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Stable silicon isotope fractionation reflects the routing of water through a mesoscale hillslope

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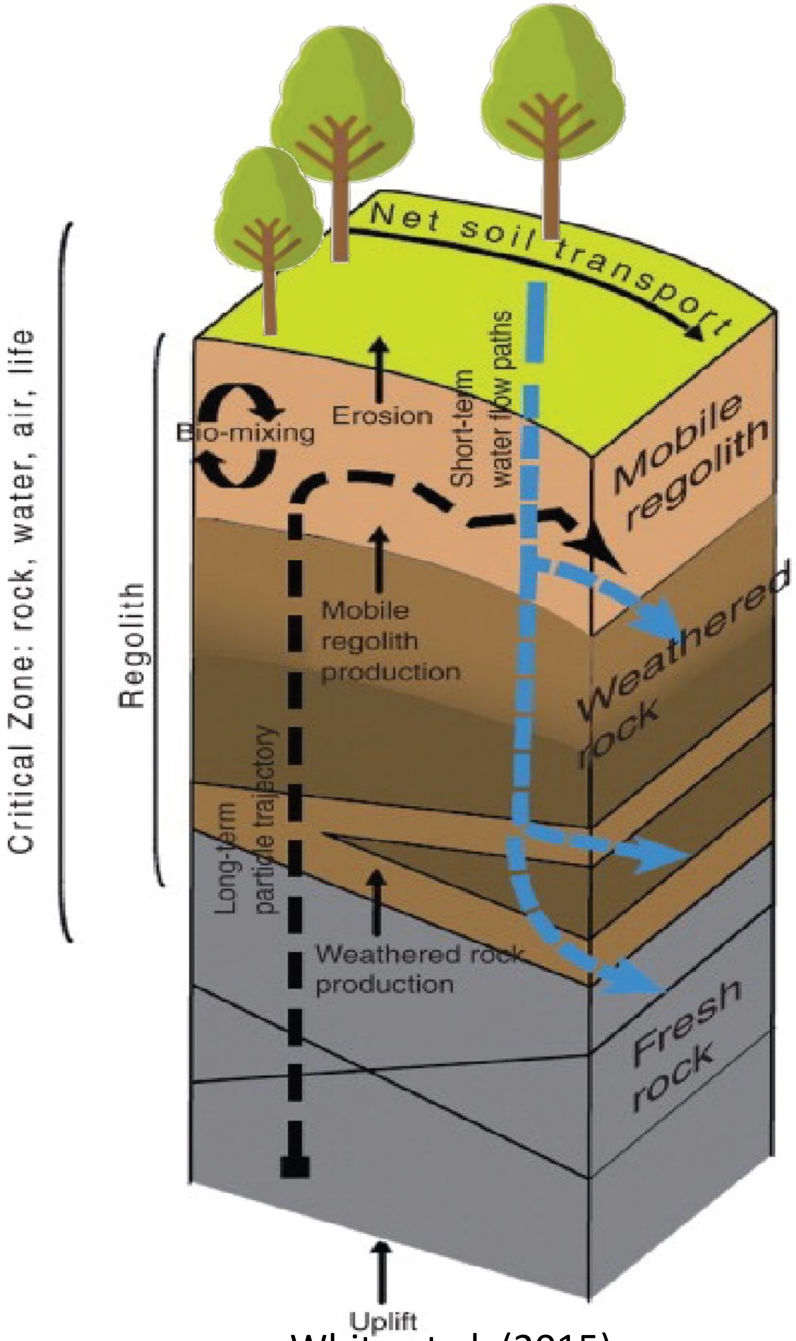
Image from @biosphere2 Instagram

Critical Zones (CZ)

- Outer layer of Earth's surface from the top of vegetation canopy to lowest depths of groundwater
- Water infiltrates subsurface of CZ at various depths to cause rock weathering
- Why do we care about weathering in the CZ:
  - Silicate weathering regulates atmospheric carbon on geologic timescale
  - Releases nutrients to biosphere
  - Sets chemistry of streams feeding larger rivers, reservoirs and aquifers
  - Evolving weather patterns, ecosystem shifts, temperature feedbacks, etc. due to Climate Change

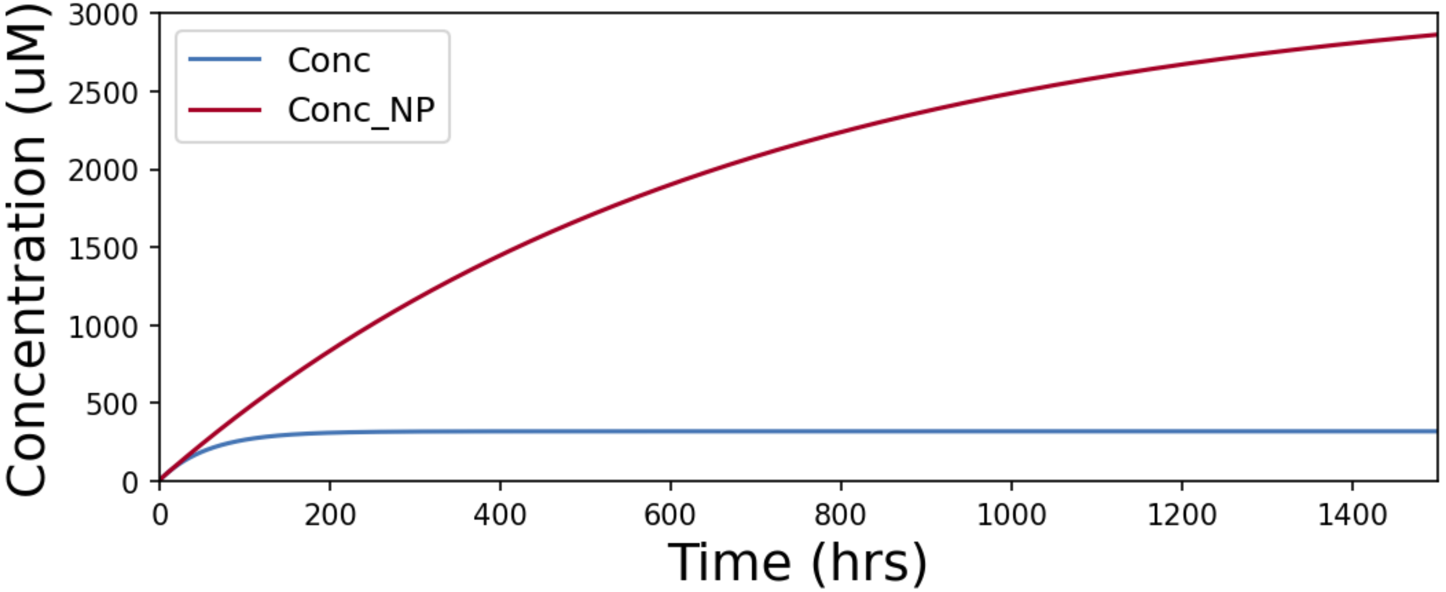


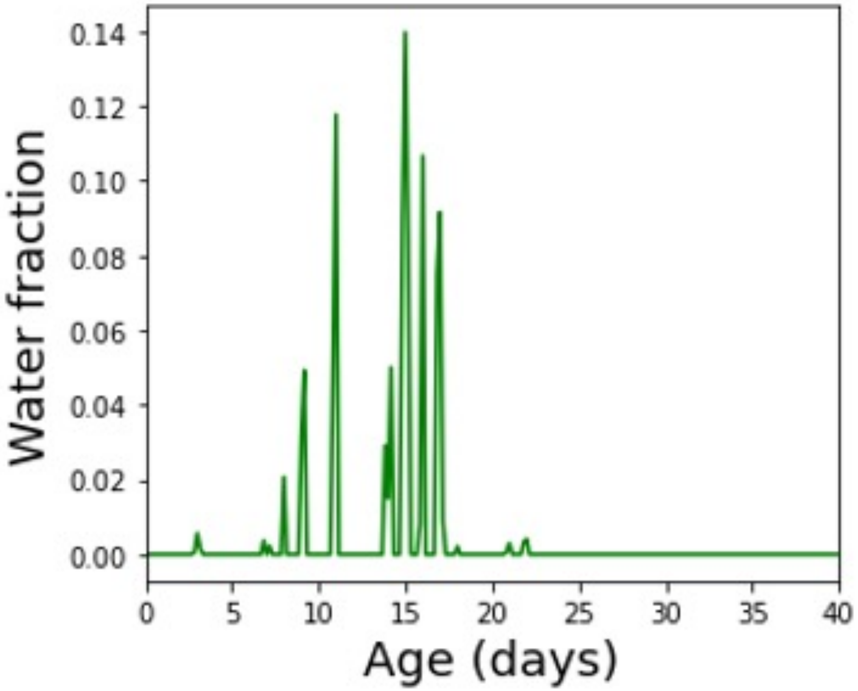
White et al. (2015)

Headwater Streams as Indicator of Ecosystem Health

- Surface and subsurface instruments within the catchment are great for specific local measurements
- Headwater streams integrate contributions across the entire catchment
  - How do individual factors show up in stream chemistry: weathering, vegetation, climate, contaminants, flow path, etc.?

What Does Chemistry Reveal about Hydrology

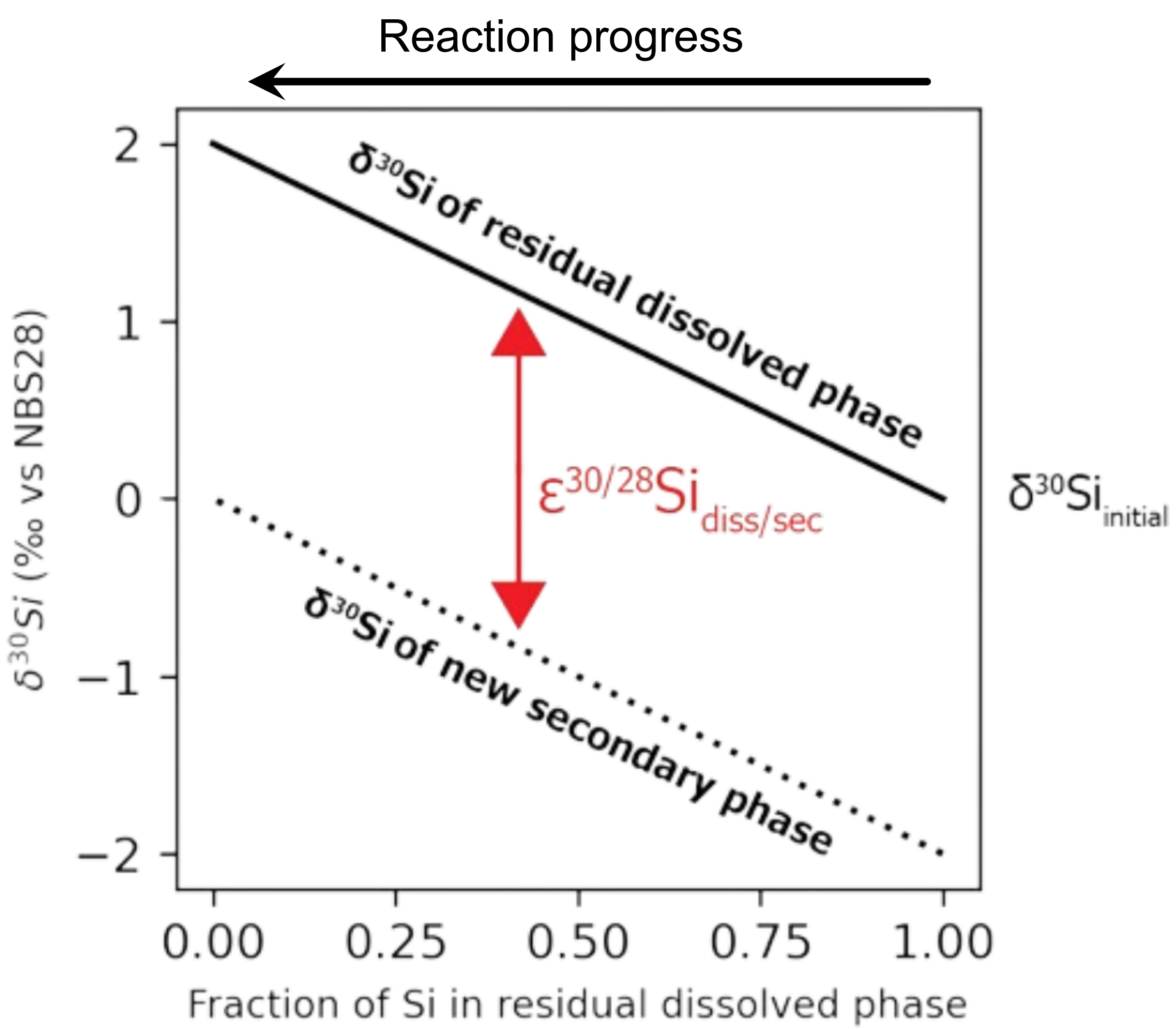




- Older water has more time to react in the subsurface (increased concentrations)
- Discharge is a cumulation water ages: Concentration-Discharge (C-Q)
  - Interpreting weathering from C alone is challenging due to equifinality from factors such as: Secondary mineral formation, incongruency, nutrient cycling, and cation exchange

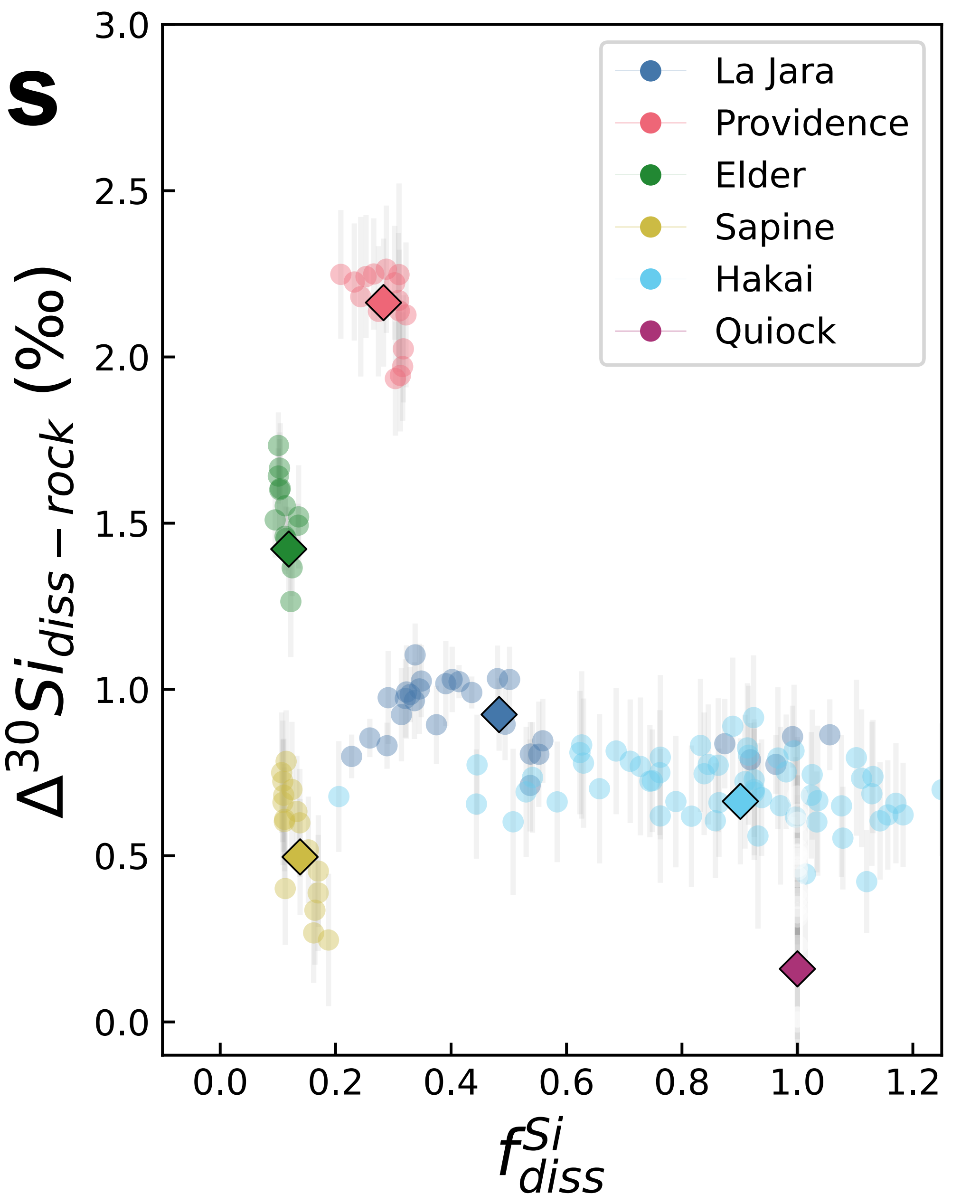
Si Isotope System

- Silicon has three stable isotopes: ^{28}Si, ^{29}Si, and ^{30}Si
- No mass dependent fractionation during congruent dissolution
- Mass dependent fractionation during secondary mineral precipitation and plant uptake
- $\alpha_{30/28} = \frac{rate_{^{30}Si}}{rate_{^{28}Si}}$
- $\varepsilon^{30/28} = (\alpha_{30/28} - 1) * 10^3$



δ^{30}Si in Upland Watersheds

- $f_{diss}^{Si} = \frac{(\frac{Si}{Na})_{stream}}{(\frac{Si}{Na})_{Bedrock}}$
  - Low f_{diss}^{Si}: More Si lost to secondary phases
  - f_{diss}^{Si} = 1: congruent dissolution



Altered from Fernandez et al. (2022)

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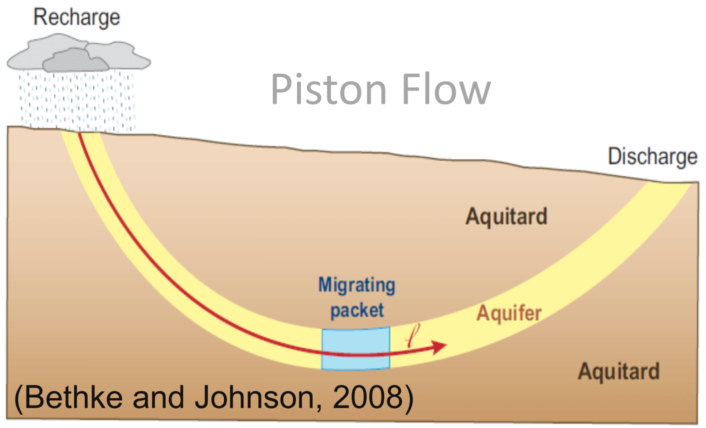
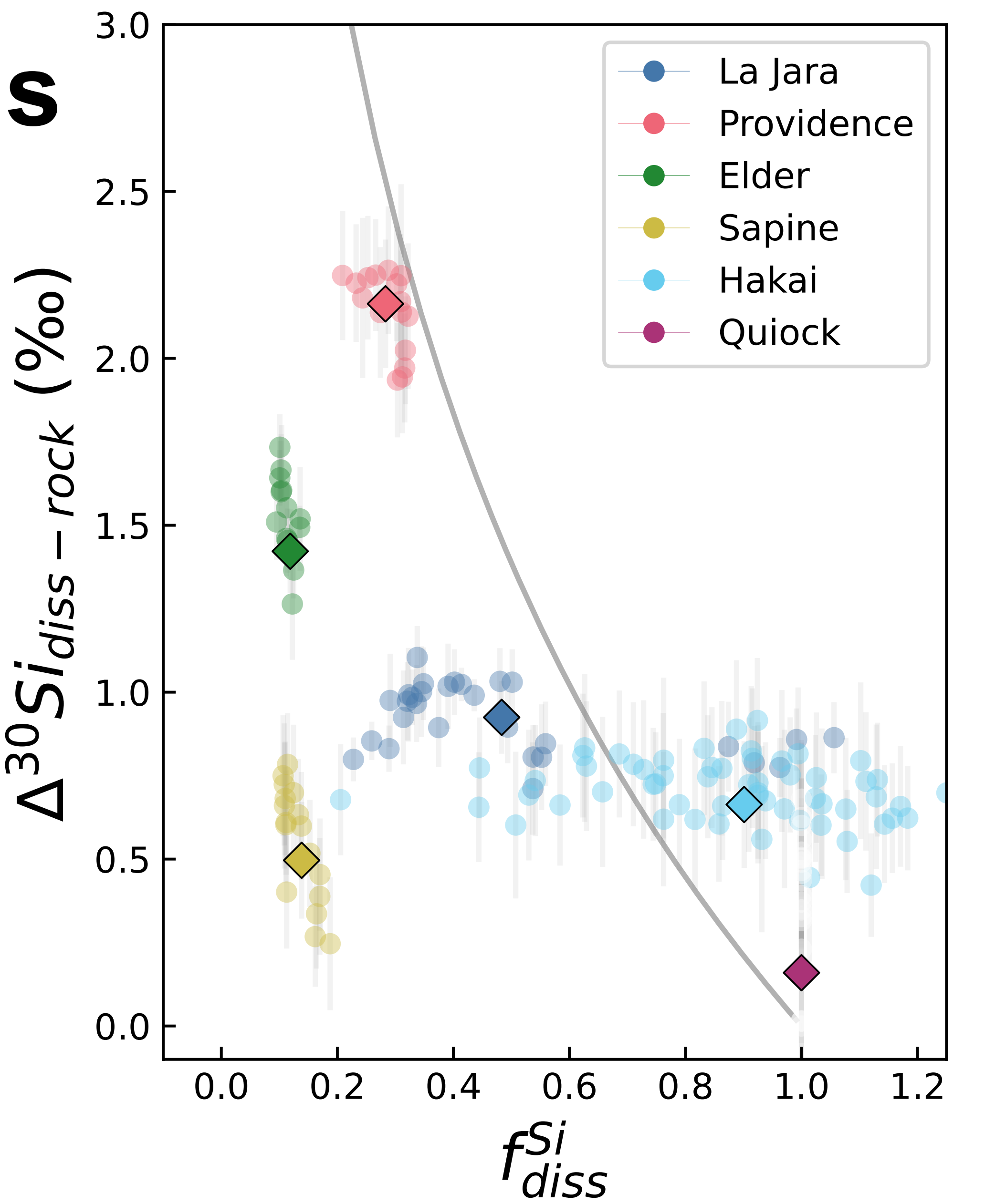
- Piston flow





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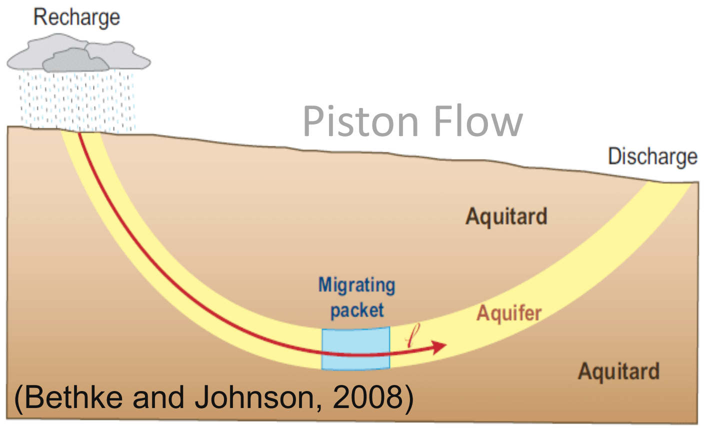
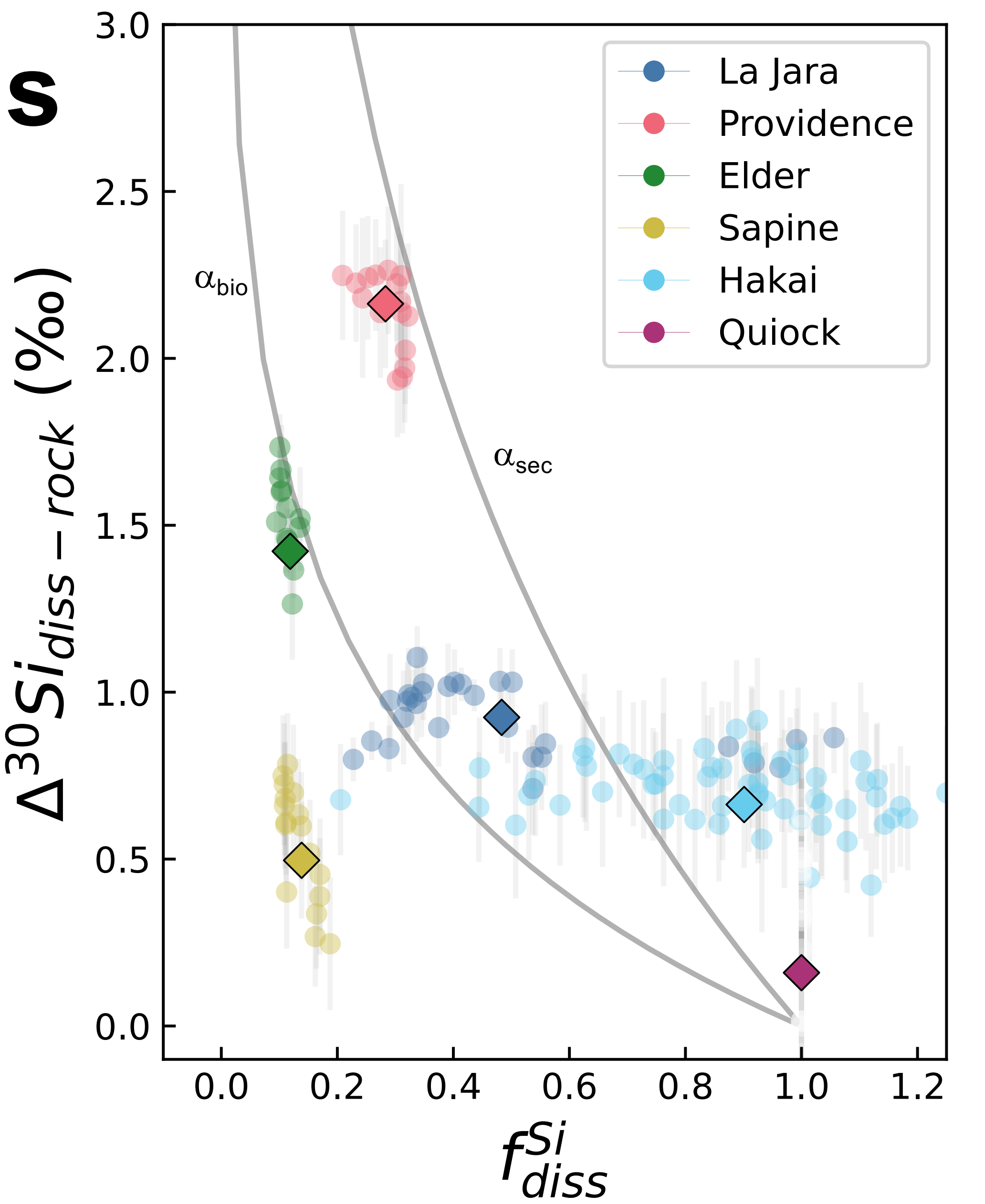
- Piston flow
- Range in fractionation factors
  - α_{sec}=0.9980
  - α_{bio}=0.99924



(Bethke and Johnson, 2008)



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- Range in fractionation factors
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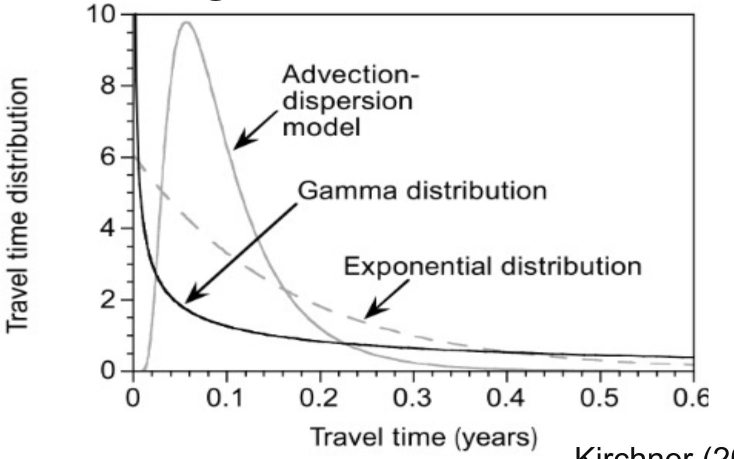
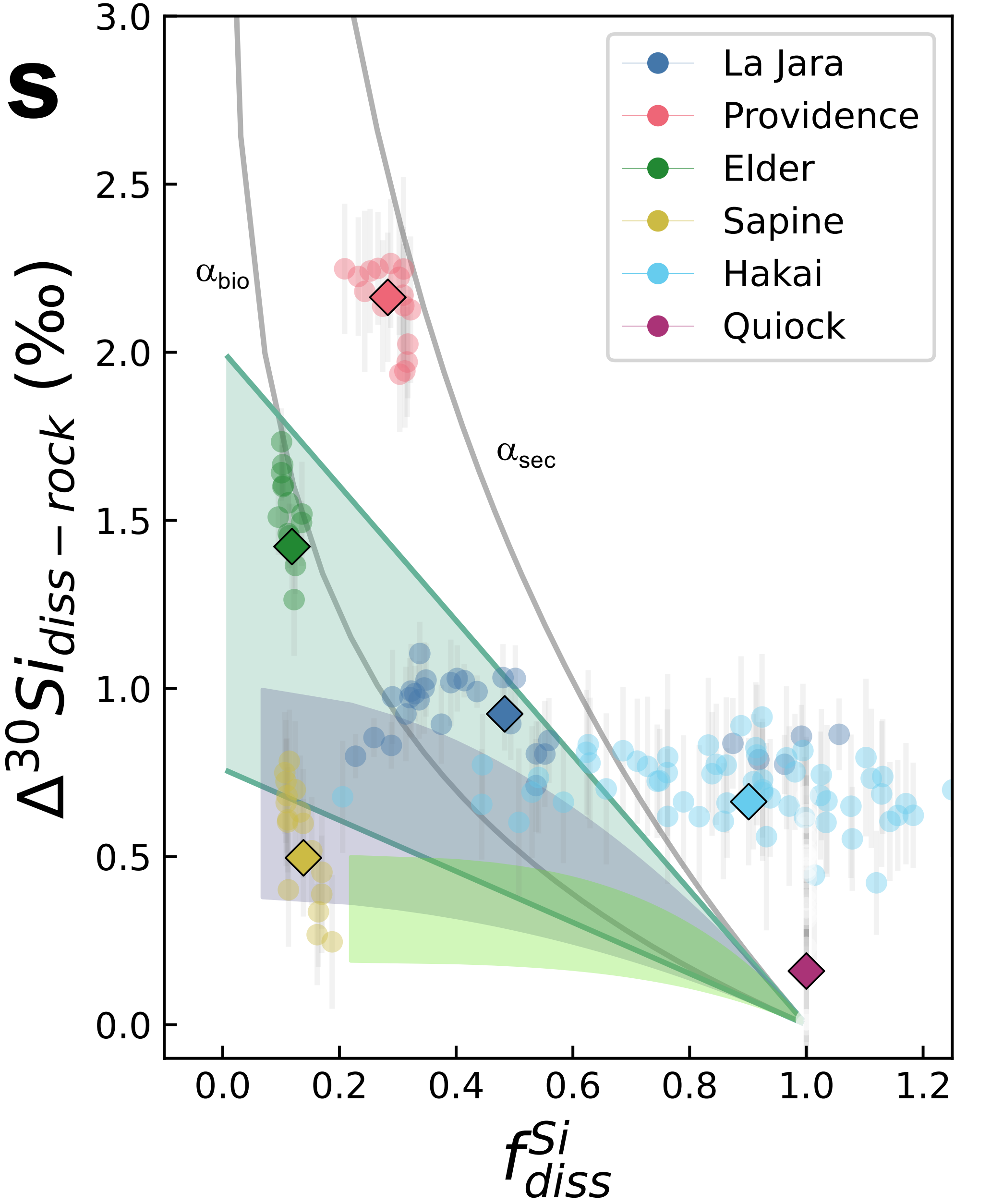
- Range in Transit Time Distribution (TTD)



Kirchner (2000)

Piston Flow
Exponential
Gamma TTD (a=0.5)
Gamma TTD (a=0.25)



Altered from Fernandez et al. (2022)

Landscape Evolution Observatory (LEO)

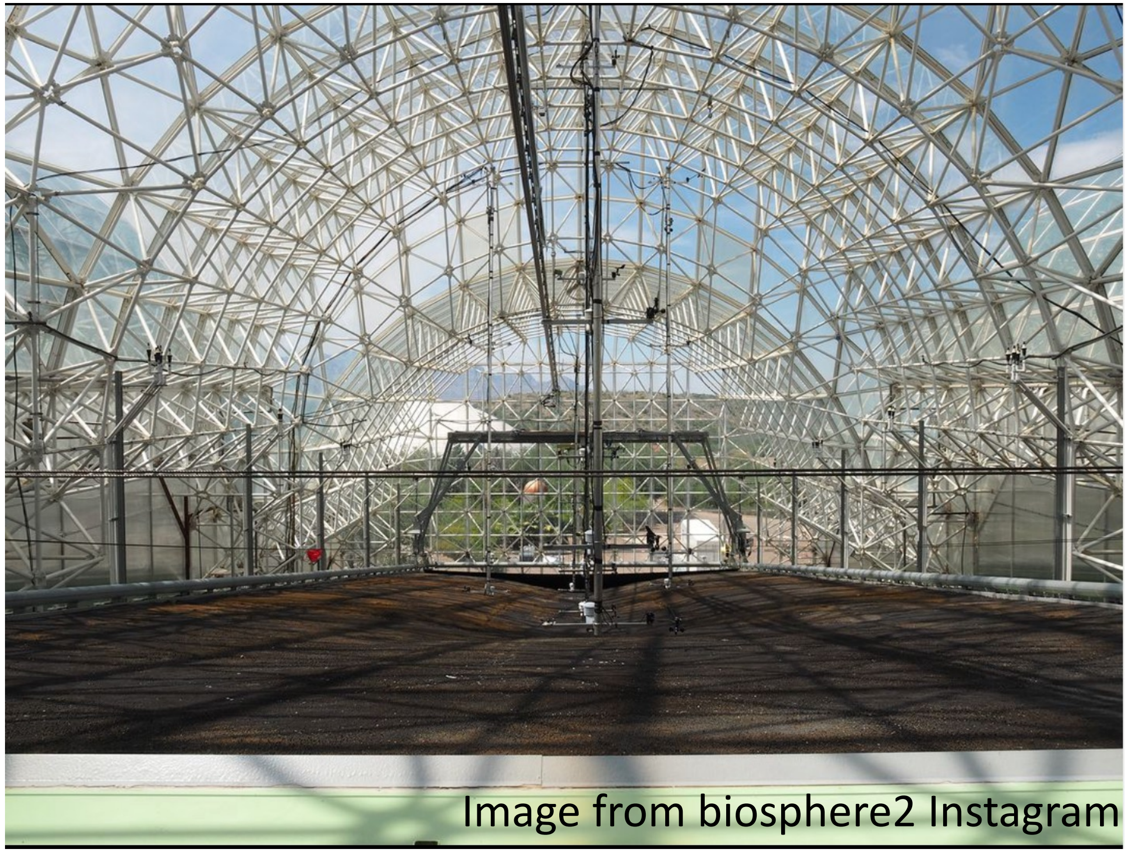


Image from biosphere2 Instagram

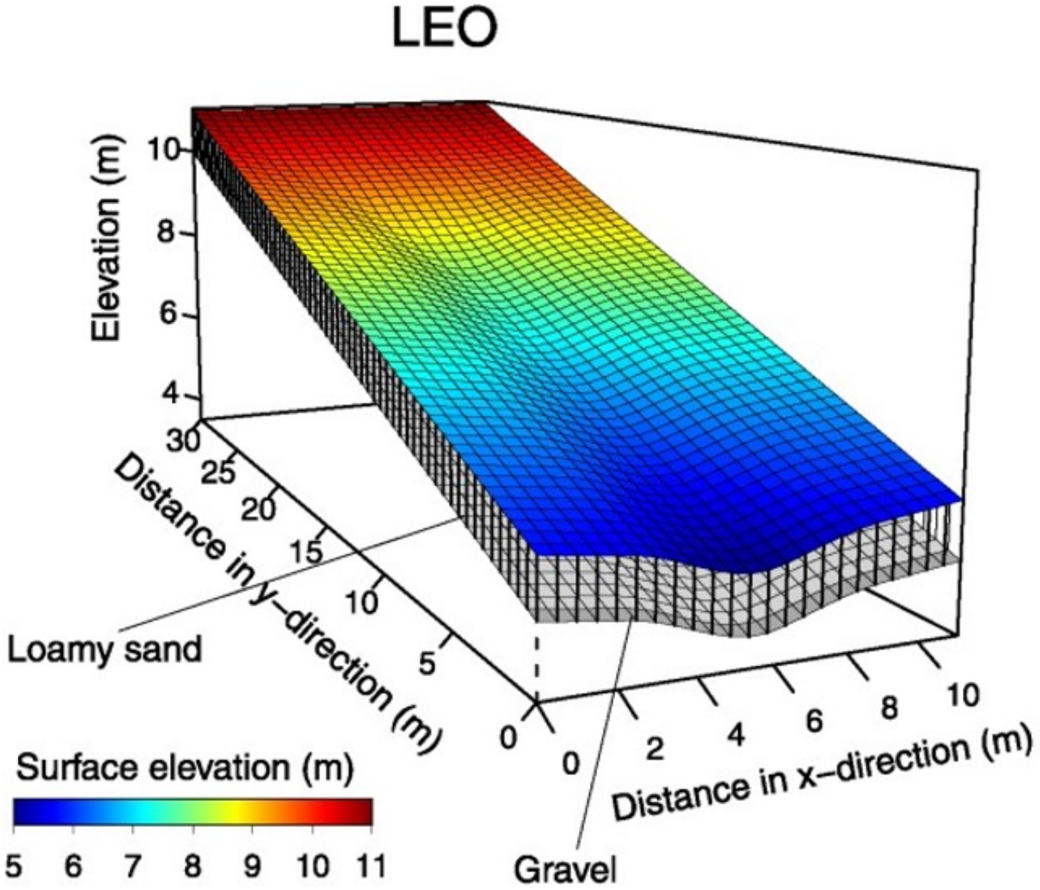
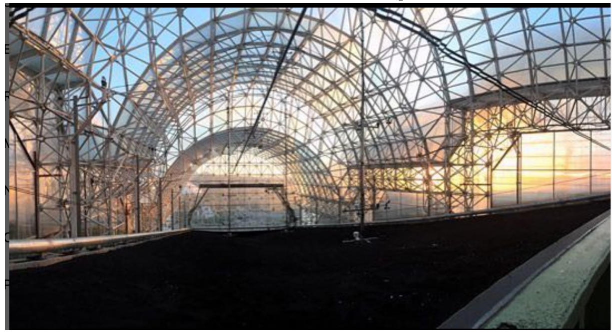


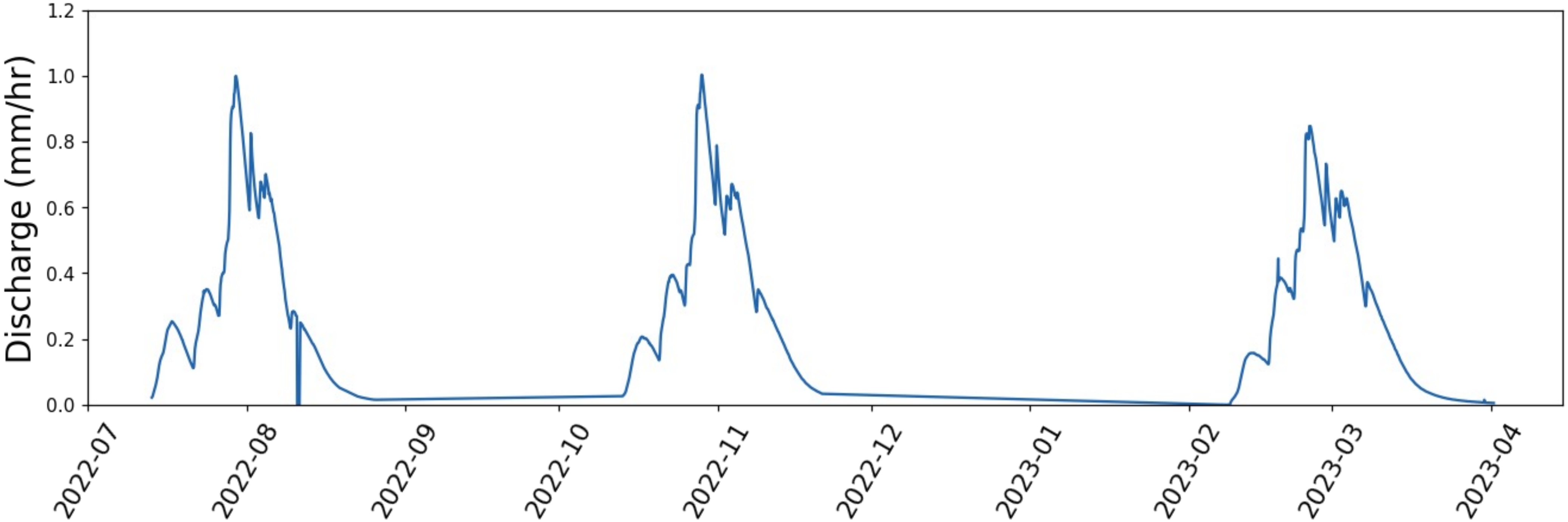
Image from Hazenberg et al. 2016

- Biosphere 2 Facility in Tucson, AZ
- LEO acts like watershed but is much simpler.
- Three identical 30 by 11 by 1-meter hillslopes filled with crushed basalt

Concentration-Ratio-Discharge Experiment

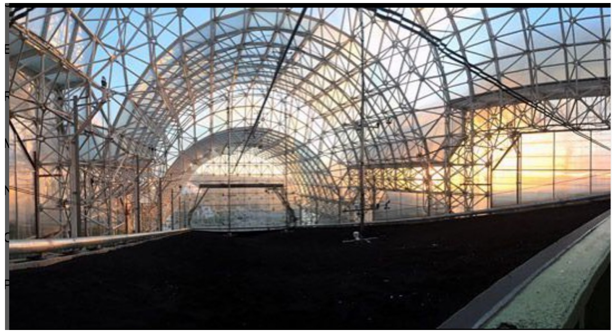
- Three 30-day pulses spaced by 30-60-90 day dry periods
- Each driven by randomly generated irrigation schedule (Kim and Troch 2022)

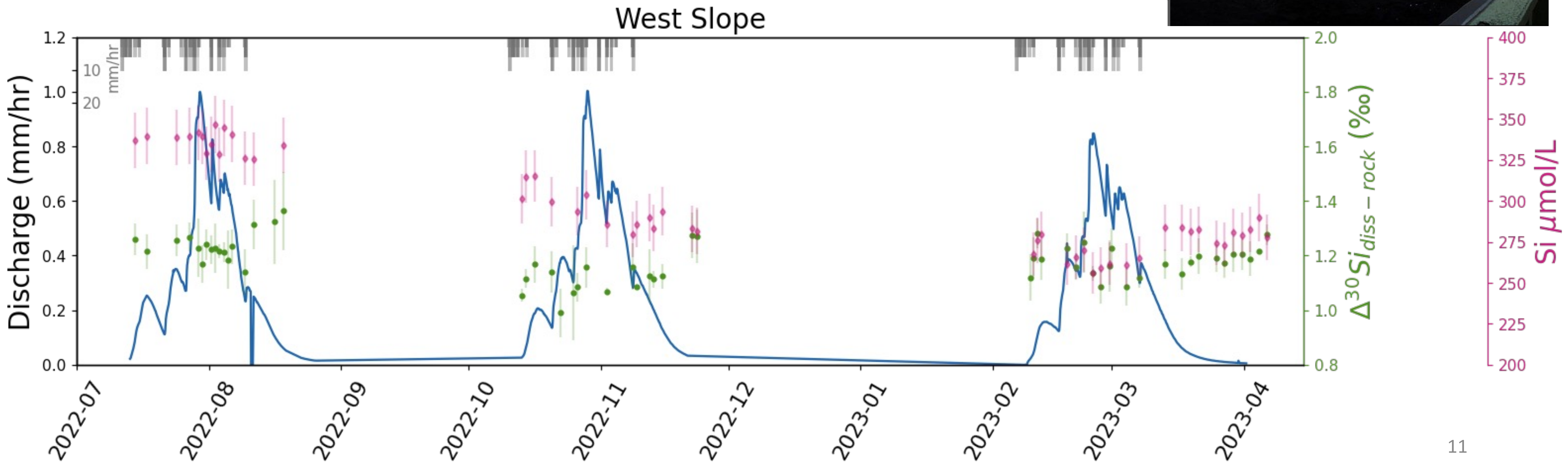




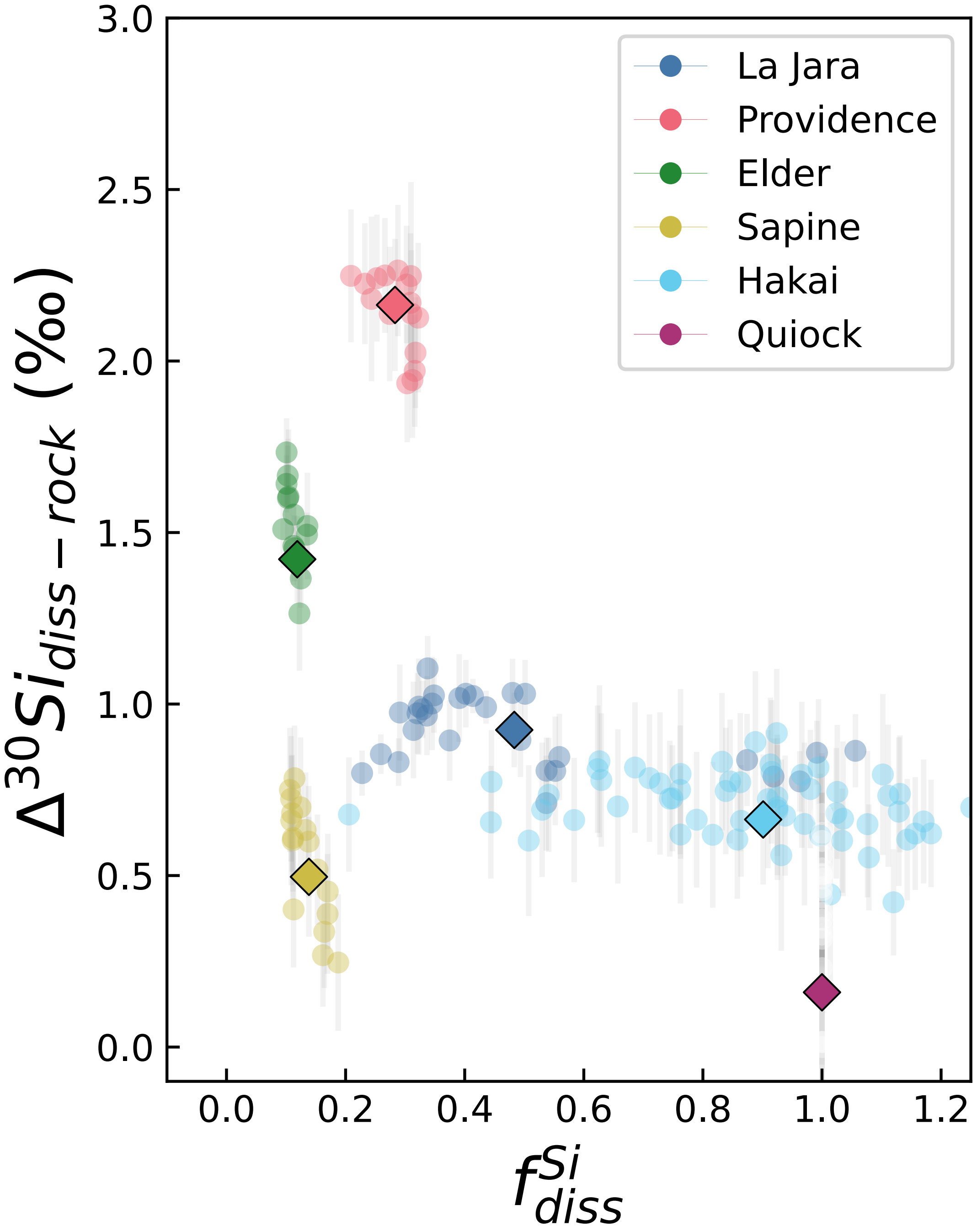
Concentration-Ratio-Discharge Experiment

- Three 30-day pulses spaced by 30-60-90 day dry periods
- Each driven by randomly generated irrigation schedule (Kim and Troch 2022)
- δ^{30}Si remains stable across all three pulse events





LEO Compared to Upland Watershed



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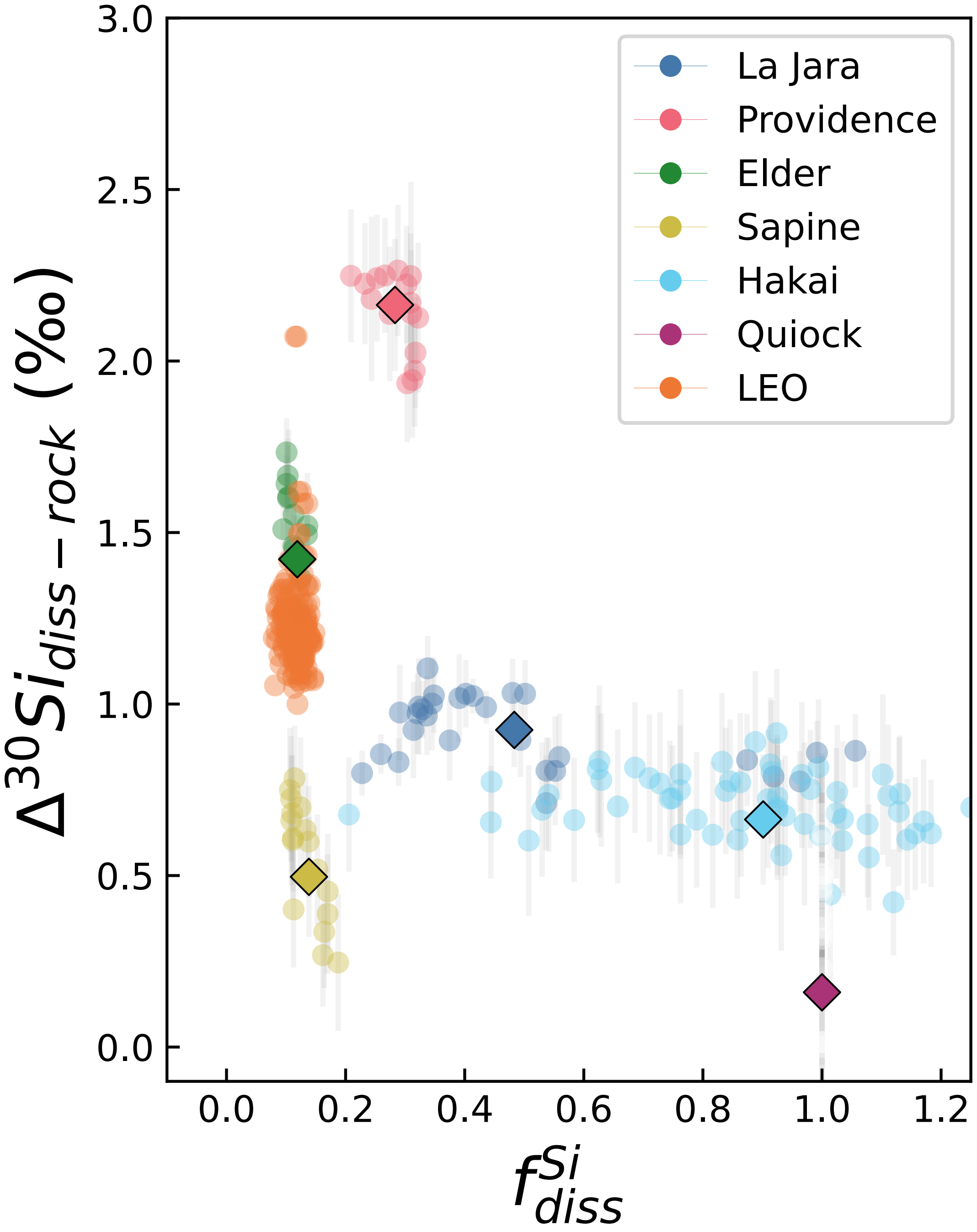
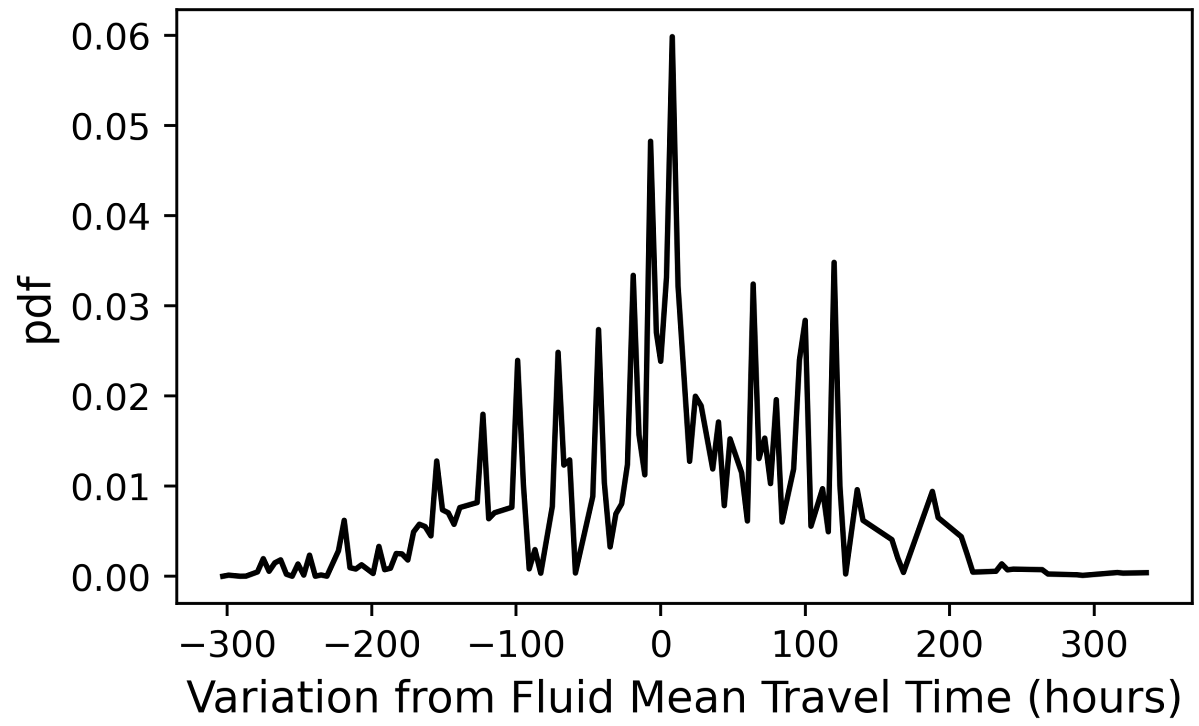
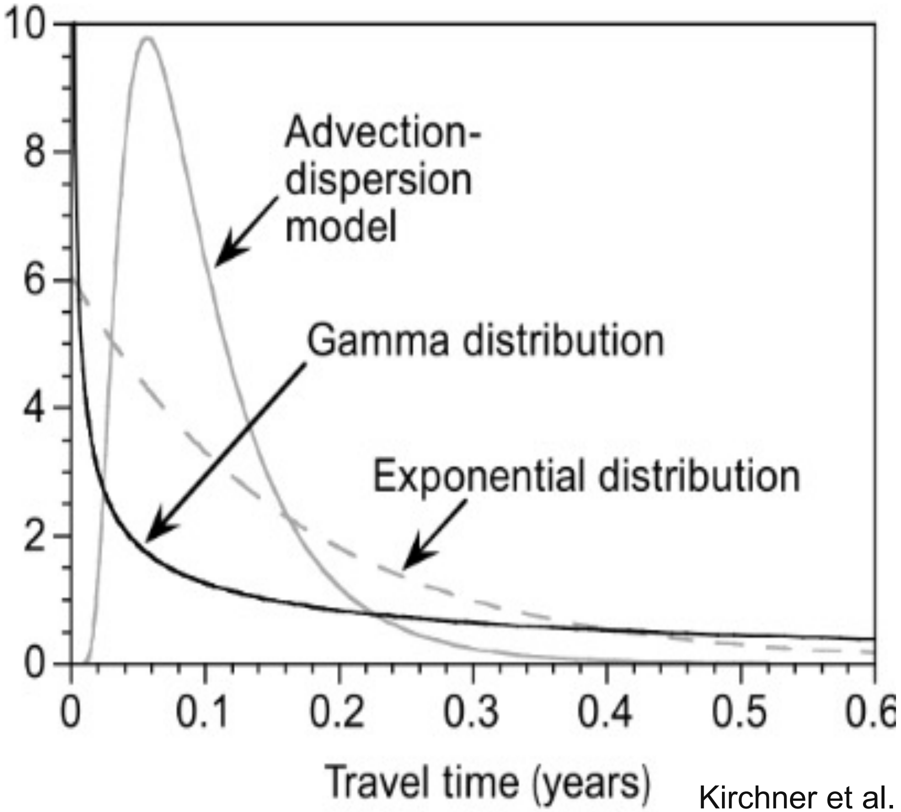


LEO Transit Time Distribution (TTD)

Combination of 7 TTDs from pulse 3
Age 0 = mean fluid age



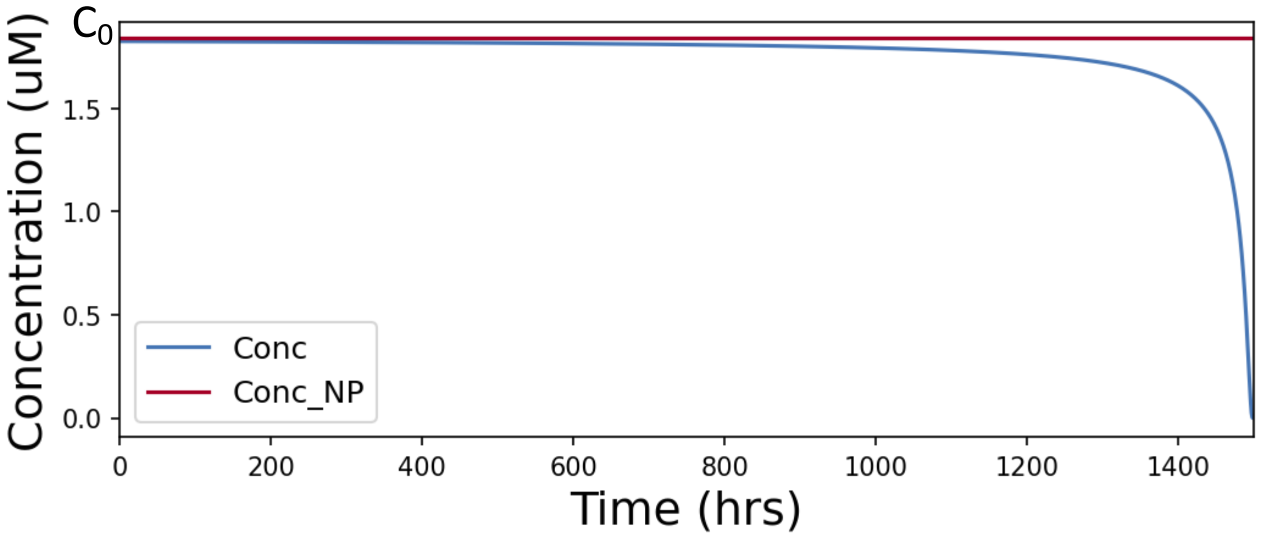


Kirchner et al. (2000)

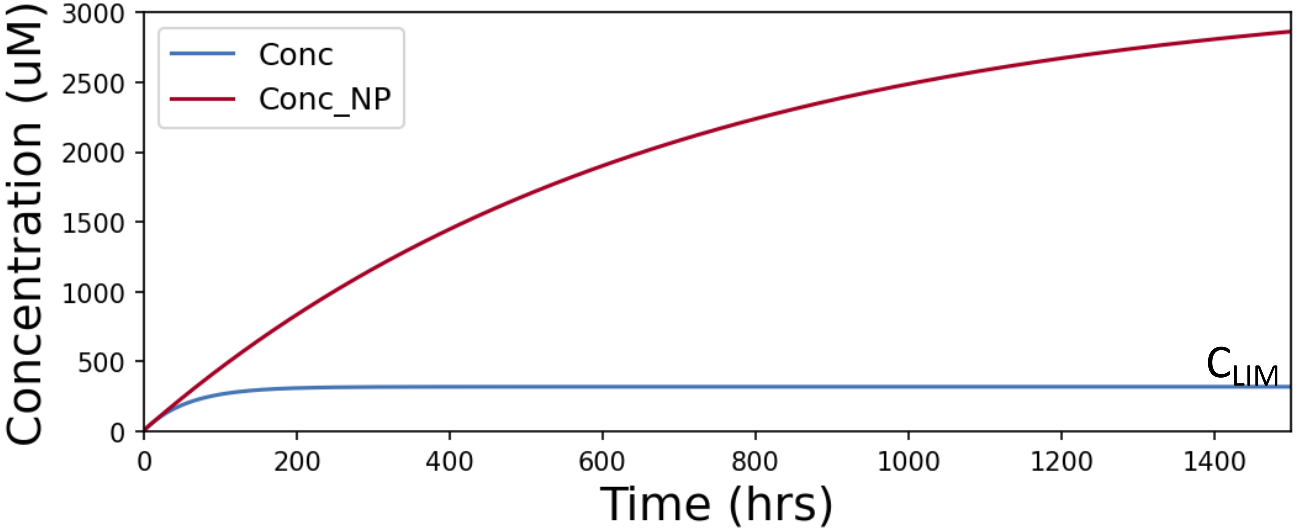
LEO TTD pdf

Common TTD shapes

Competing Reactions Model



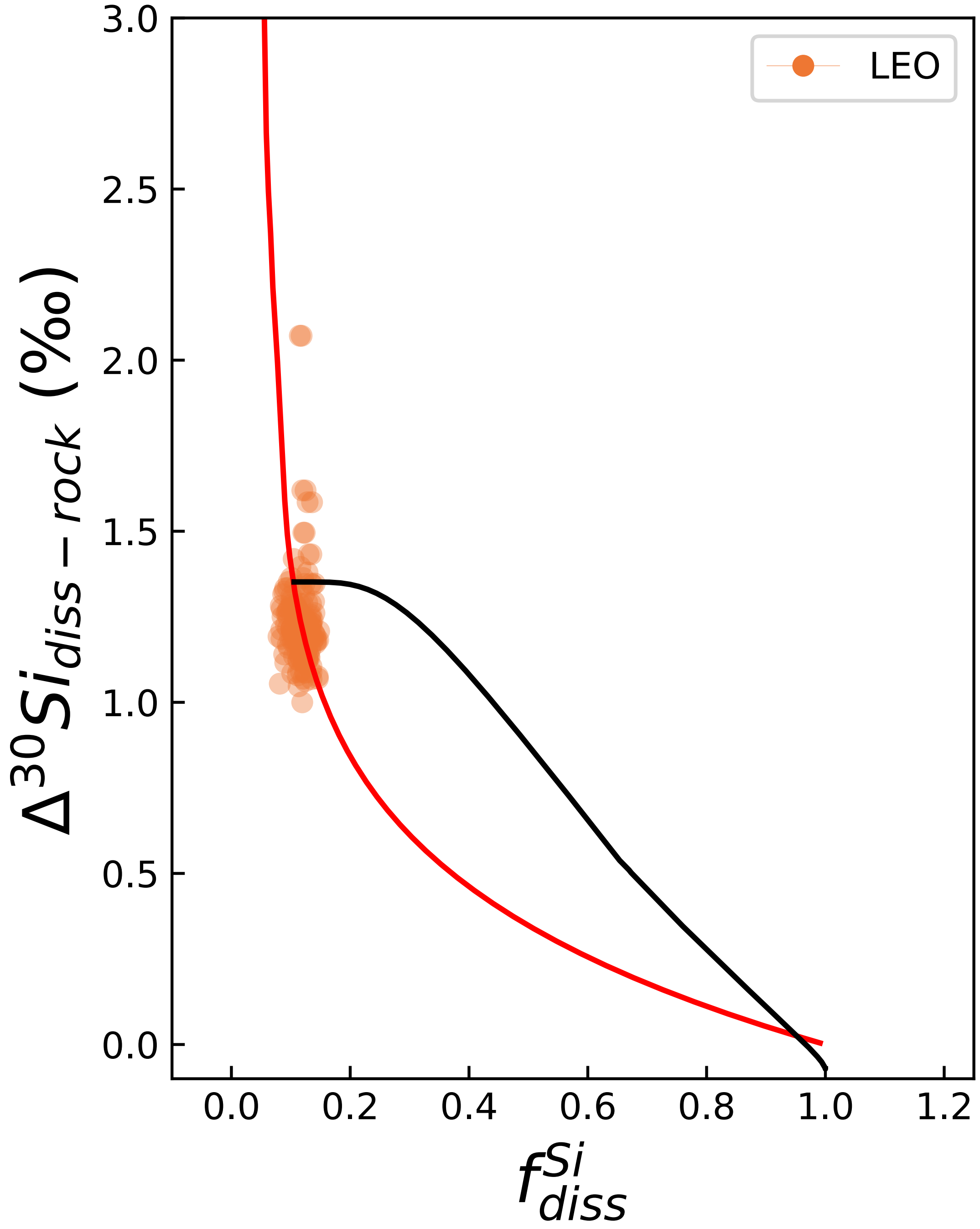
- Single reaction progressively removing Si from C_0
- $C(t) = C_0 * \exp(-kt)$
- Conc_NP = Concentration of element excluded from secondary phase



- Two reactions:
  - Dissolution of Si into solution
  - Precipitation of Si out of solution
- Equilibrates at C_{LIM}
- $C(t) = C_{LIM} + (C_0 - C_{LIM}) \exp\left(-\frac{k_{eff}}{C_{LIM}} t\right)$

LEO TTD fit requires a fractionation factor of α = 0.9995 and strong f_{diss}^{Si} relationship

LEO TTD Competing reaction fit requires a fractionation factor of α_{sec} = 0.9985 and α_{diss} = 1 No f_{diss}^{Si} dependence <0.25

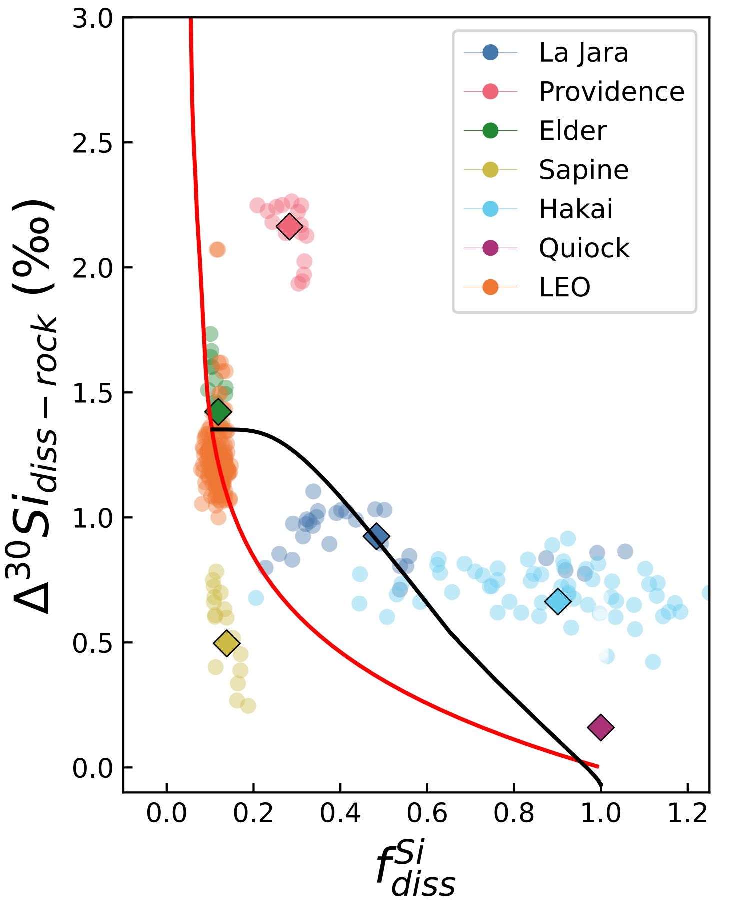


LEO TTD (Fernandez et al. 2022 model)

LEO TTD: Competing Reaction Model

Conclusions

- Controlled hillslope systems such as LEO provide a unique research opportunity with known fractionation pathways and transit time distributions
- A minimalist model for isotope fractionation during mineral weathering subject to a constrained fluid TTD accounts for the observed relationship between solute depletion and Si isotope signatures at LEO
- This work opens the possibility to revisit published Si isotope time series in upland watersheds using a competing reaction model



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