Integrating geochemical tracers with physics-based modeling to understand Rio Icacos storm response

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Rio Icacos Study Area

326 ha monolithogic catchment
50 Ma quartz diorite
4200mm annual rainfall
22° C mean annual temp

Research Approach:
- Understand tracer behavior in soils, porewaters
- Link tracer to stream chemistry, infer solute sources and flowpaths
- Test inferences against simulations (physics-based hydrology model)

Critical Zone Exploration Network
**Geochemical and Isotopic Trace**

*Germanium*

Ge substitutes for Si in minerals, behaves like Si in solution.

**Silicon tracer:**

Ge/Si ratios in water reflect fractionation by weathering and biological cycling.
Streamwater Ge/Si ratios reflect mixing

![Graph showing the relationship between Ge/Si ratios and 1/Si](image-url)
Streamwater Ge/Si ratios reflect mixing
Streamwater Ge/Si ratios reflect mixing
Example Event: 6-24-2006 Storm

Precip. = 3.3 cm in ~2 hours
Example Event: 6-24-2006 Storm

![Graph showing Ge/Si (µmol/mol) vs. Discharge (m³/sec)]

- **Falling**
- **Rising**
Example Event: 6-24-2006 Storm

Three component mixing

Fraction

Time

Error bars reflect propagation of analytical and endmember uncertainty
Hydrologic Model  \textit{InHM} VanderKwaak and Loague

Physics-based 3-D integrated subsurface-surface hydrologic model

- Surface
- Porous Media
- Macropore

FLOW and TRANSPORT

Parameterized with hydrometric and physical data from site

(soil characteristic tables, hydraulic conductivity, porosity)

Finite element grid from DEM
Soil, saprolite, bedrock layers
Model Performance: July-August 2007

“flashiness” requires dominance of overland flow
TDR data: hillslope site

Model simulation: hillslope site

Model Performance: July-August 2007
Model Tracers

Synthetic hydrograph separation

6-24-2006 Storm

Diagram showing the separation of total discharge, event water, and pre-event water over time. The Y-axis represents the fraction, while the X-axis represents time (hours). The graph helps in understanding the timing and proportion of different water components in the hydrograph.
June Event: Surface flow velocity (m/s) at max Q
June Event: Surface “Event” tracer at max Q
June Event: Porous Media “Pre-Event” tracer at max Q
Conclusions

Geochemistry

- Streamwater Ge/Si data indicate three components to stormflow
- Shallow/overland flow component dominates most of hydrograph
- A soil matrix component becomes significant at the end of hydrograph recession

Model

- Model indicates catchment “flashiness” controlled by (Hortonian) overland flow rather than macropores
- Application of model tracers indicate dominance of “event water” delivered by overland flow early in event, and displaced “pre-event water” during hydrograph recession.

Model serves as a useful test of geochemical inferences, some consistency, but may be failing to capture some...
Oxygen Isotopes - trace ‘new’ vs. ‘old’ water

Discharge (ft³/sec)

-2.5
-2.7
-2.9
-3.1
-3.3
-3.5

δ¹⁸O(‰)

Rising Limb
Falling Limb

Baseflow = -2.7

Rain (6-24-06 event) = -3.3
Isotope Hydrograph Separation

% Contribution

Time (hours)

Falling Limb

Pre-event water

Event water
Solute sources from a soil perspective
Both of these tracers have paleoceanographic applications as well.
87Sr/86Sr ratios reflect age and Rb/Sr ratio of rocks and minerals

Cation tracer:

Sr isotope ratios in water reflect source of cations

(mineral weathering, ion exchange, weathering)
Ge/Si Geochemistry "pseudo-isotopic" behavior

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<th>IVB</th>
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<td>50</td>
<td>Sn</td>
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<tr>
<td>82</td>
<td>Pb</td>
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Ge substitutes for Si in the silicate lattice (Goldschmidt's “camouflage”)

1 to 5 atoms of Ge per million silicon atoms
Ge/Si Geochemistry "pseudo-isotopic" behavior

$pK_{\text{dis}}^{Ge} = 9.3$
$pK_{\text{dis}}^{Si} = 9.8$
Model of Ge/Si fractionation during incongruent silicate weathering

after Murnane and Stallard, 1990; Froelich et al., 1992
Ge/Si fractionation in synthetic allophane

- 52 ppm Si, 55 ppm Al
  - Ge/Si = 1.0 µmol/mol

NaOH titration, 5 days @ 90°C

- 24 ppm Si, 1.6 ppm Al
  - Ge/Si = 0.5 µmol/mol

- 52 ppm Si, 55 ppm Al
  - Ge/Si = 1.3 µmol/mol

Neoformed allophane
Soil solids
Perspective
Luquillo Ridgetop Saprolite Core Profiles

Weathering profiles aren’t like sediment cores...
Conveyor belt goes UP
(landscape eroding 25-50 m/my)
Hillslope Soil Profile

40 cm
On Ridgetops, this saprolite-bedrock contact is at 800cm depth
Solid-phase Ge/Si ratios (μmol/mol)

Opal Phytoliths: 0.1 to 0.5

Soil = 2.5

Saprolite = 2.8 to 3.3

Regolith Minerals
Kaolinite = 5.9
Altered Biotite = 5.3
Quartz = 0.5

Primary Minerals
Hornblende = 6.6
Biotite = 5.5
Plagioclase = 1.5
Quartz = 0.5
“Immobile Element” Mass Balance Framework

Fractional net loss (or gain) of a mobile element $j$ (e.g. Si) calculated relative to immobile element $i$ (Nb, Zr)

$$
\tau_{j, w} = \left( \frac{C_{j, w}}{C_{j, p}} \times \frac{C_{i, p}}{C_{i, w}} \right) - 1
$$

**Positive tau** = gain of mobile element

**Negative tau** = loss of mobile element
Solid-phase Ge/Si ratios (µmol/mol)

Weathering Ge/Si Fractionations

\( \tau_{\text{Si}} = 0.6 \)  
\( \tau_{\text{Si}} = 0.4 \)

Soil  
\( \tau_{\text{Si}} = 2.5 \)

Saprolite  
\( \tau_{\text{Si}} = 2.8 \) to 3.3

Quartz Diorite  
\( \tau_{\text{Si}} = 2.0 \)

Weathering

- Biotite \( \rightarrow \) Kaolinite and Kaolinite \( \rightarrow \) Solution
- Plagioclase \( \rightarrow \) Kaolinite

Ge/Si soln = 3.7
Ge/Si soln = 0.4
Ceramic-cup pressure-vacuum water samplers (lysimeters)
 Nested Lysimeters in deep saprolite
15cm to >800cm

Ridgetop Site (LG-1)
Soil and Saprolite Porewaters \textit{Ridgetop Site LG-1} (WEBB project suction lysimeters)

**Predictions**

\[ \text{Ge/Si}_{\text{soln}} = 3.7 \]

\[ \text{Ge/Si}_{\text{soln}} = 0.4 \]

Not Seeing 0.4 here…
“Landslide Water”

\[ \text{Si} = 340 \, \mu\text{mol/L} \]

\[ \text{Ge/Si} = 0.3 \, \mu\text{mol/mol} \]
Stream Perspective

Rio Icacos at Flood Stage, Nov ‘06
USGS Stream Gauge
Silica

![Graph showing Silica concentration against discharge (ft³/sec)]

- **Baseflow**
- **Rising Limb**
- **Falling Limb**
1) Define “groundwater” and “soilwater” endmembers (Si concentration and Ge/Si) based on data

2) Use Ge/Si (“R”) to partition Si flux into “groundwater” and soilwater components

\[ f_g = \frac{R_t - R_s}{R_g - R_s} \]

3) Multiply Si fluxes by endmember Si concentrations to determine water flux of components

4) Close water balance by adding “Si free water”
Hydrograph Separation Based on Ge/Si and [Si]

- **Rising**
- **Falling Limb**

**% Contribution**
- Soil water
- Groundwater
- Si-free water

**Time (hours)**

0 2 4 6 8 10
Hydrograph Separations Based on Ge/Si and [Si]

![Graph of hydrograph separations showing time (hours) and percentage contribution of Soil water, Si-free water, and Groundwater in the Falling Limb phase.](Image)
"Storm Flow" Conditions: Subsurface stormflow dominates: Soils contribute to solute load
Dilute solutions with high Ge/Si (\&^{87}\text{Sr}/^{86}\text{Sr})
Carried by “New Water”

"Base Flow" Conditions: Groundwater discharge maintains streamflow. Solute load reflects *incongruent weathering of primary silicates*
Concentrated solutions with low Ge/Si, (\&^{87}\text{Sr}/^{86}\text{Sr})
Carried by “Old Water”
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

InHM
VanderKwaak and Loague

Porosity

porosity

0.32
0.3
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

*InHM*
VanderKwaak and Loague

Total Hydraulic Head
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

*InHM*
VanderKwaak and Loague

Saturation
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

InHM
VanderKwaak and Loague

Porous media flow velocity (m/s)
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

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Model Slice - Flow Velocity
Hydrologic Model

Physics-based 3-D integrated subsurface-surface hydrologic model

InHM
VanderKwaak and Loague

Model Slice - Flow Velocity
Hydrologic Model

Synthetic storm hydrograph
Hydraulic Conductivity determined by Guelph Permeameter

Conductivity (cm/min)

Depth (cm)

Hill Slope

Stormflow zone?