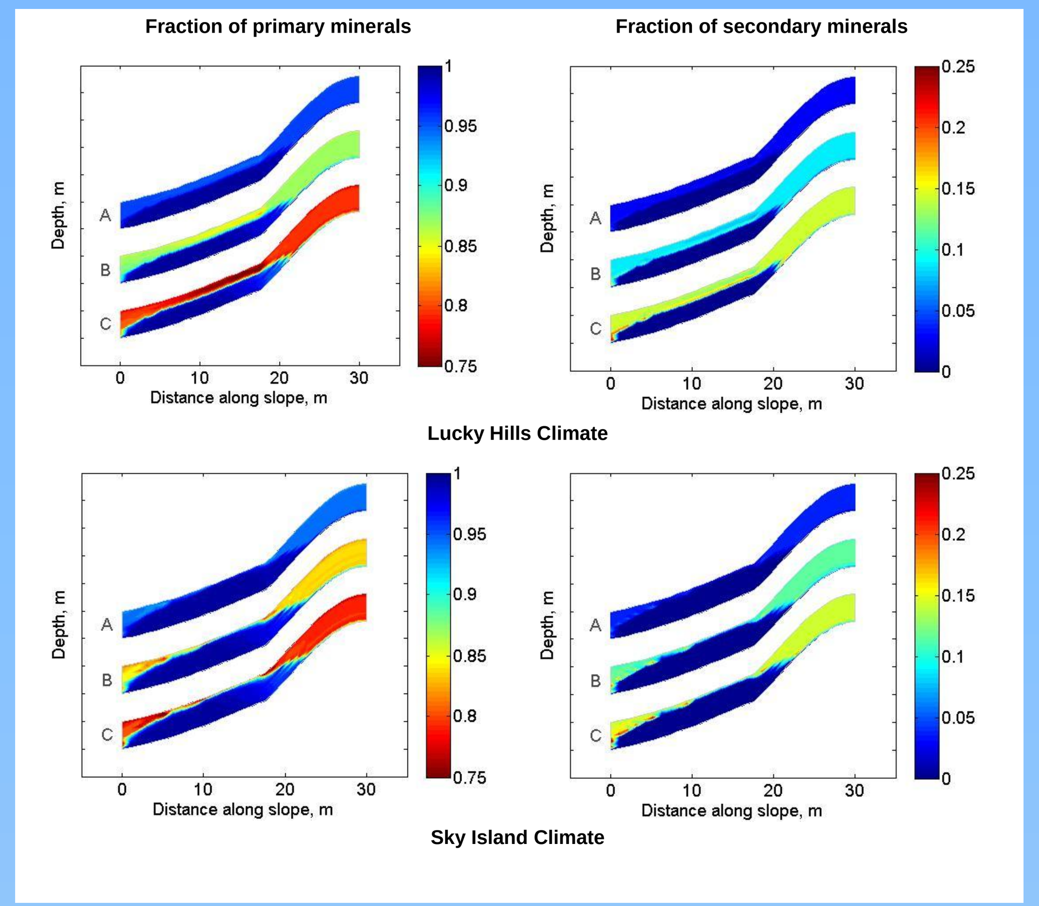


Figure 3. Fraction of primary (left) and secondary (right) minerals as a function of time. Top two plots are after (A) 168 days or 3 years; (B) 560 days or 10 years; and (C) 1000 days or 18 years of Lucky Hills climate. Bottom two plots are after (A) 222 days or 3 years; (B) 740 days or 10 years; and (C) 1000 days or 14 years of Sky Island climate rainfall. Initial fraction of primary minerals equaled one. Initial fraction of secondary minerals equaled zero.

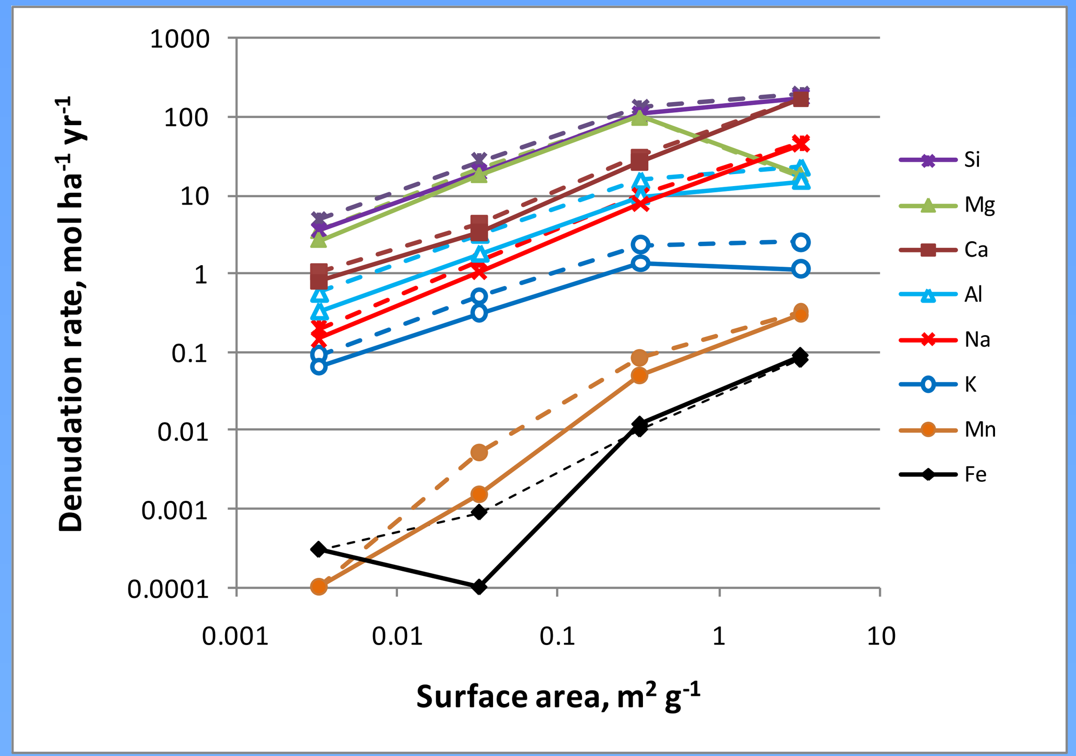


Figure 4. Hillslope chemical denudation rate for lithogenic elements (mol $ha^{-1}\ yr^{-1}$) as a function of grain surface area and climate regime. Solid lines represent values for Lucky Hills Climate, dashed lines for Sky Island Climate.

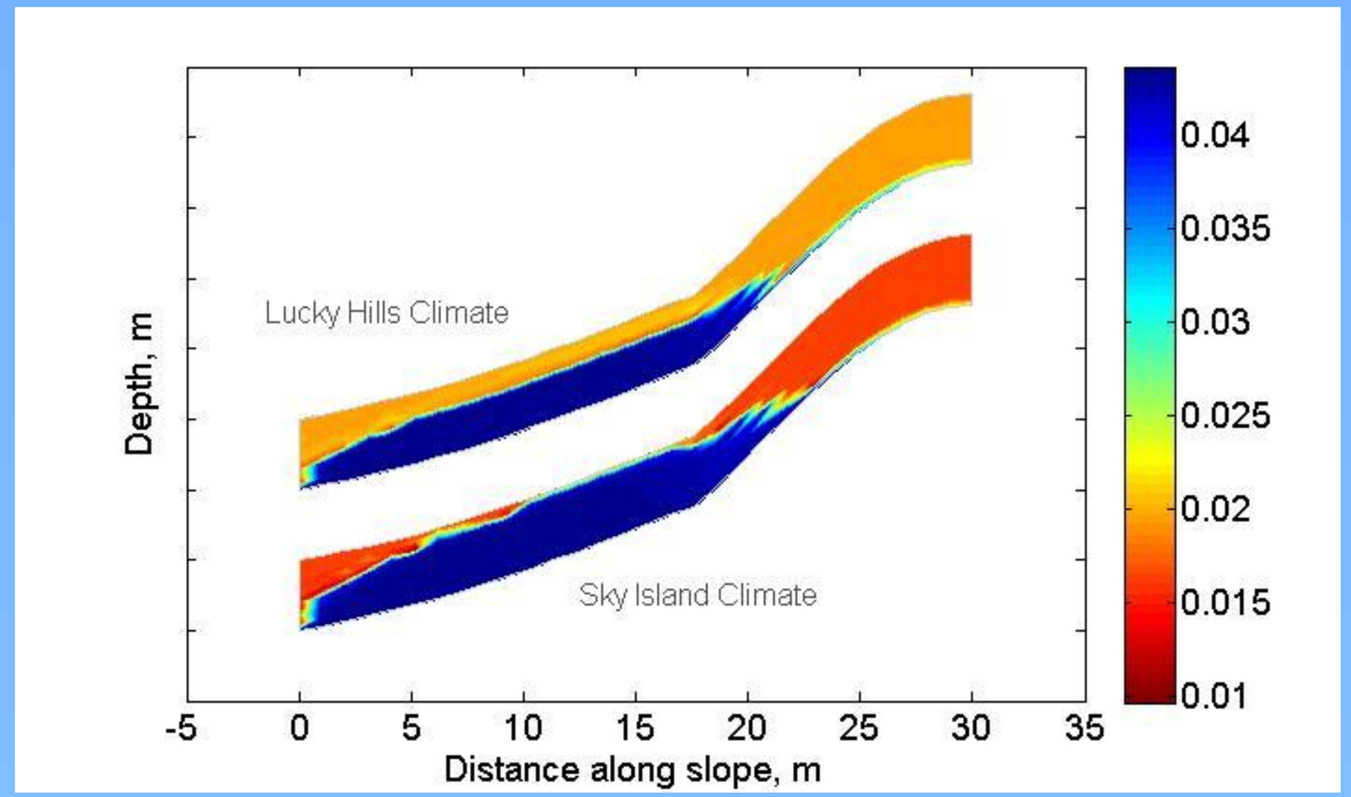


Figure 5. Map of the Rosetta-calculated K_{sat} values (m h^{-1}) based on the change in mineral volumes and associated particle sizes over 10 years for two climates. Y-axis tick mark spacings equal 1 m.

- Smectite was the principal neophase formed in both climatic regimes, particularly in the vadose zone
- Solutions in the groundwater zone were strongly undersaturated with respect to goethite (α-$Fe^{III}OOH$) and pyrolusite ($Mn^{IV}O_2$), whereas vadose zone solutions were at equilibrium or supersaturated with respect to these same phases in response to oxygen availability
- The patterns for both dissolution and precipitation followed the flow patterns for both climates
- Hillslope chemical denudation increased with surface area; calculated denudation rates for the measured mineral surface area (3.2 $m^2\ g^{-1}$) were in line with field observations (White and Blum, 1995).
- All areas of the hillslope showed a change in K_{sat} because of incongruent weathering processes, with the Sky Island climate having a greater reduction in the K_{sat}, and the Lucky Hills climate having a reduction throughout a larger areal extent, consistent with a more extensive vadose zone.

Conclusions

Spatially distributed flow characteristics, including velocity and saturation, strongly influence the predicted extent of incongruent mineral weathering and neo-phase precipitation on the hillslope, resulting in change in particle size and saturated hydraulic conductivity and creating a feedback to hillslope hydrology.