

非传统稳定同位素在表生地球过程的应用: **Li**和**K**为例

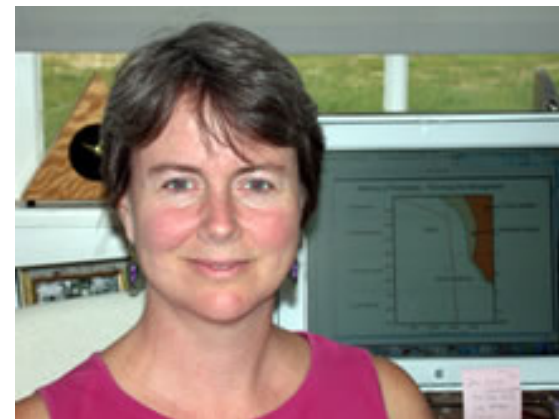
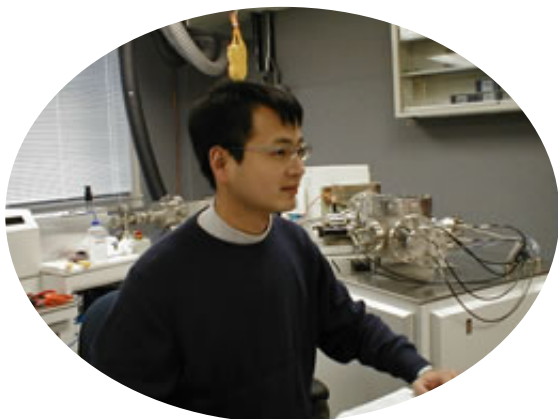


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Assistant Professor
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Earth and Planetary Science Letters 243 (2006) 701–710

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Diffusion-driven extreme lithium isotopic fractionation in country rocks of the Tin Mountain pegmatite

Fang-Zhen Teng*, William F. McDonough, Roberta L. Rudnick, Richard J. Walker

Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20742, U.S.A.

Outline



1. Introduction

2. Chemical weathering in modern environments

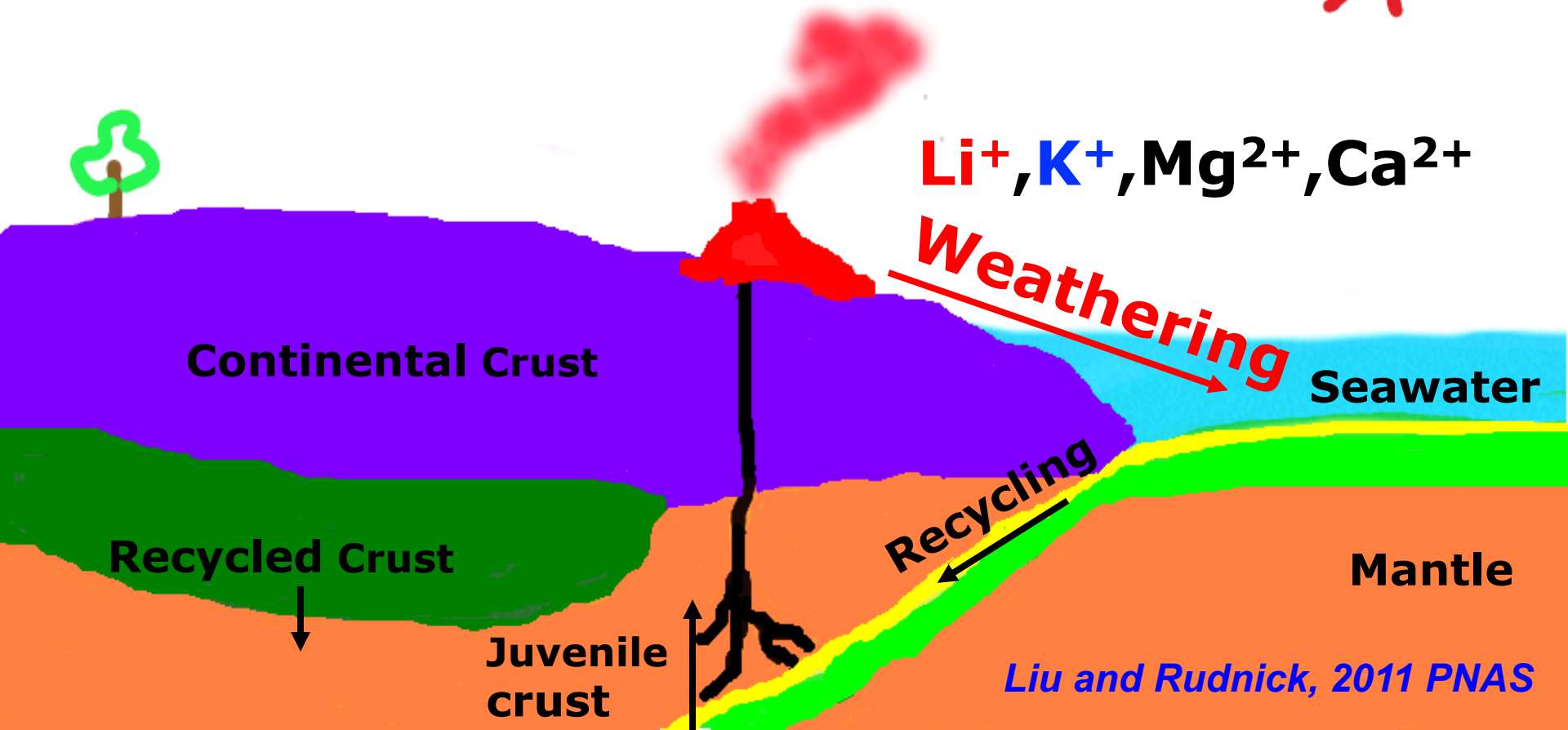
3. Weathering and global ocean cycle in Earth's history

4. Conclusions and outlook

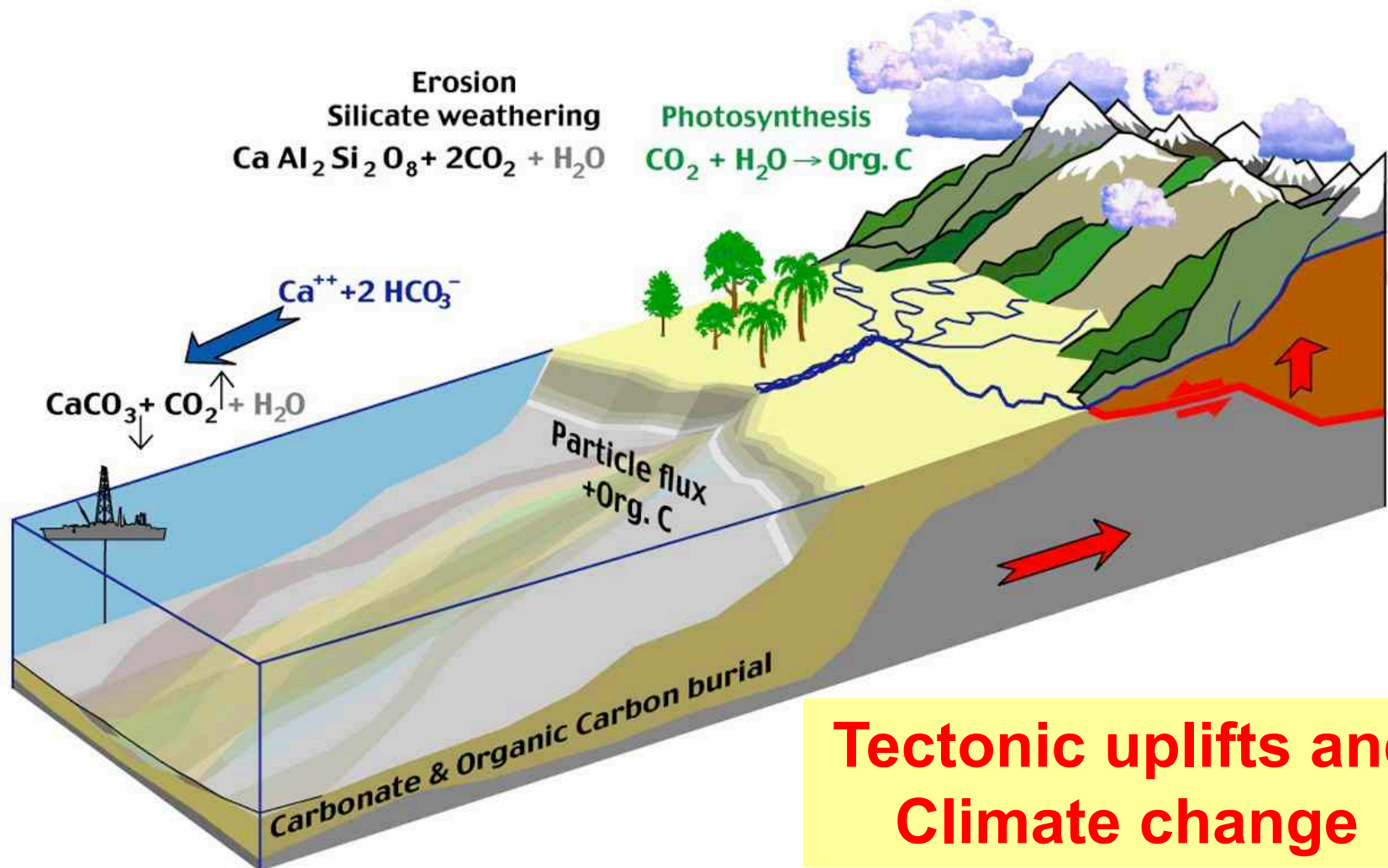
1. Introduction

Why study chemical weathering?

>15% mass of original juvenile crust lost due to continental weathering and erosion



Why study chemical weathering?



Why lithium?

FirstView

Association between naturally occurring lithium in drinking water and suicide rates: systematic review and meta-analysis of ecological studies

Anjum Memon  (a1), Imogen Rogers (a1), Sophie M. D. D. Fitzsimmons  (a1), Ben Carter (a2) ... 

DOI: <https://doi.org/10.1192/bjp.2020.128> Published online by Cambridge University Press 07 July 2022



Ptable
.com

La Lanthanum 138.90547	Ce Cerium 140.116	Pr Praseodymium 140.90765	Nd Neodymium 144.242	Pm Promethium (145)	Sm Samarium 150.36	Eu Europium 151.964	Gd Gadolinium 157.25
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)

Lithium pioneer: Lui-Hueng Chan (1939-2007)

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0016-7037/88/\$3.00 + .00



Variation of lithium isotope composition in the marine environment: A preliminary report

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(Received September 2, 1987; accepted in revised form March 22, 1988)

Abstract—The Li isotopic compositions of ocean waters, lake waters, hydrothermal solutions, altered and unaltered basalts have been determined using the technique of thermal ionization mass spectrometry of lithium tetraborate. Seawater appears to be homogeneous in Li isotopic composition. The mean $\delta^6\text{Li}$ value is $-32.3 \pm 0.5\text{‰}$, relative to an isotopic standard. Three lakes studied (Lake Tanganyika, Caspian Sea and Dead Sea) yield $\delta^6\text{Li}$ similar to the seawater isotopic composition. A fresh basalt glass from 21°N, East Pacific Rise displays a $\delta^6\text{Li}$ value of -4.7‰ . A hydrothermal solution from a 21°N vent field has $\delta^6\text{Li}$ of -10‰ , indicating incomplete extraction of Li from the igneous minerals or partial retention in secondary phases. The alteration margin of a basalt from the Mid-Atlantic Ridge has $\delta^6\text{Li}$ of -8.4‰ . The isotope data of submarine basalts suggest preferential removal of ^6Li from seawater into alteration minerals during low temperature weathering. The $\delta^6\text{Li}$ values of two hydrothermal solutions from Guaymas Basin were found to be -5‰ and -10‰ . The results can be interpreted as the net effect of Li addition from basalt and sediments and incorporation in hydrothermal precipitates as the hydrothermal fluids interact with basin sediments.

The observed enrichment of ^7Li in seawater relative to submarine hydrothermal solutions, its principal Li input, is tentatively attributed to isotopic fractionation associated with low temperature alteration of seafloor basalt and incorporation in authigenic sediments. It appears that the Li isotope system may have characteristics that can resolve the mass balance of Li in the ocean.

Potassium pioneers:



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Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



High-precision analysis of potassium isotopes by HR-MC-ICPMS

Yan Hu^{a,*}, Xin-Yang Chen^a, Ying-Kui Xu^{a,b}, Fang-Zhen Teng^{a,*}

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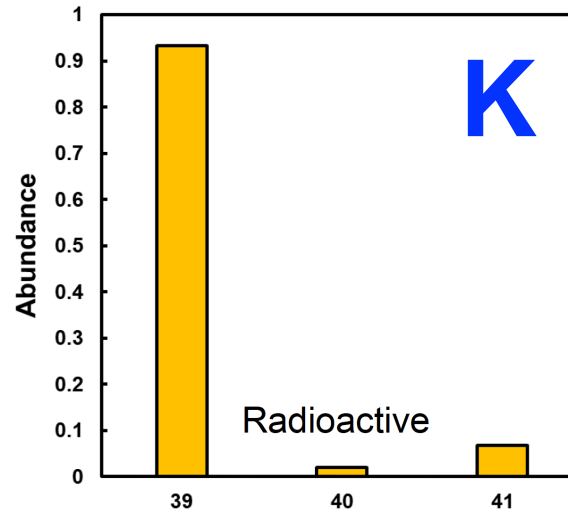
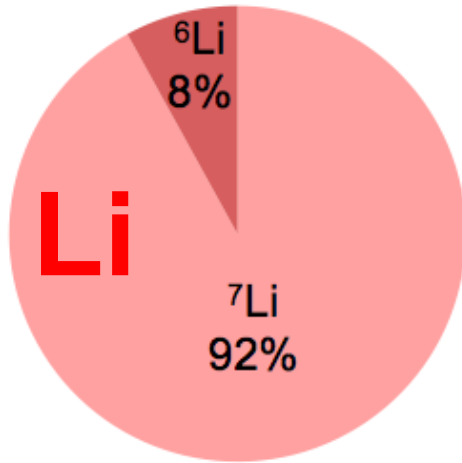
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Cite this: *J. Anal. At. Spectrom.*, 2019, 34, 160

High-precision potassium isotopic analysis by MC-ICP-MS: an inter-laboratory comparison and refined K atomic weight†

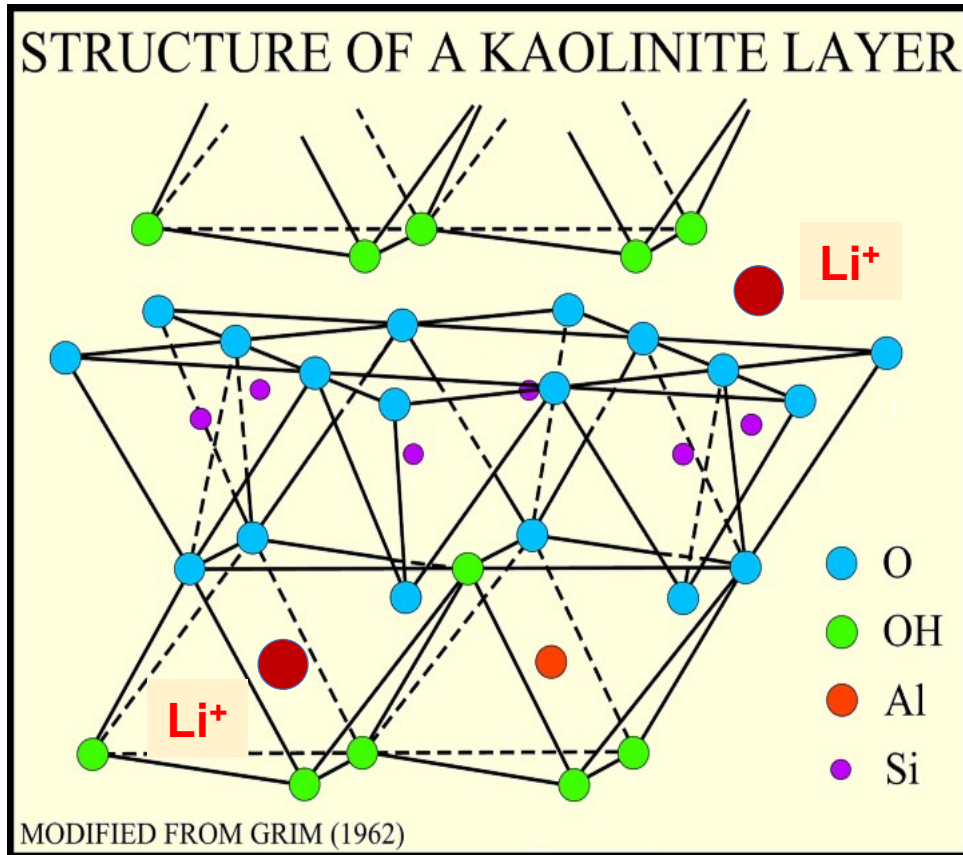
Heng Chen, Zhen Tian, Brenna Tuller-Ross, Randy L. Korotev and Kun Wang *

Why **Li** and **K**?



- Incompatible – enriched in continental crust
- Soluble in fluid and can be incorporated/sorbed to clay
- Monovalent (not affected by redox)
- Enriched in silicates, poor in carbonates
- **K** – important nutrient, **Li** – NOT a nutrient

How do **Li isotopes** fractionate?



Heavy isotope

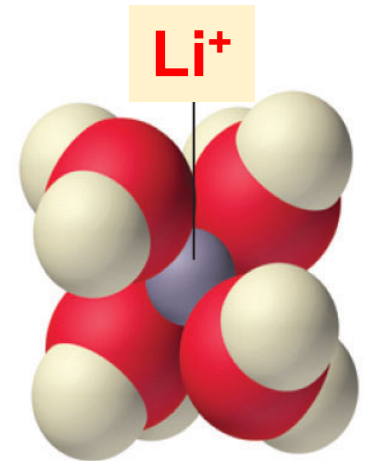
High bonding energy site

Low coordination number

Bigeleisen and Mayer (1947)

Tetrahedra,
CN=4

Octahedral,
CN=6



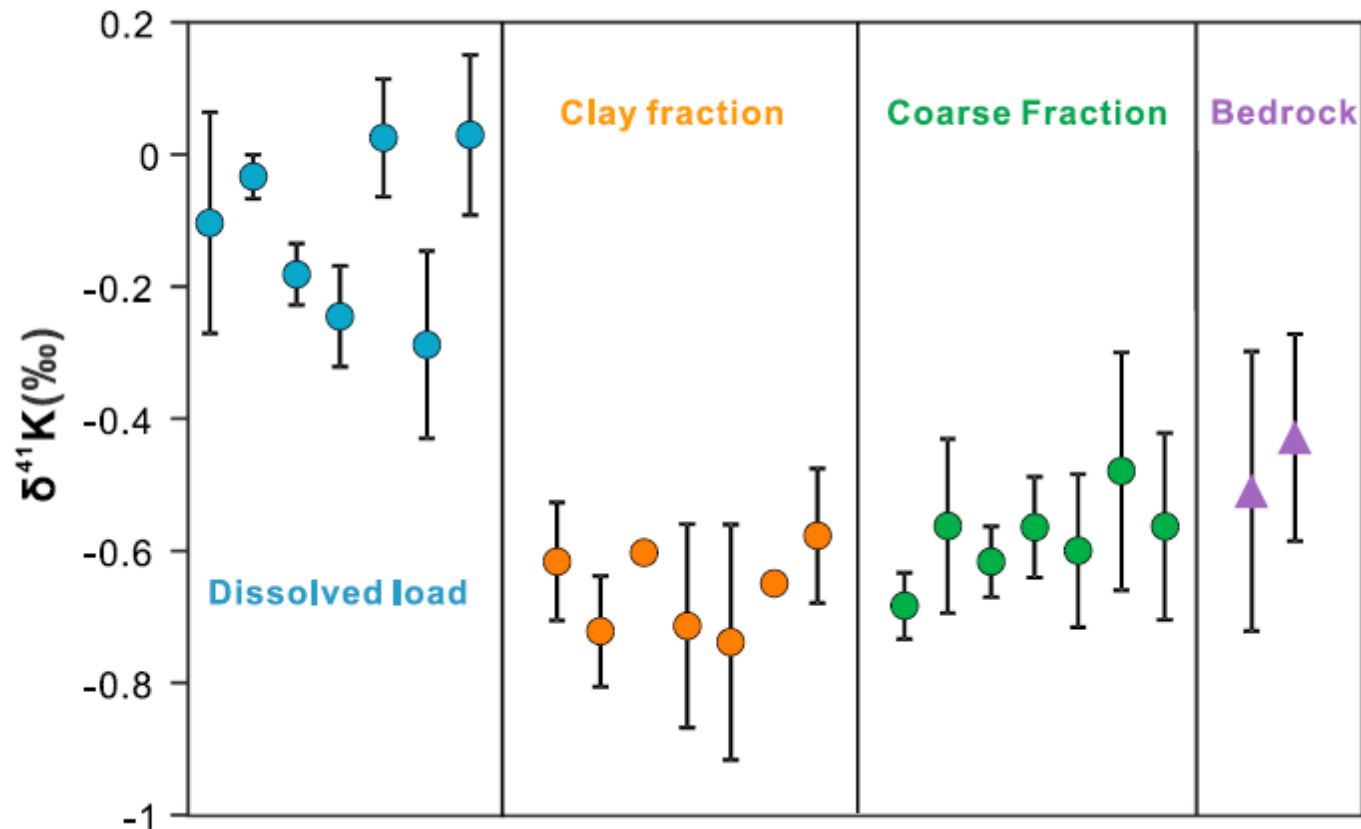
H₂O

heavy isotope (⁷Li) in **tetrahedral** sites of water

light isotope (⁶Li) in **octahedral** sites of secondary minerals

Huh et al., 1998; Liu et al., 2013; 2015; Pistiner and Henderson, 2003; PvS et al., 2006; 2009; Rudnick et al., 2004; Teng et al., 2004; Williams and Hervig, 2005; Vigier et al., 2008; Wimpenny et al., 2015

How do **K** isotopes fractionate?



heavy isotope (⁴¹K) in water

light isotope (³⁹K) in secondary minerals

Chen et al., 2020; S. Li et al., 2019; Teng et al., 2020; Zeng et al., 2019

Global **Li** and **K** cycle

Riverine input

$\text{Li}_f = \sim 10 \text{ Bmol/yr}$, $\delta^7\text{Li} = 23\text{‰}$
 $\text{K}_f = \sim 1.5 \text{ Tmol/yr}$, $\delta^{41}\text{K} = \sim -0.38\text{‰}$?

Seawater

$\delta^7\text{Li} = +31\text{‰}$
 $\delta^{41}\text{K} = +0.14\text{‰}$

Fresh basalt

$\delta^7\text{Li} = +4\text{‰}$
 $\delta^{41}\text{K} = -0.5\text{‰}$

Subduction reflux

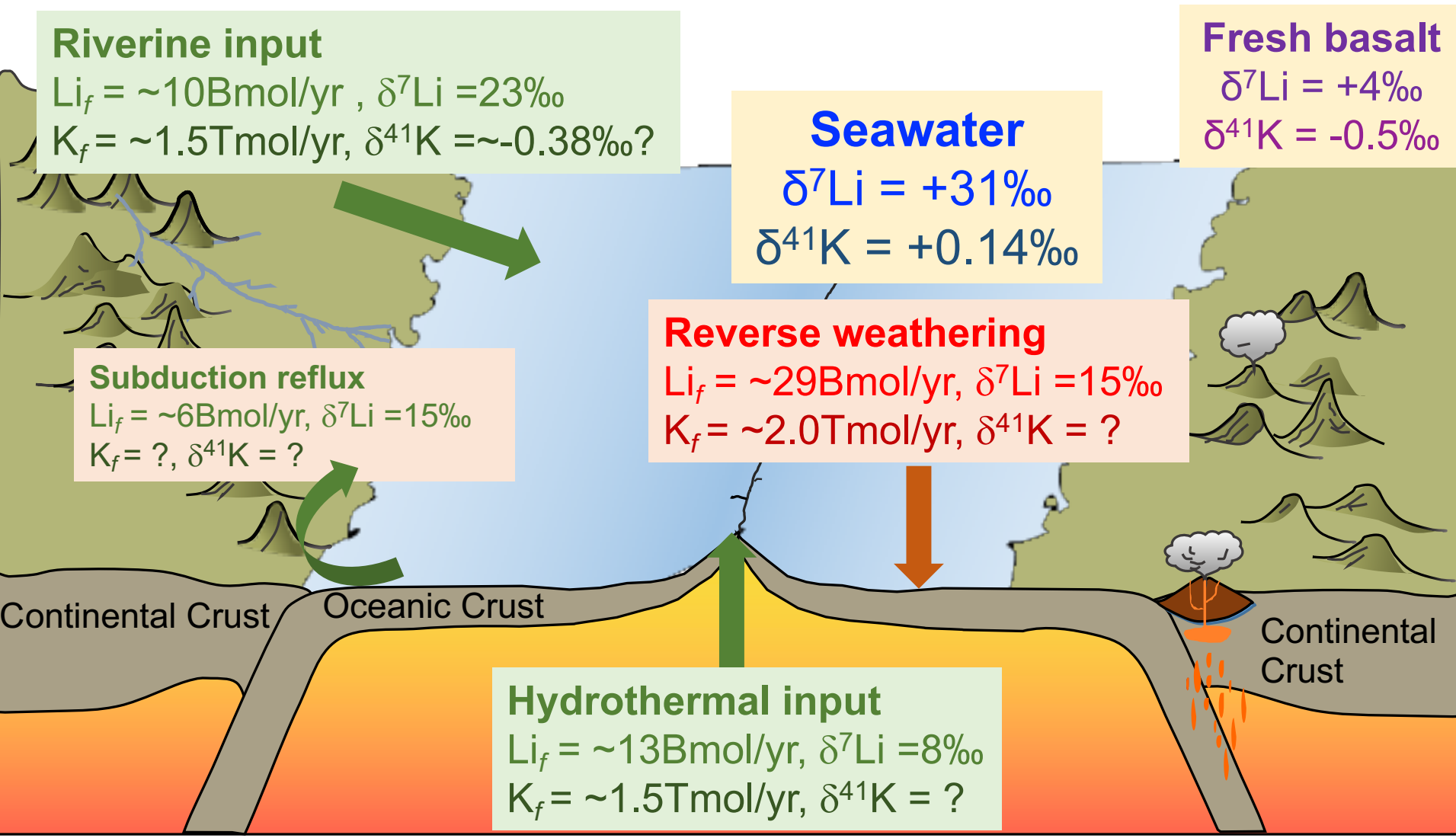
$\text{Li}_f = \sim 6 \text{ Bmol/yr}$, $\delta^7\text{Li} = 15\text{‰}$
 $\text{K}_f = ?$, $\delta^{41}\text{K} = ?$

Reverse weathering

$\text{Li}_f = \sim 29 \text{ Bmol/yr}$, $\delta^7\text{Li} = 15\text{‰}$
 $\text{K}_f = \sim 2.0 \text{ Tmol/yr}$, $\delta^{41}\text{K} = ?$

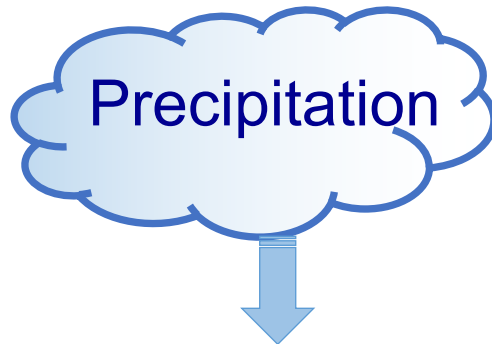
Hydrothermal input

$\text{Li}_f = \sim 13 \text{ Bmol/yr}$, $\delta^7\text{Li} = 8\text{‰}$
 $\text{K}_f = \sim 1.5 \text{ Tmol/yr}$, $\delta^{41}\text{K} = ?$



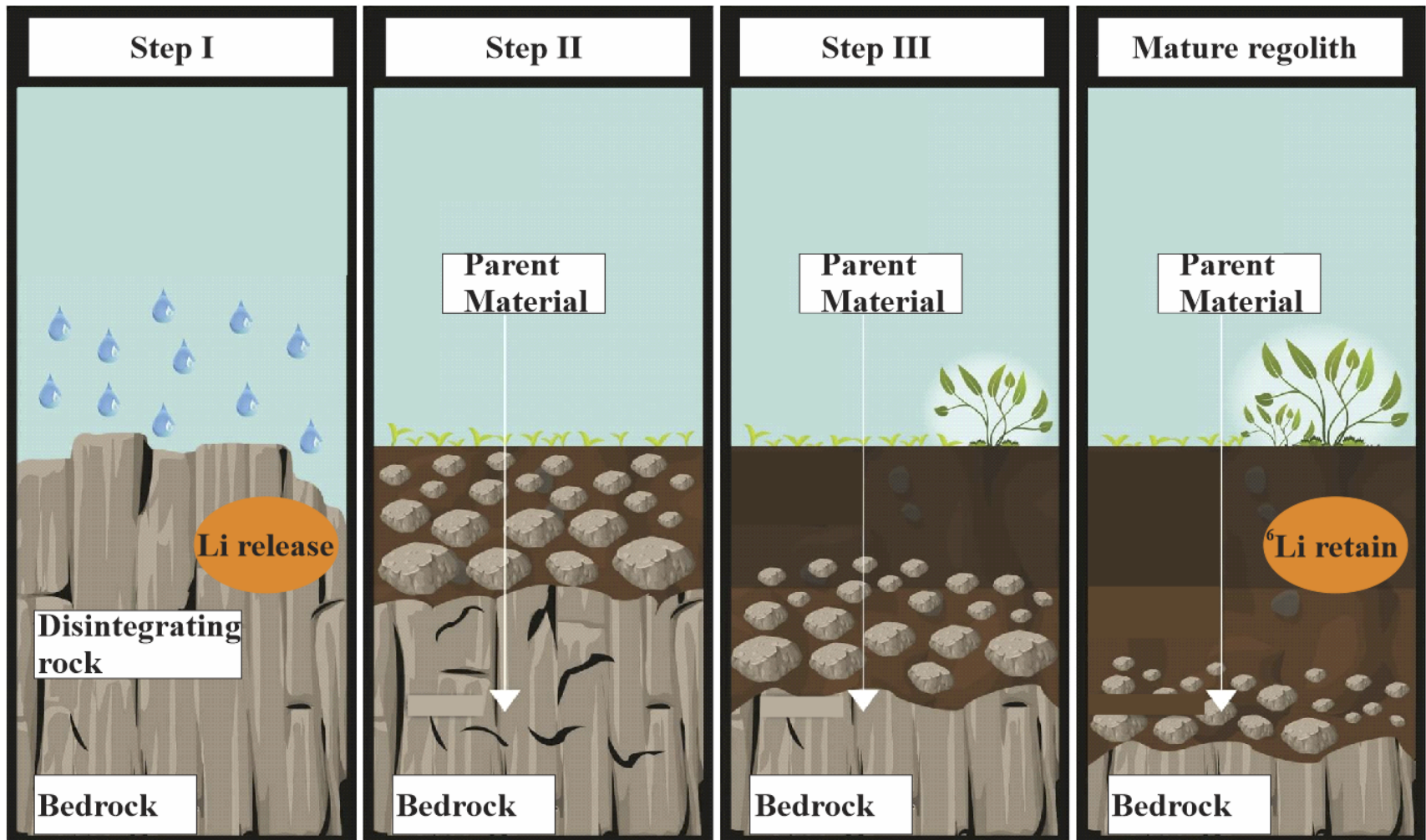
2. Chemical weathering in modern environments

Weathering process

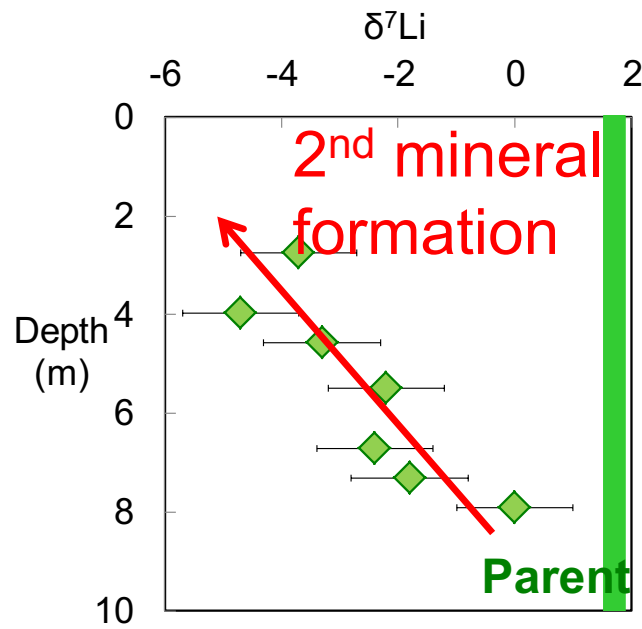
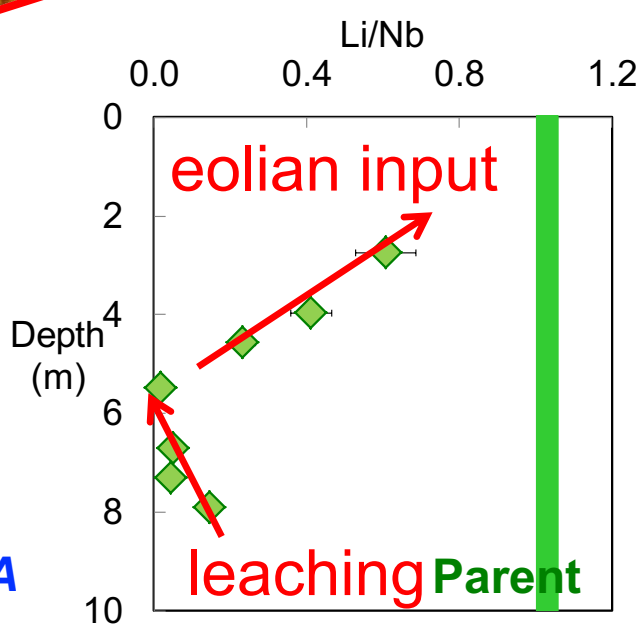
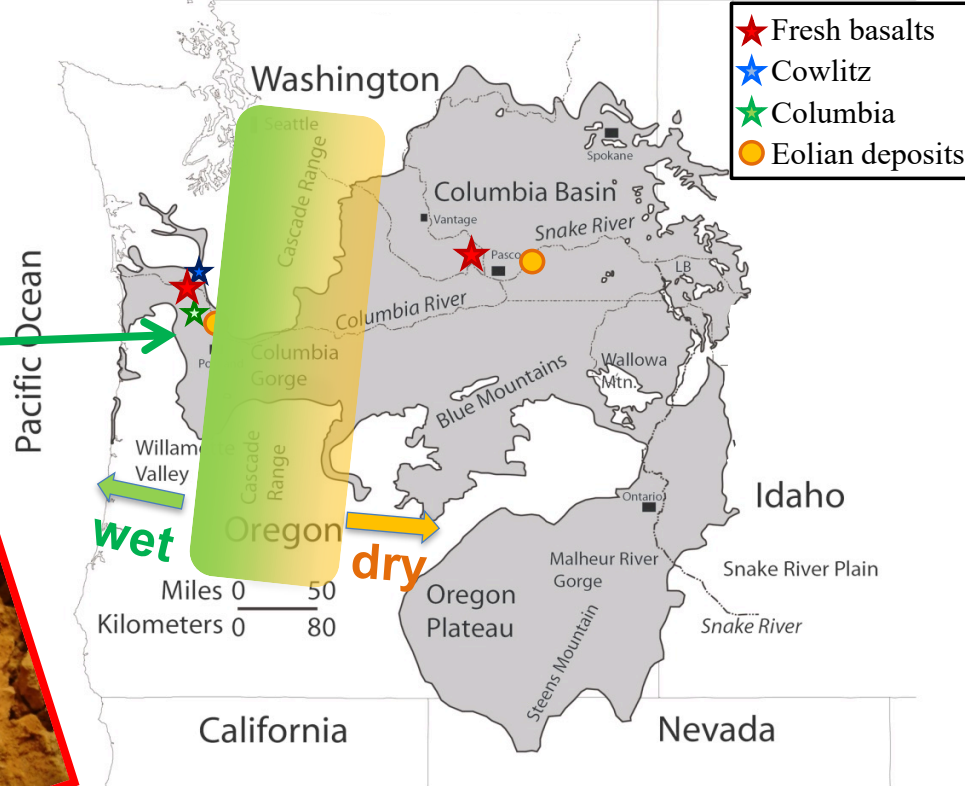
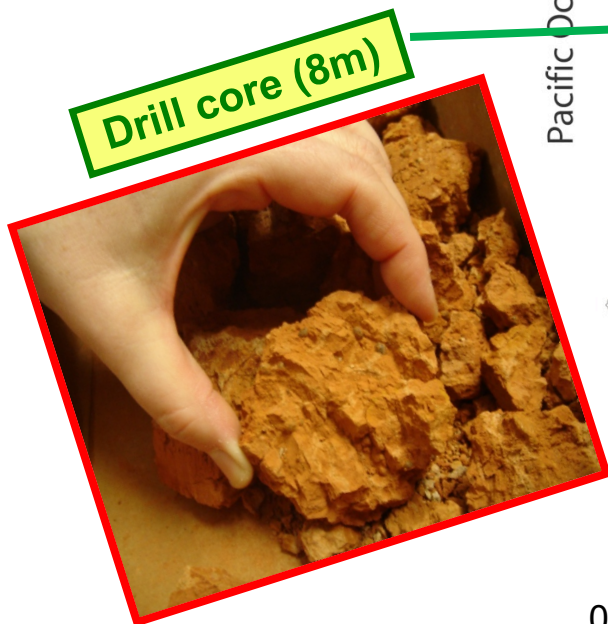


Why study regolith?

Regolith provide **accumulated knowledge** during weathering.



Regolith Li isotopes



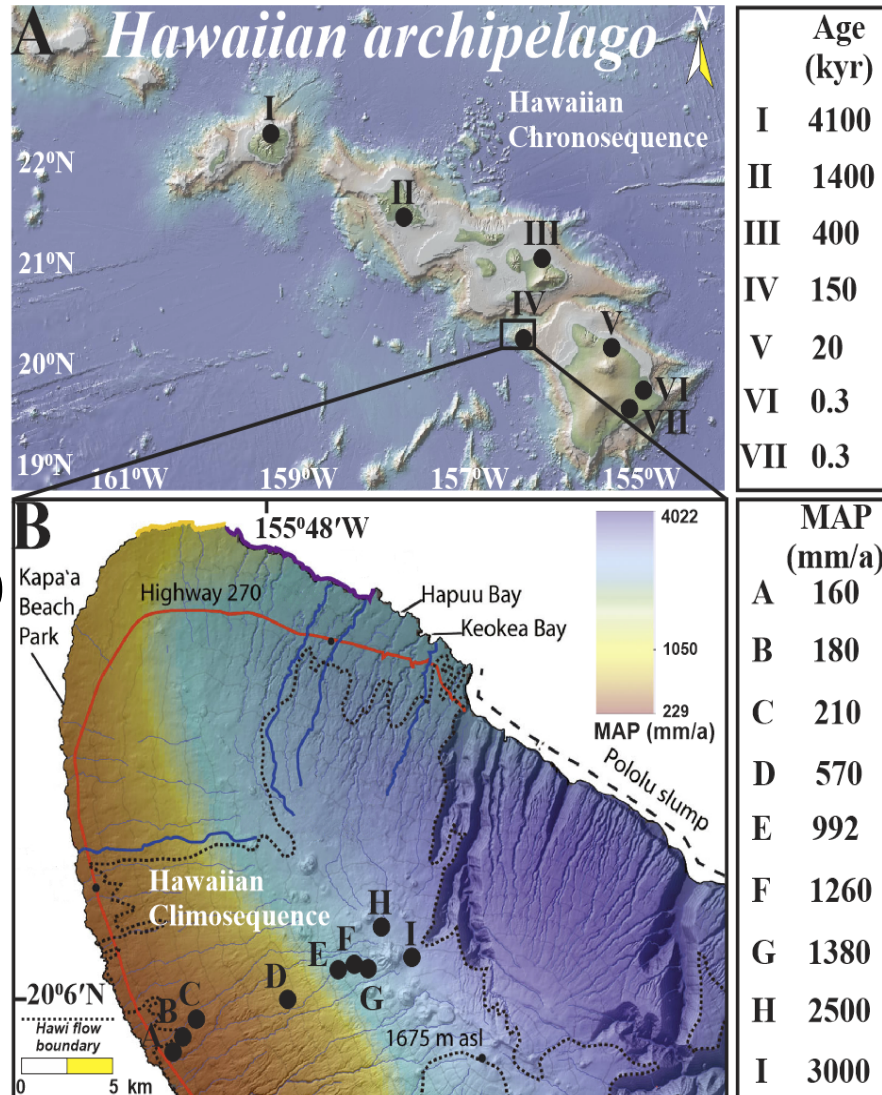
Hawaii Islands



Previous work on Li in Hawaiian regolith

MAP=2500 mm
(Age=0.3~4100 kyr)

Age=170 kyr
(MAP=160~3000 mm)

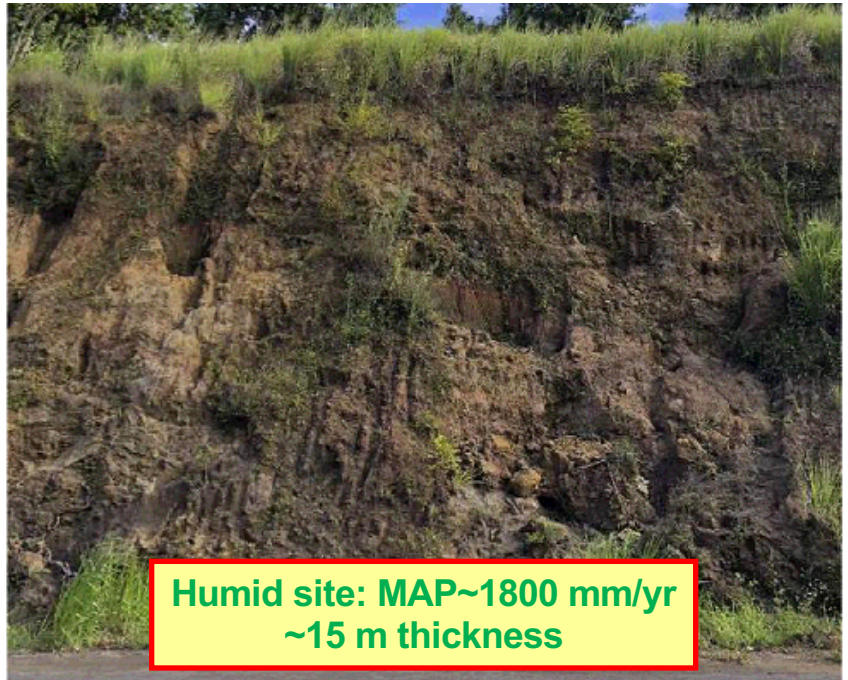
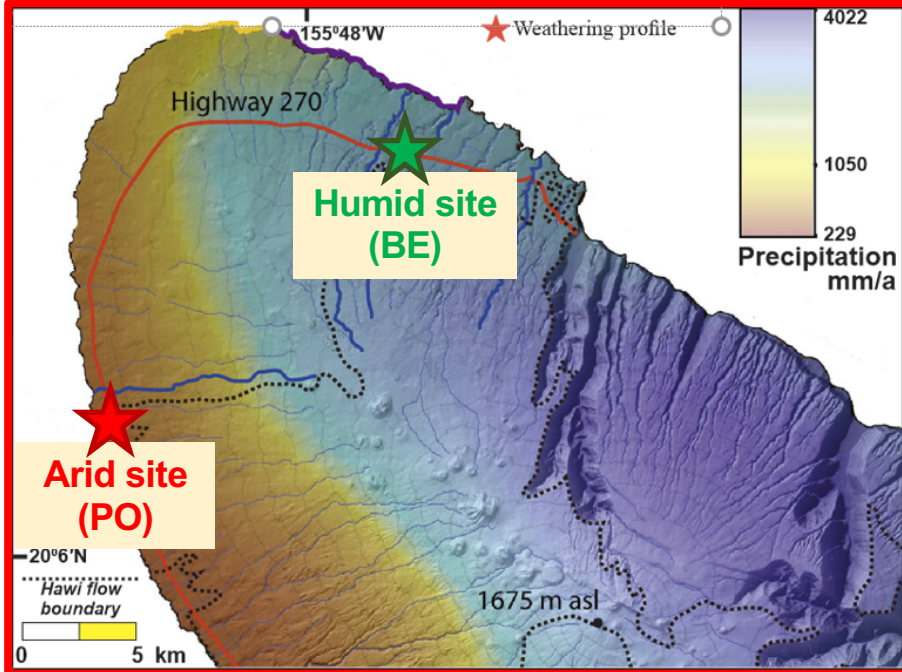
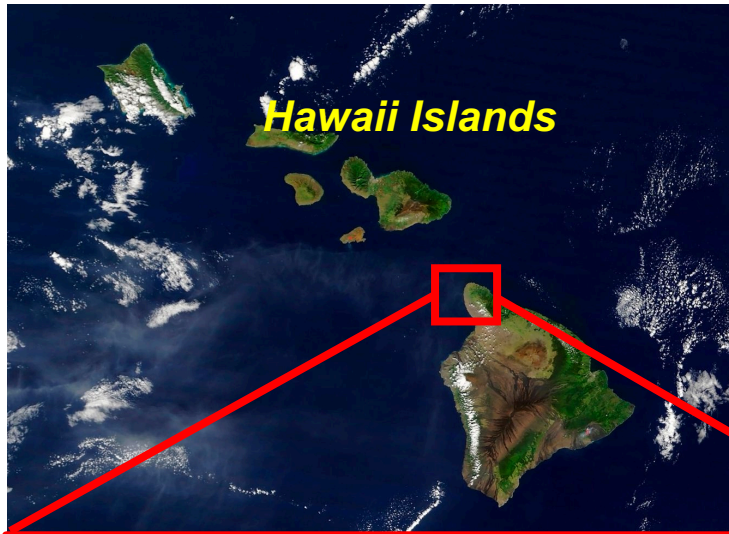


1. **Clay mineral formation** controls Li geochemistry.

2. **Eolian addition** affect Li geochemistry.

Huh et al., 2004 G^3
Ryu et al., 2014 GCA

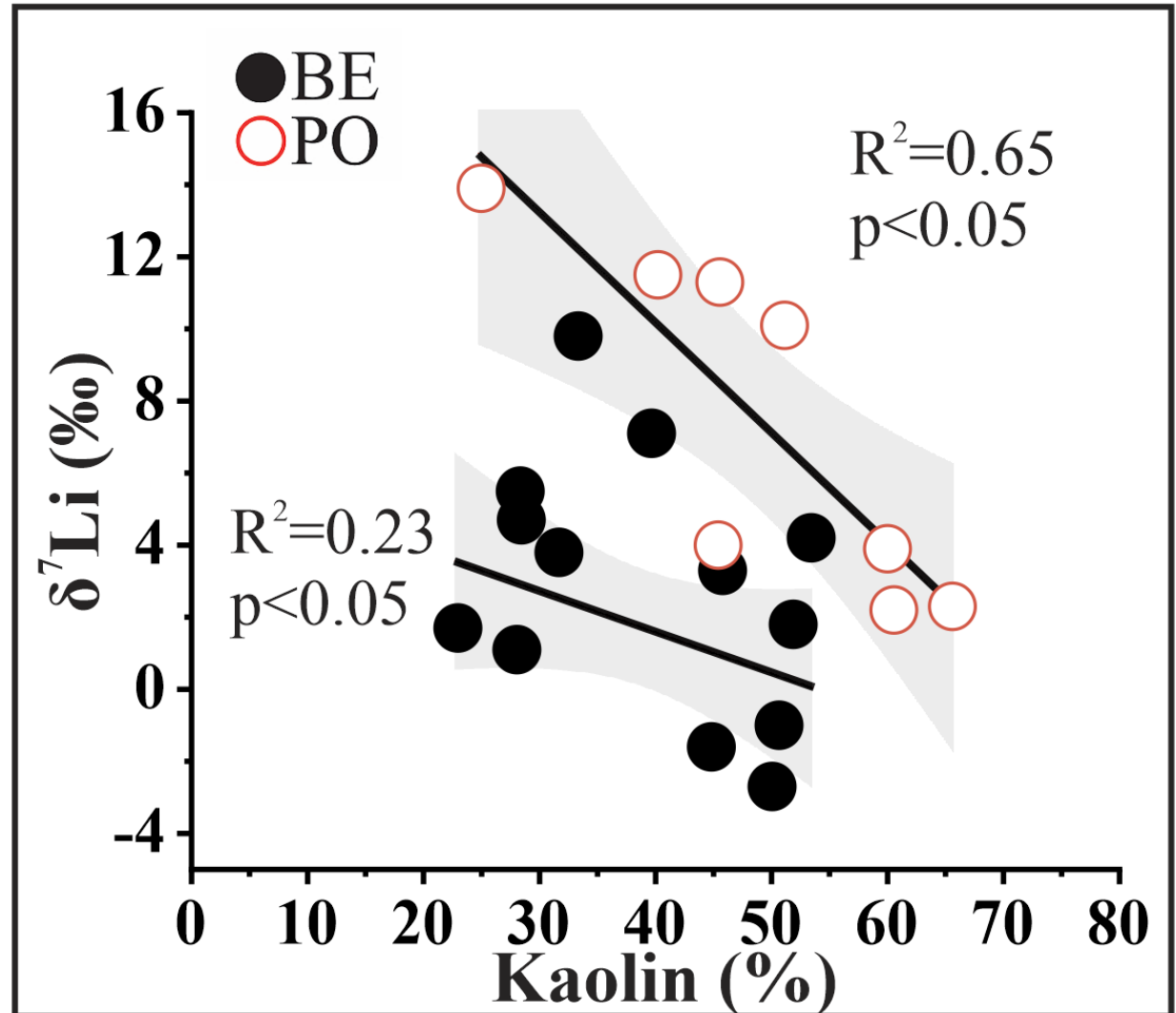
Regolith



Regolith Li isotopes

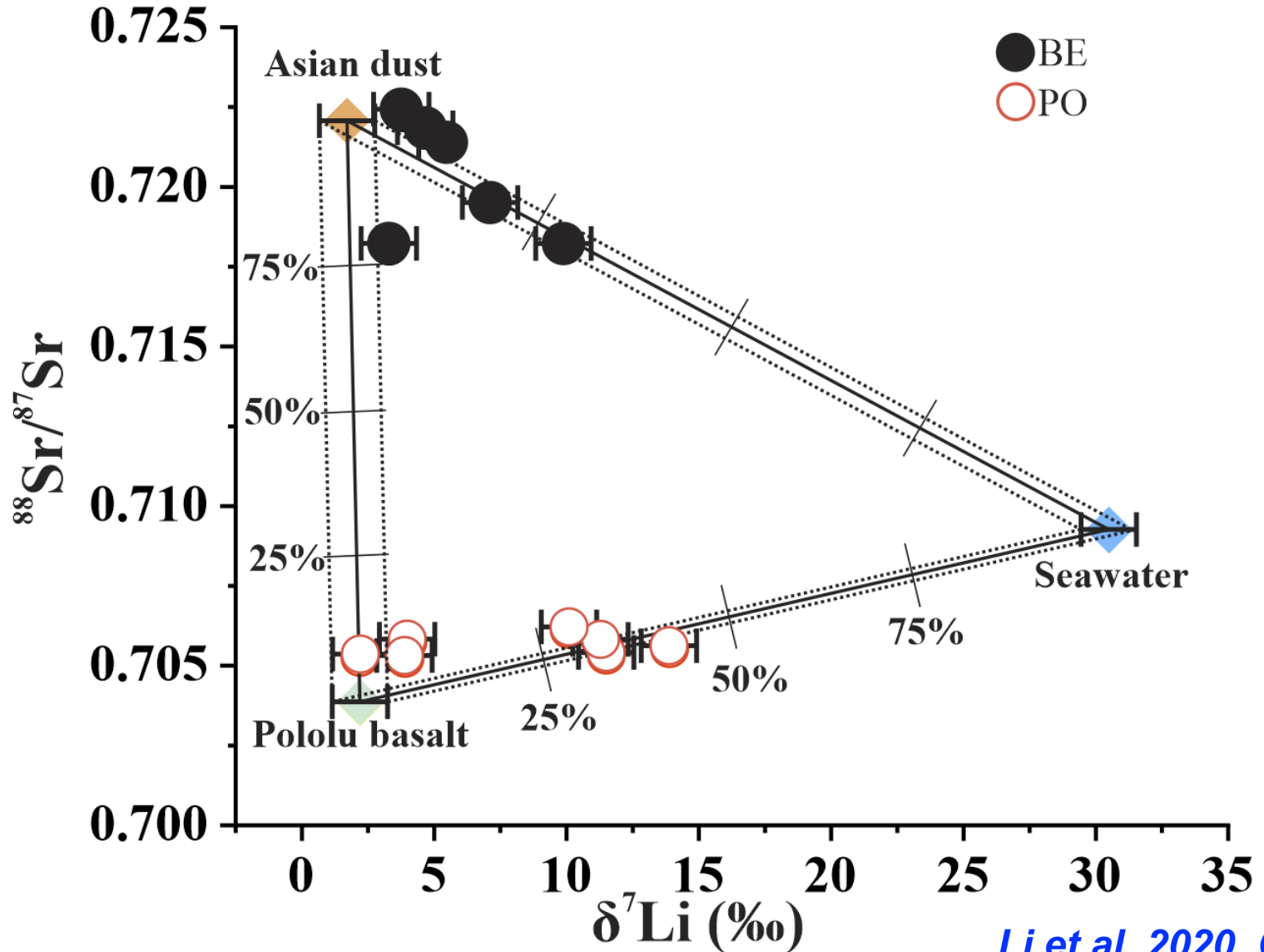


1. 2nd mineral formation



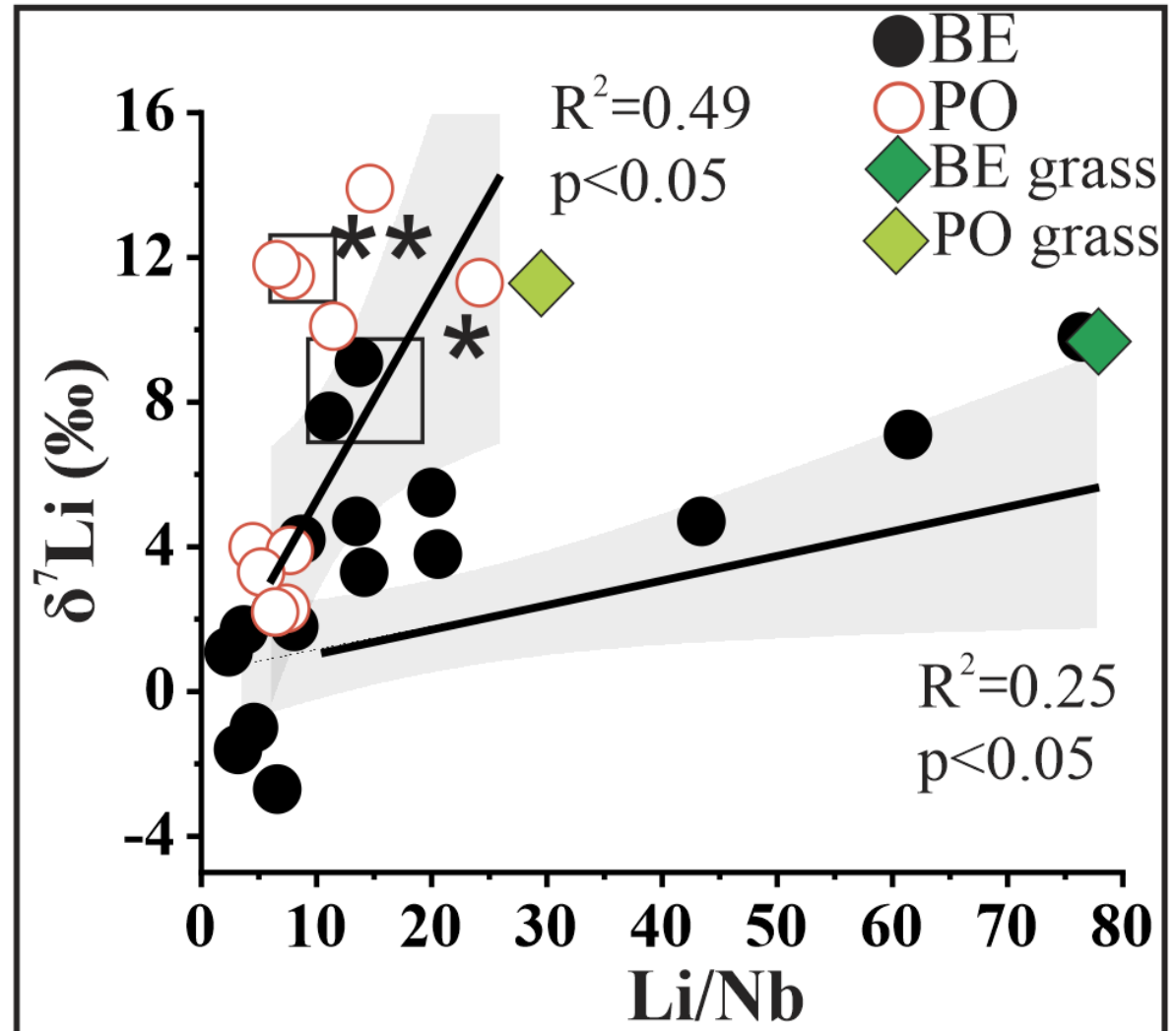
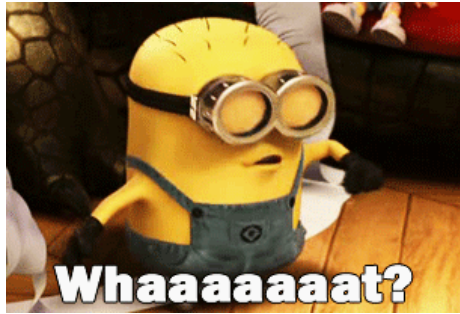
Regolith Li isotopes

2. Eolian inputs



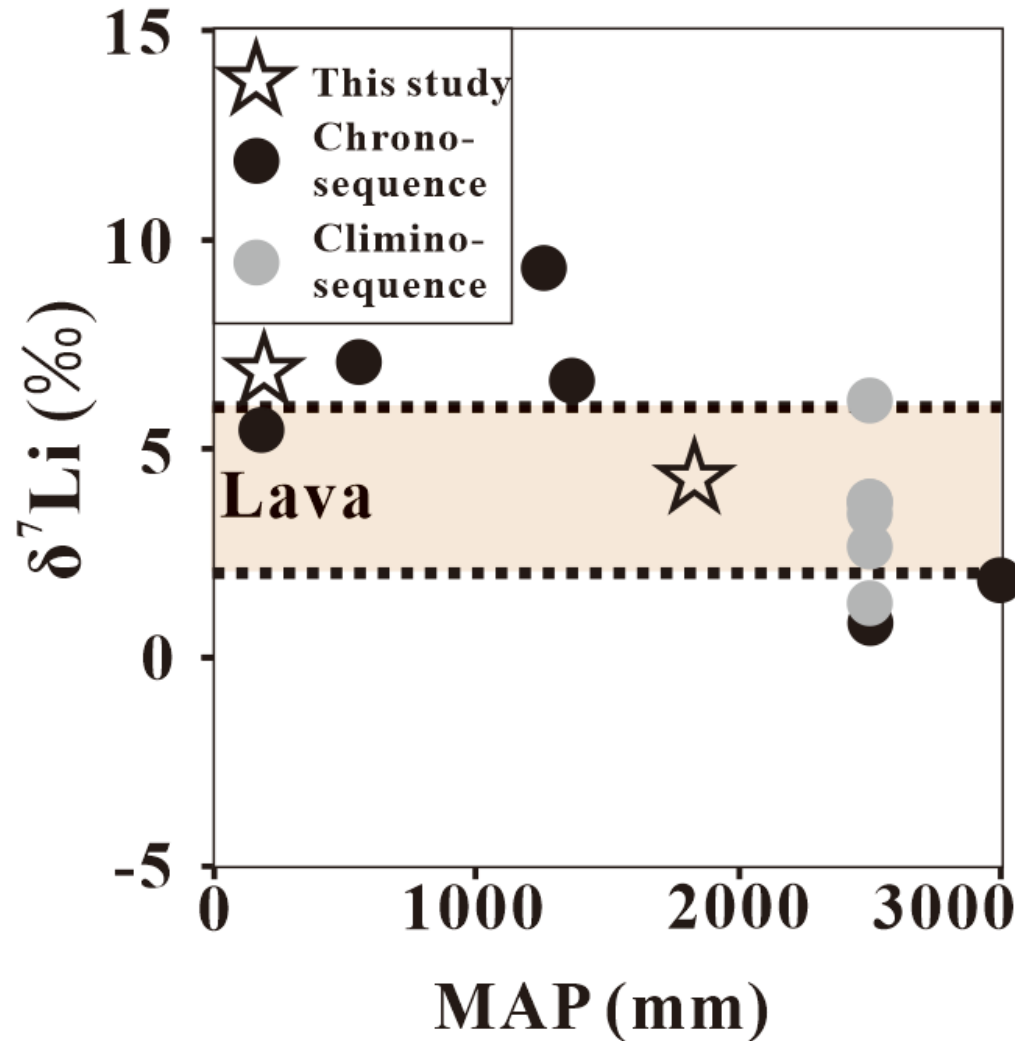
Regolith Li isotopes

3. Biological control



Hawaii Li summary

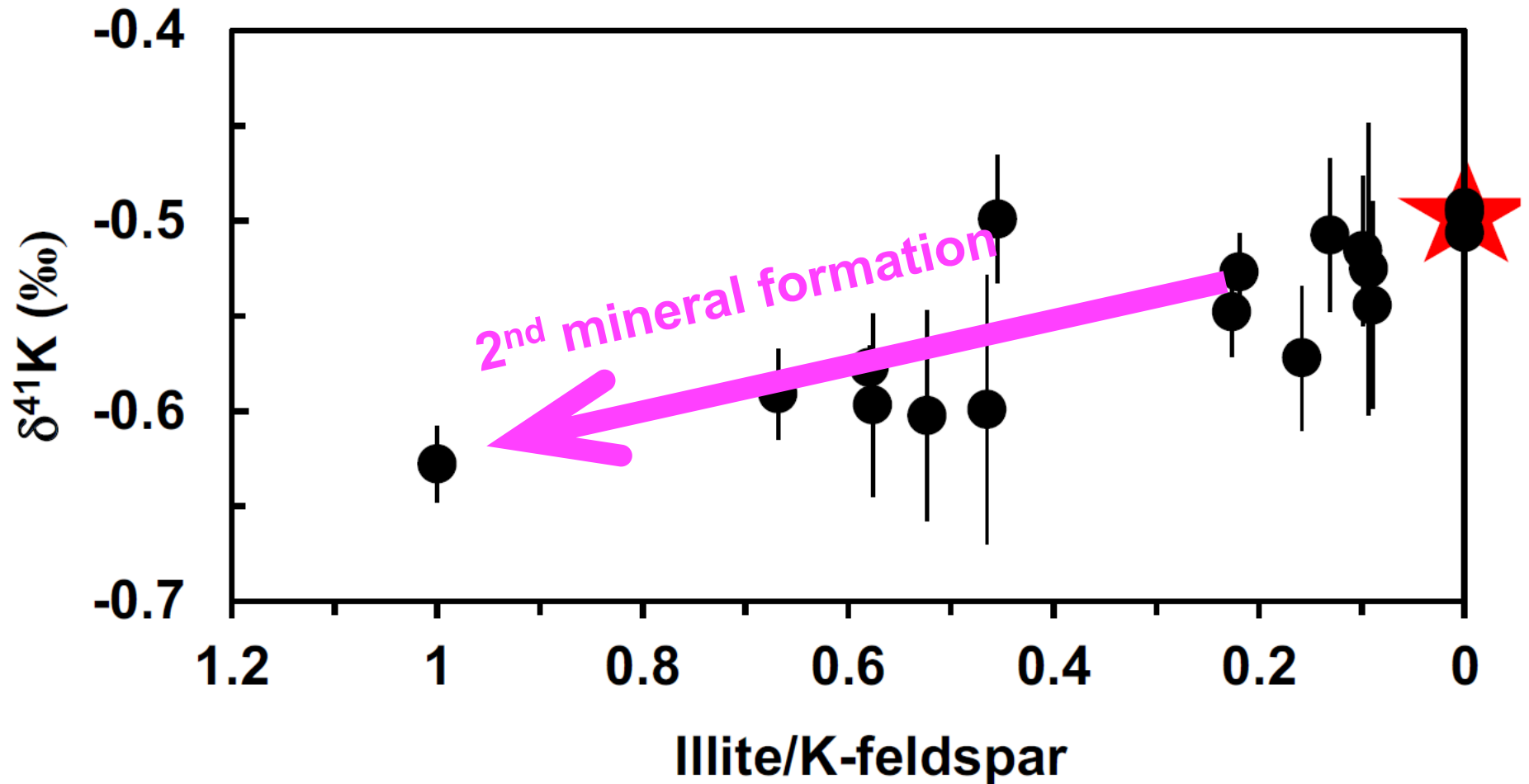
– Climate/Weathering intensity



Huh et al., 2004 G³; Ryu et al., 2014 GCA; Li et al., 2020 GCA

Regolith

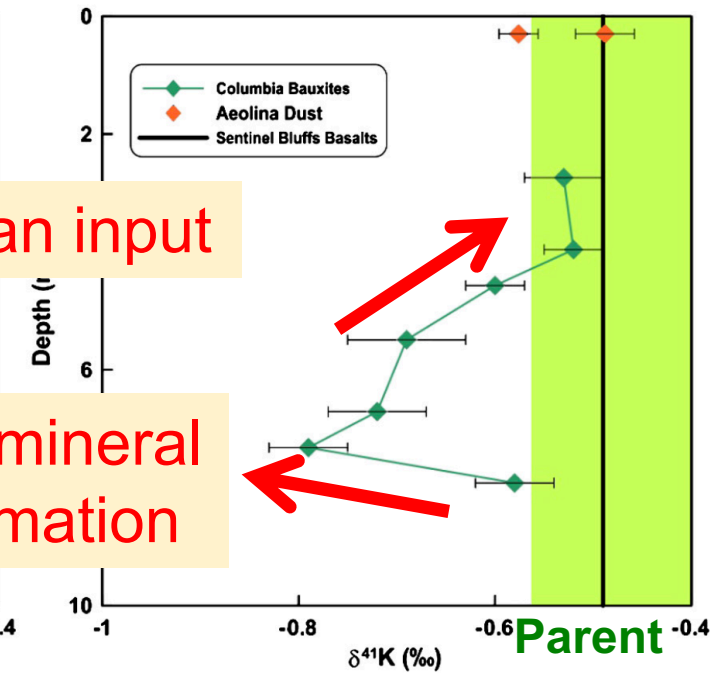
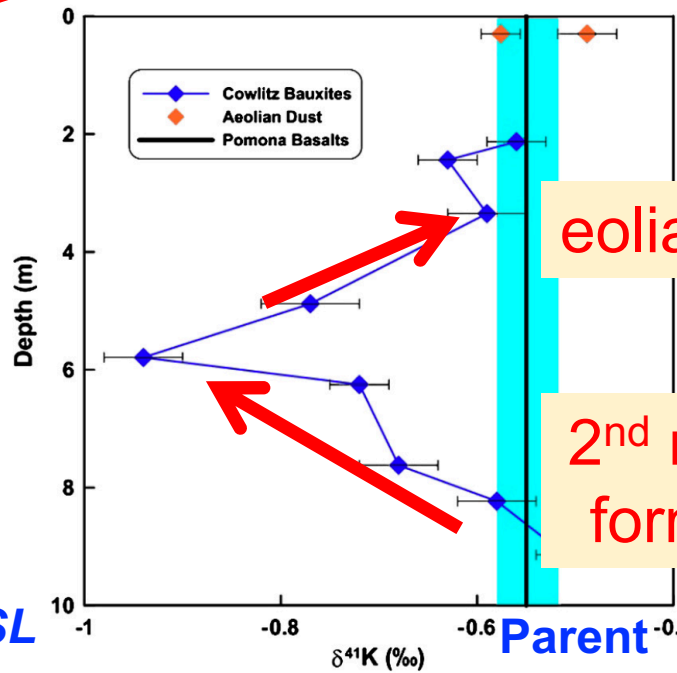
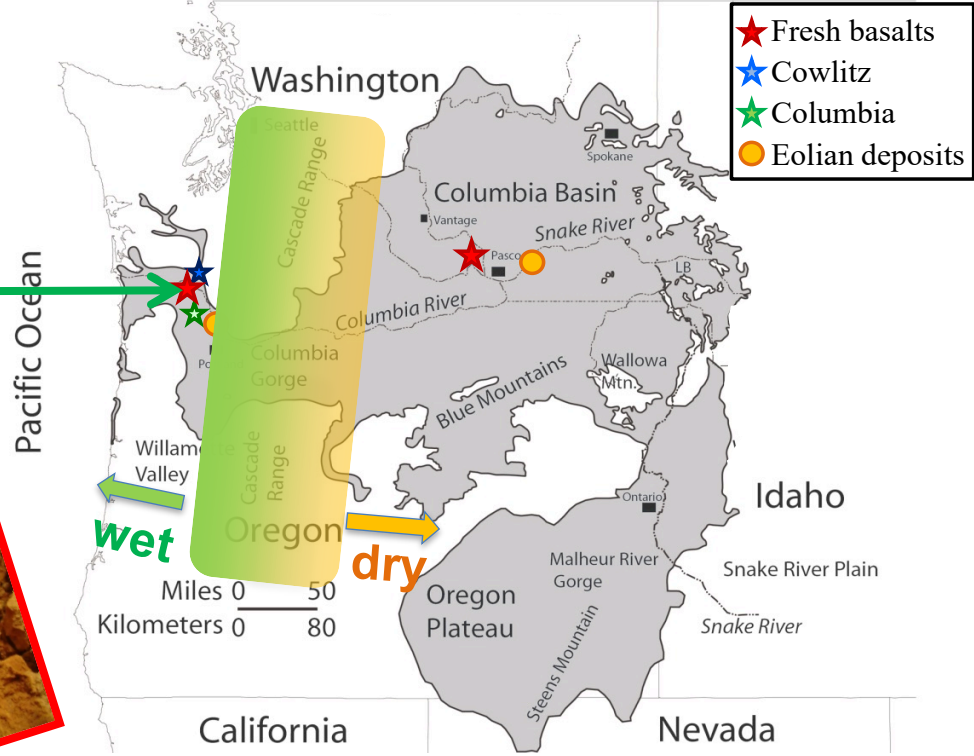
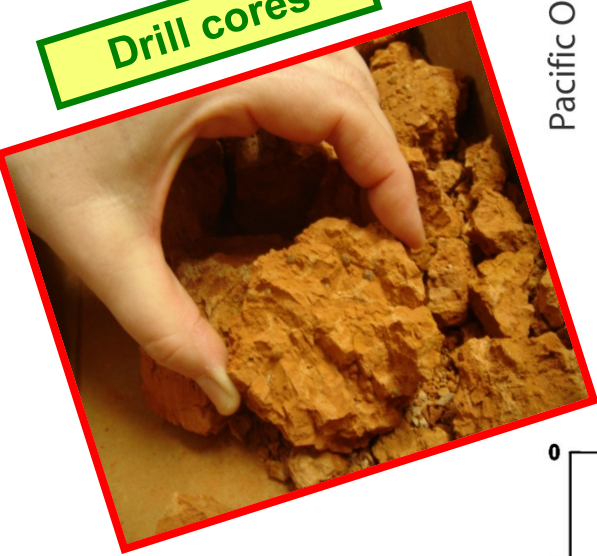
K isotopes



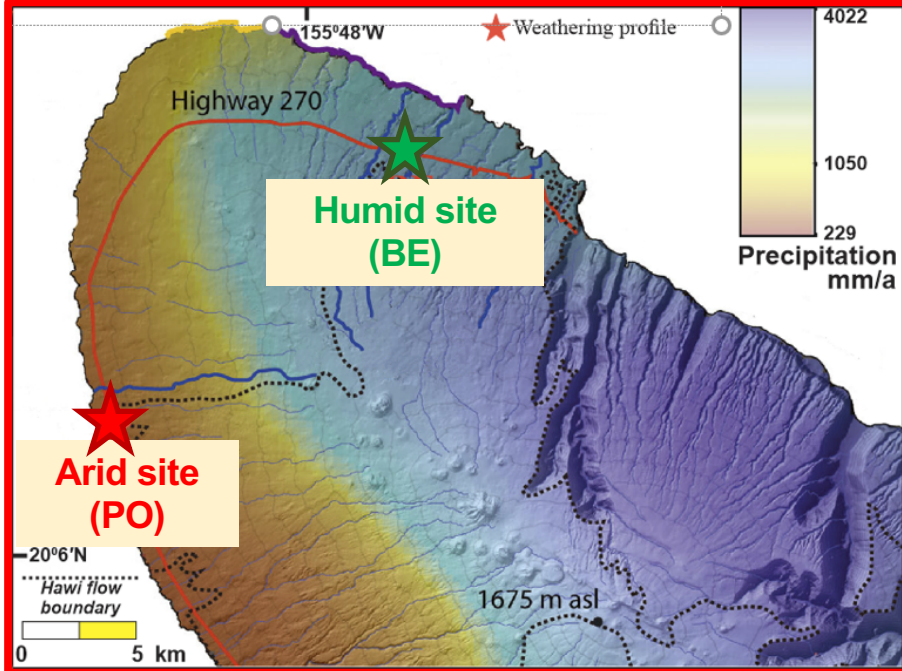
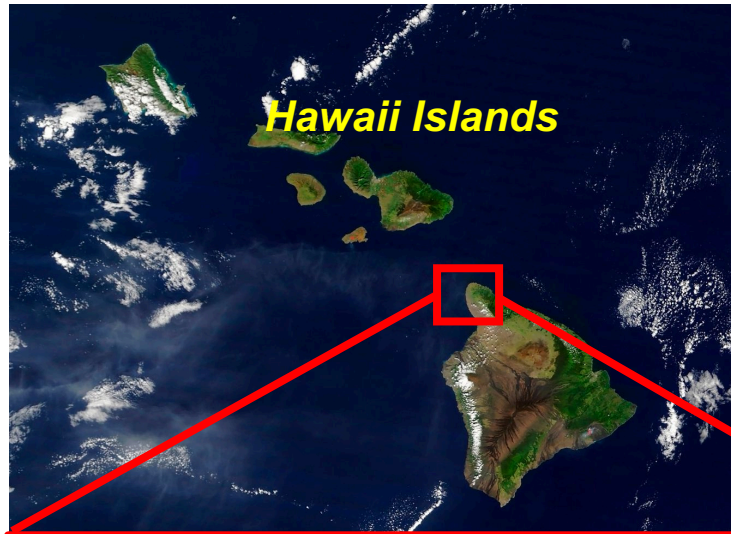
Teng et al. 2020, GCA

Regolith K isotopes

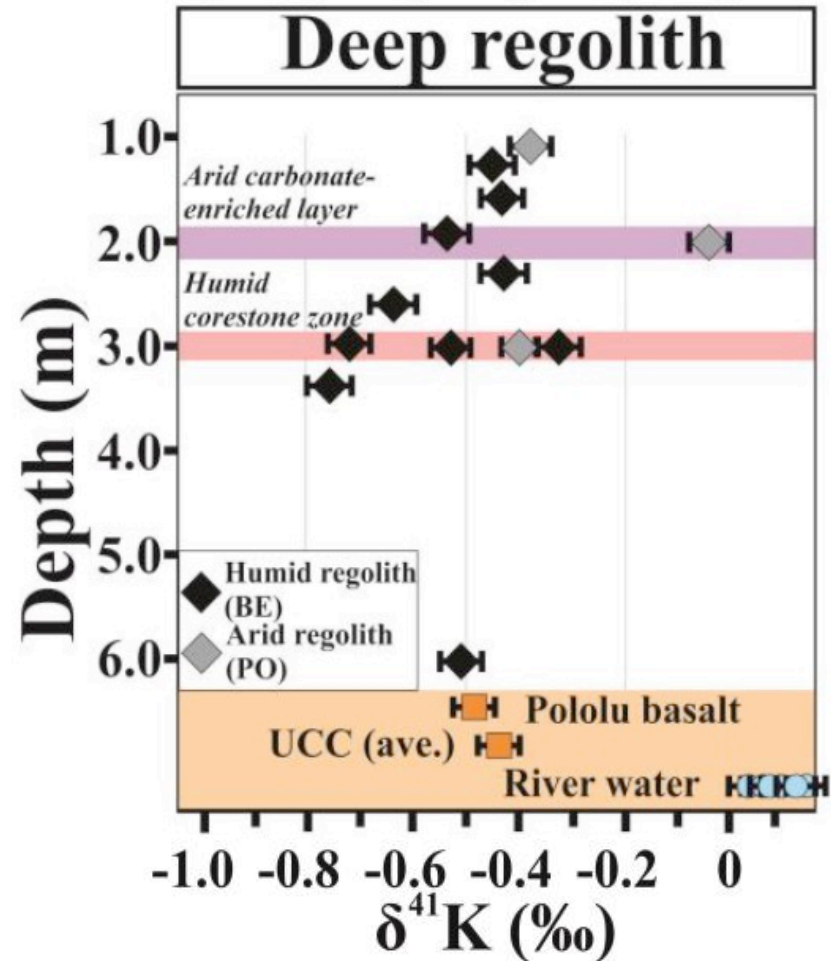
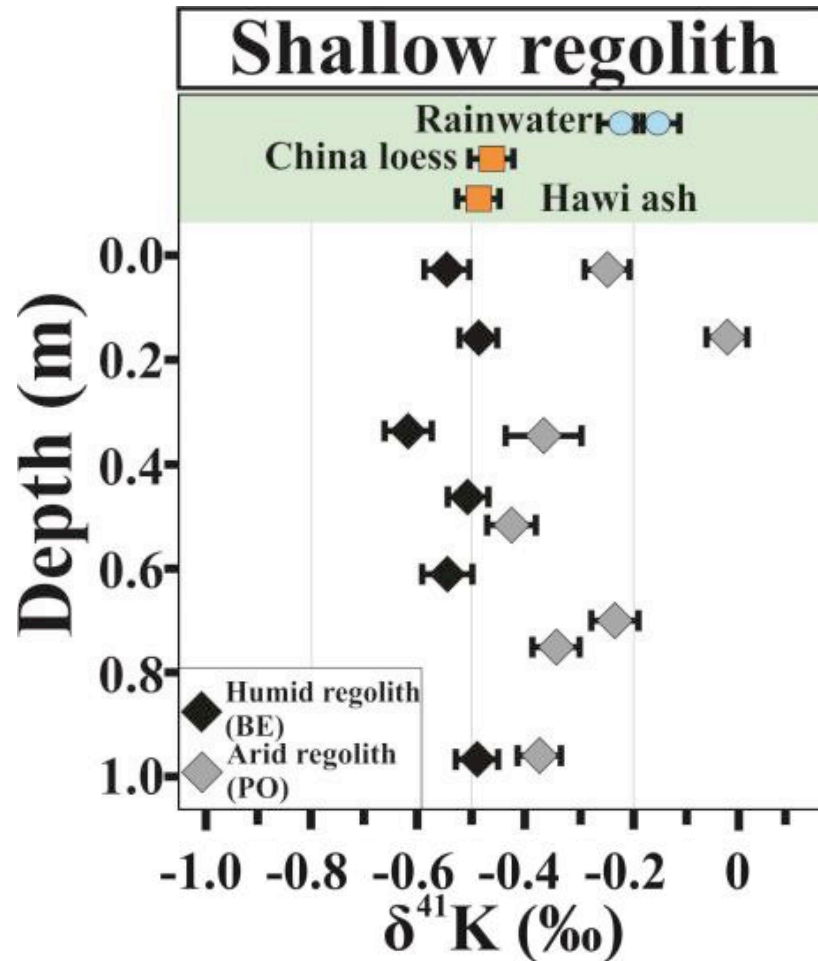
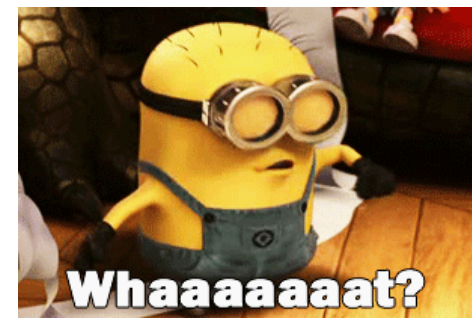
Drill cores



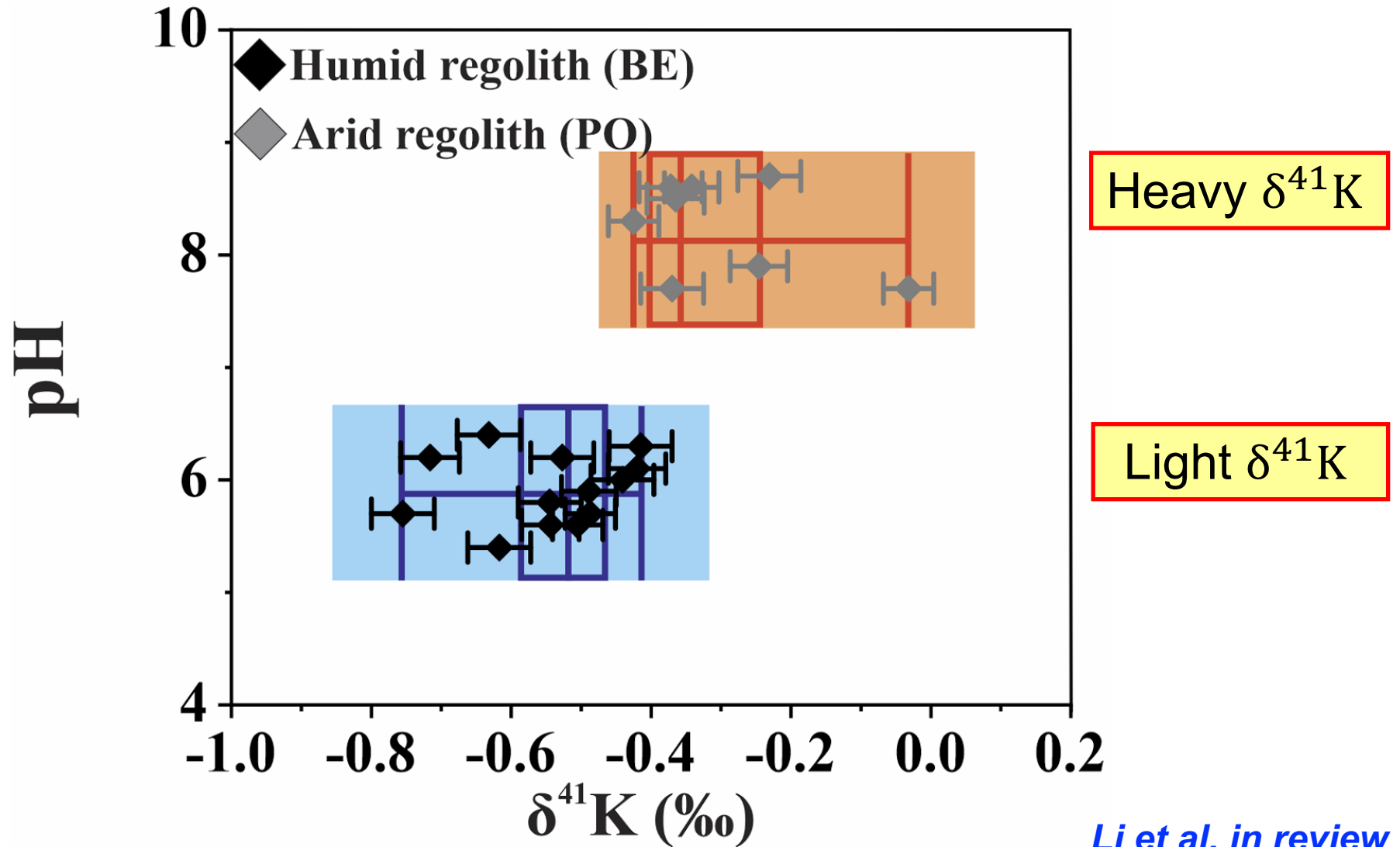
Regolith



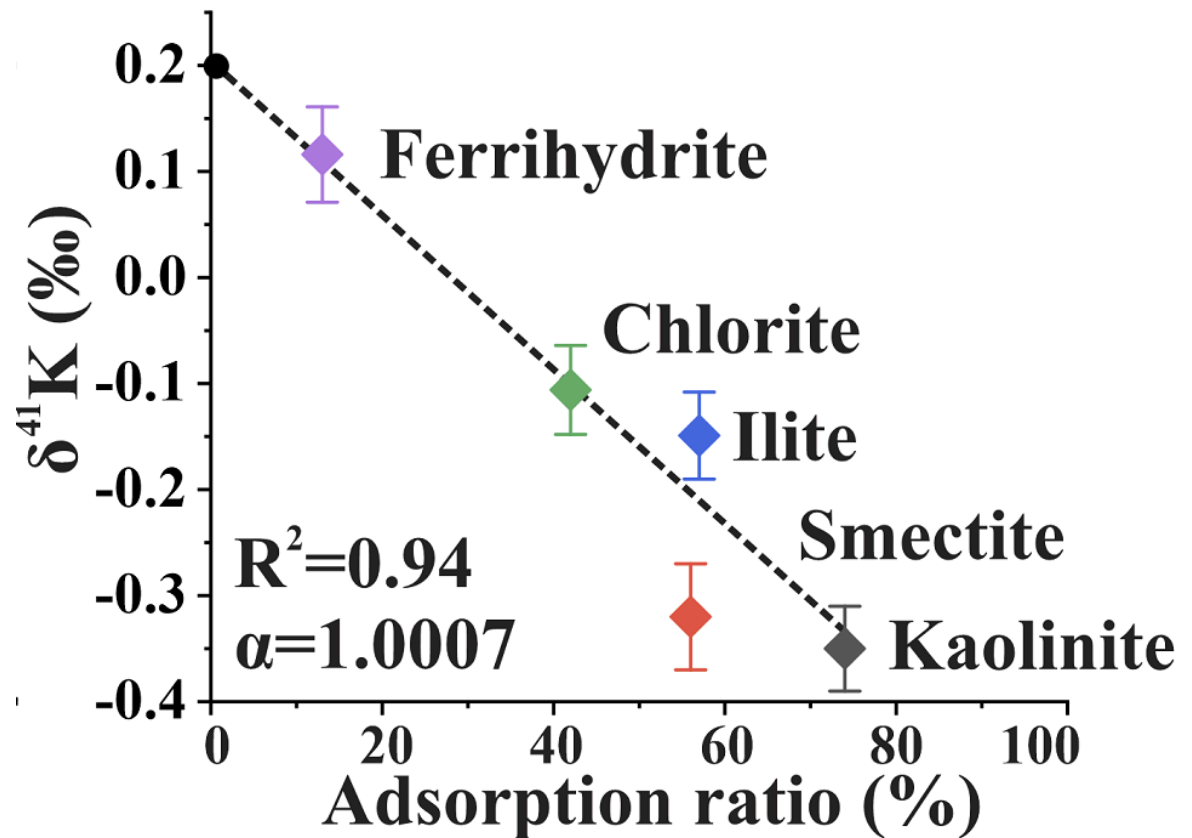
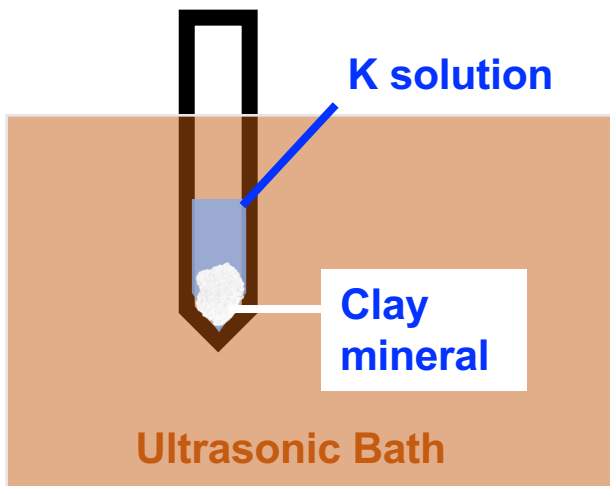
Regolith K isotopes



Strong climate (pH) control

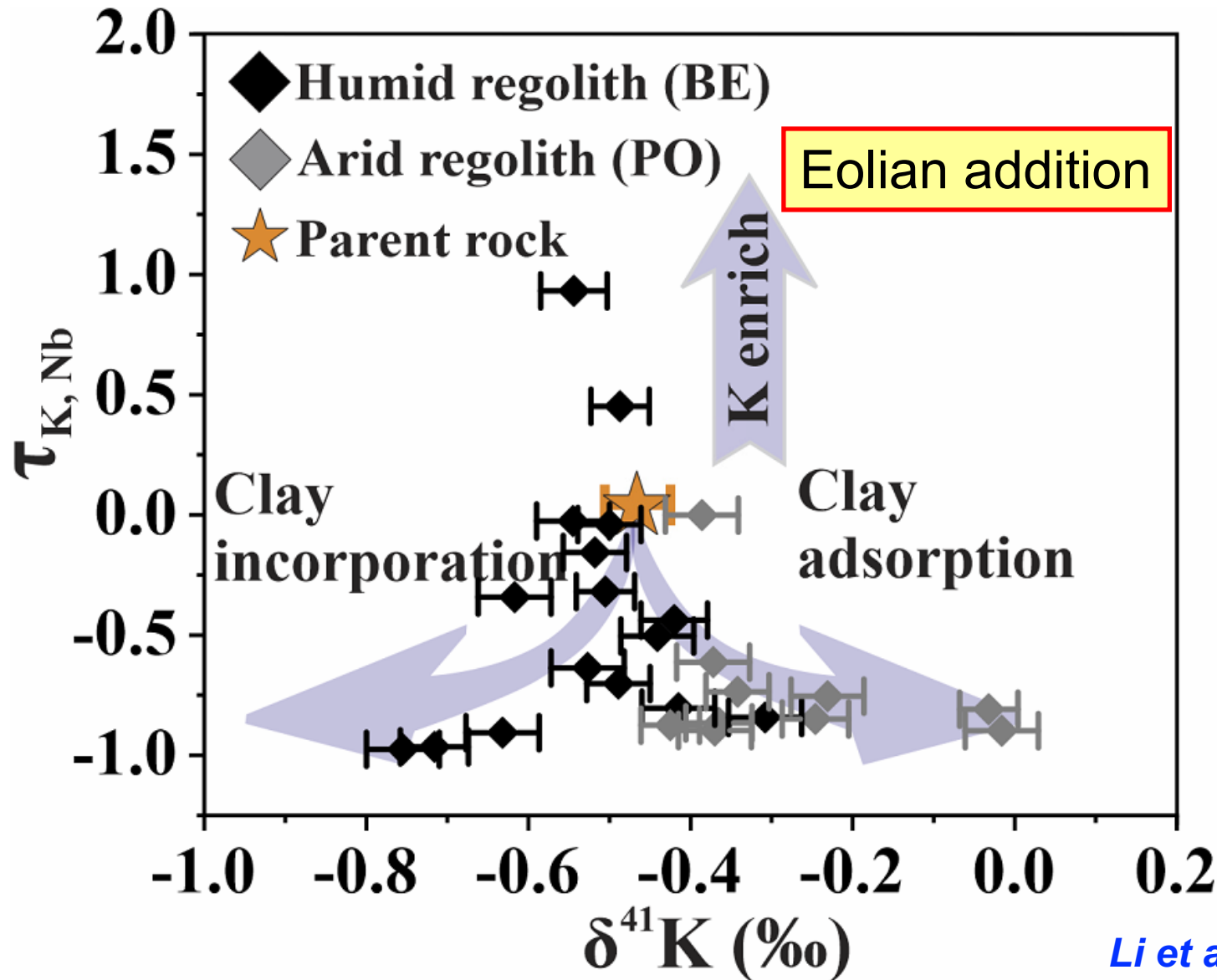


Adsorption experiment evidence



Li et al. in review

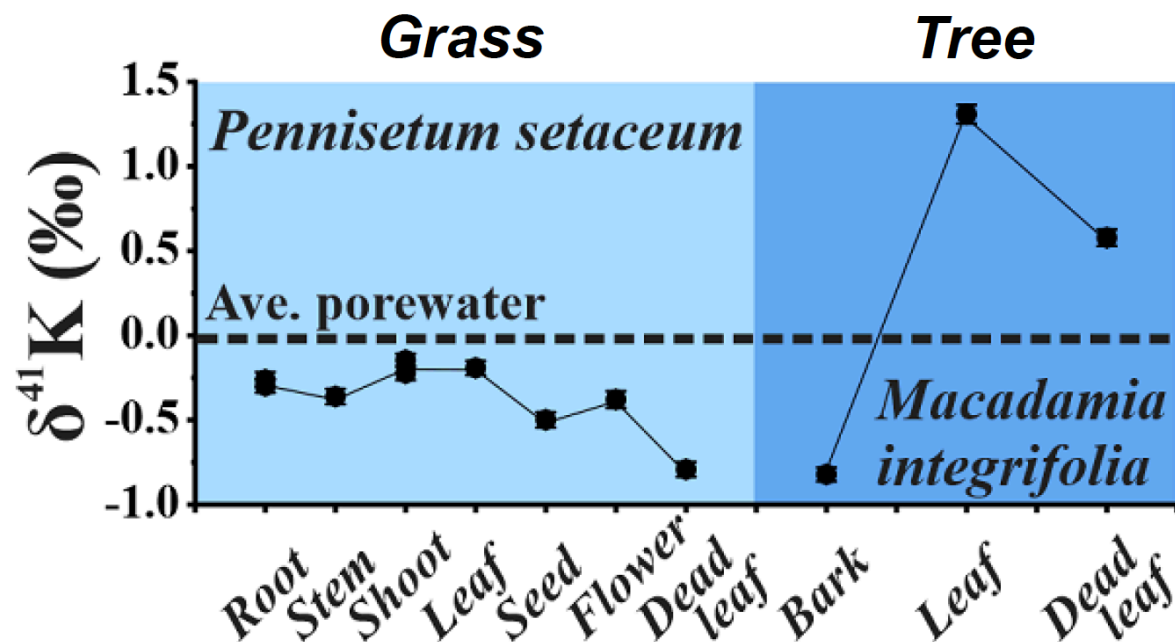
K isotope fractionation mechanisms



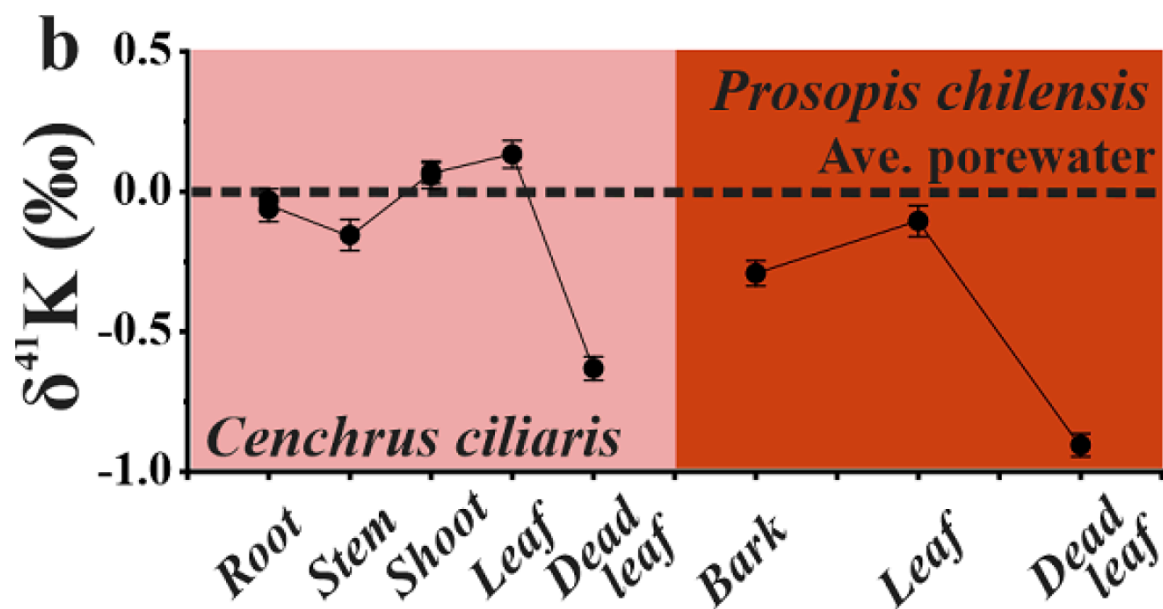
Biological control



Humid



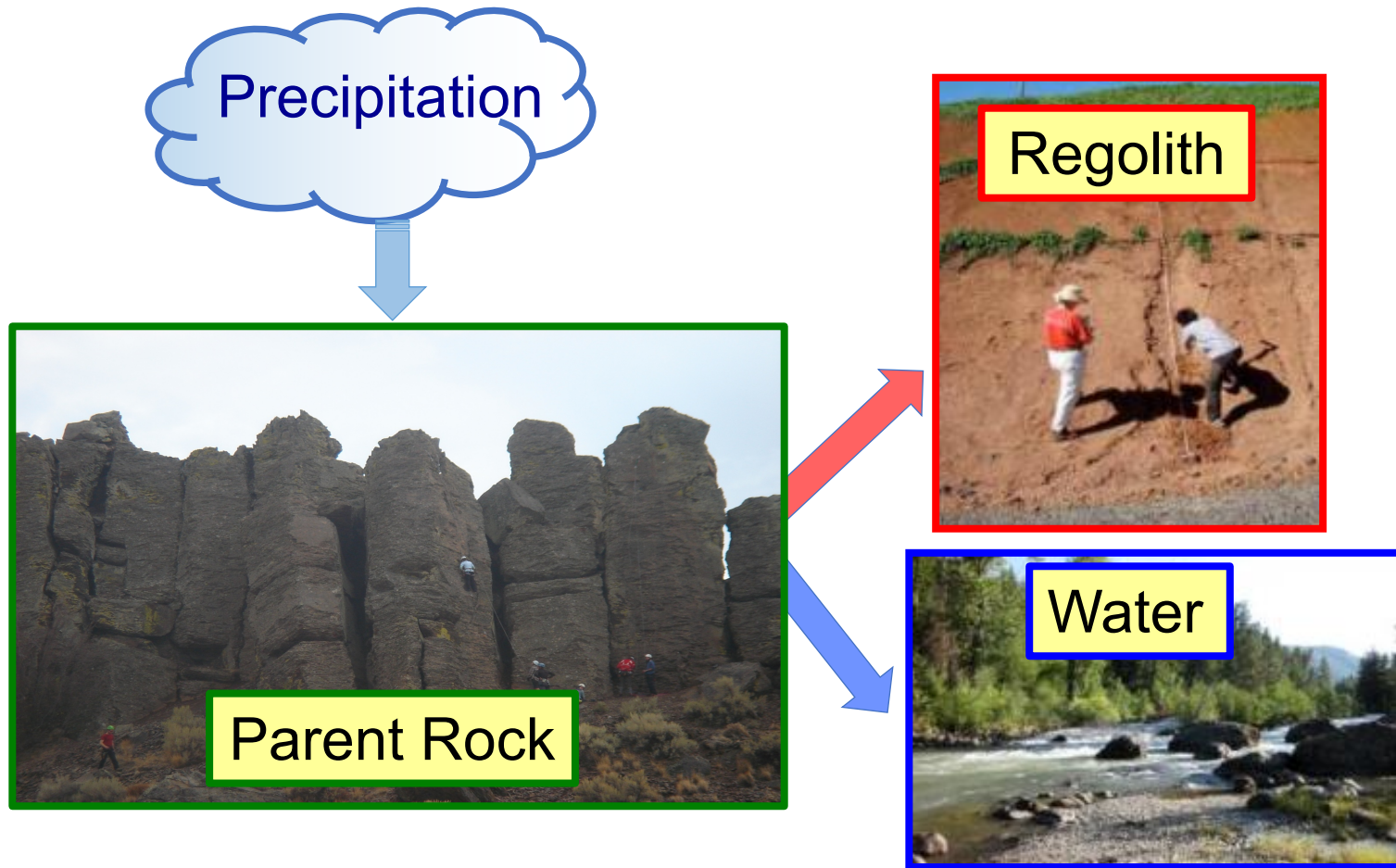
Arid

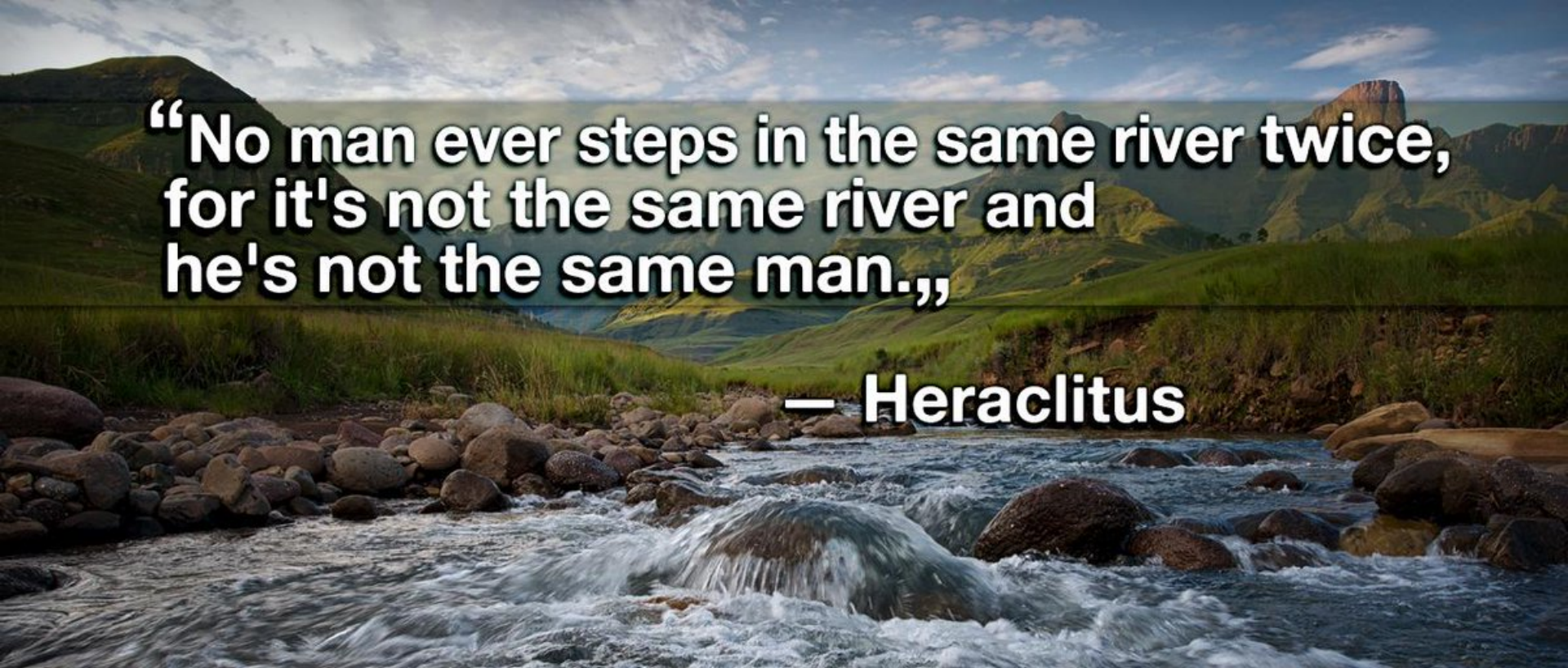


Regolith Summary

- Regolith Li and K isotope signals reflects an interplay of 2nd mineral formation, eolian addition, and biological controls.
- Li and K isotope fractionations during weathering highly depend on climate conditions.

Weathering process





**“No man ever steps in the same river twice,
for it's not the same river and
he's not the same man.,,**

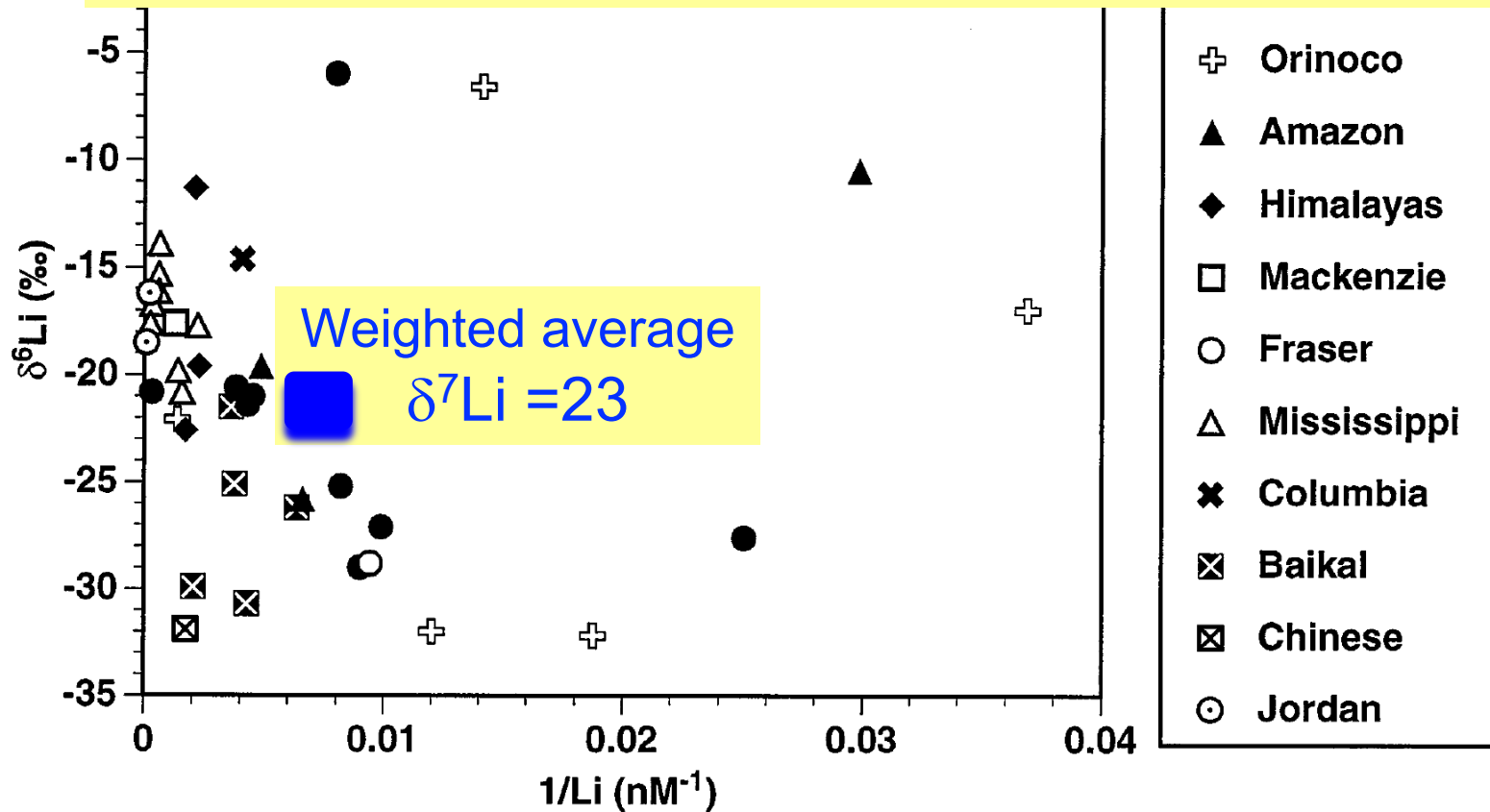
— Heraclitus

Why study (river) water?

Water provides **instantaneous knowledge** during weathering.

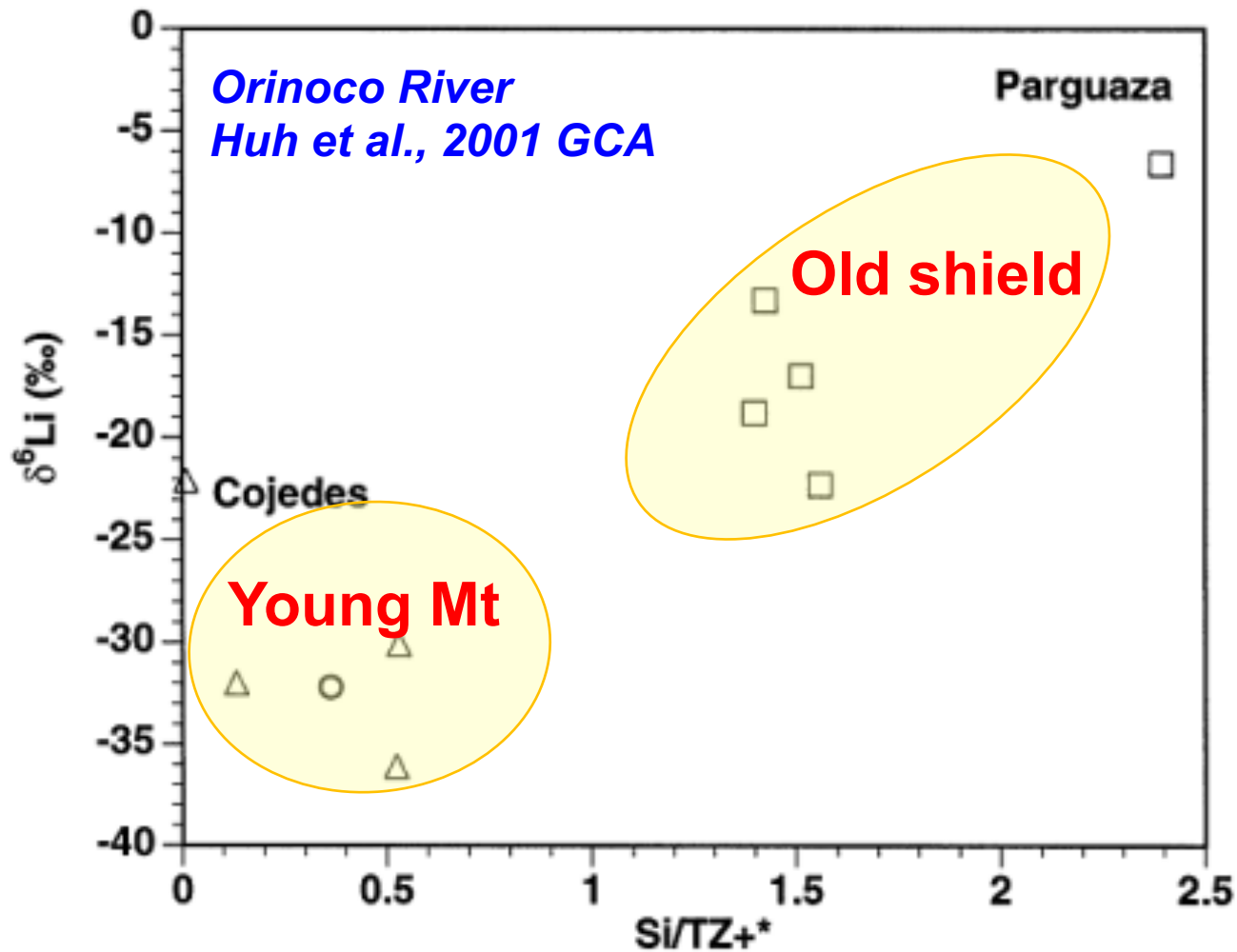
Water – World rivers

Why is $\delta^7\text{Li}$ in rivers so variable?



Huh et al., 1998, EPSL

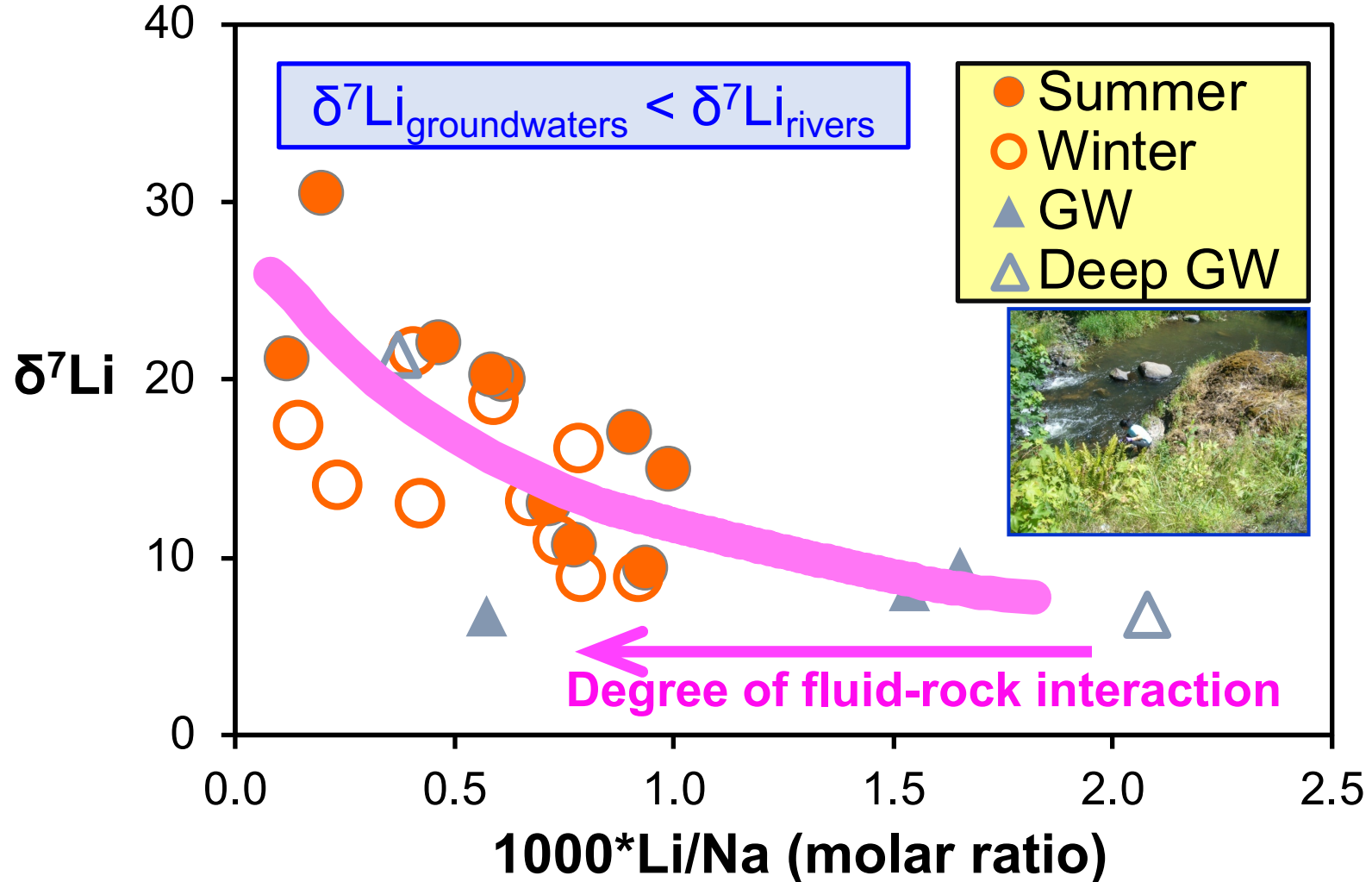
What controls $\delta^7\text{Li}$ in rivers?



$\delta^7\text{Li}$ depends on degree of weathering/weathering intensity

$\delta^7\text{Li}$ as a weathering intensity tracer?

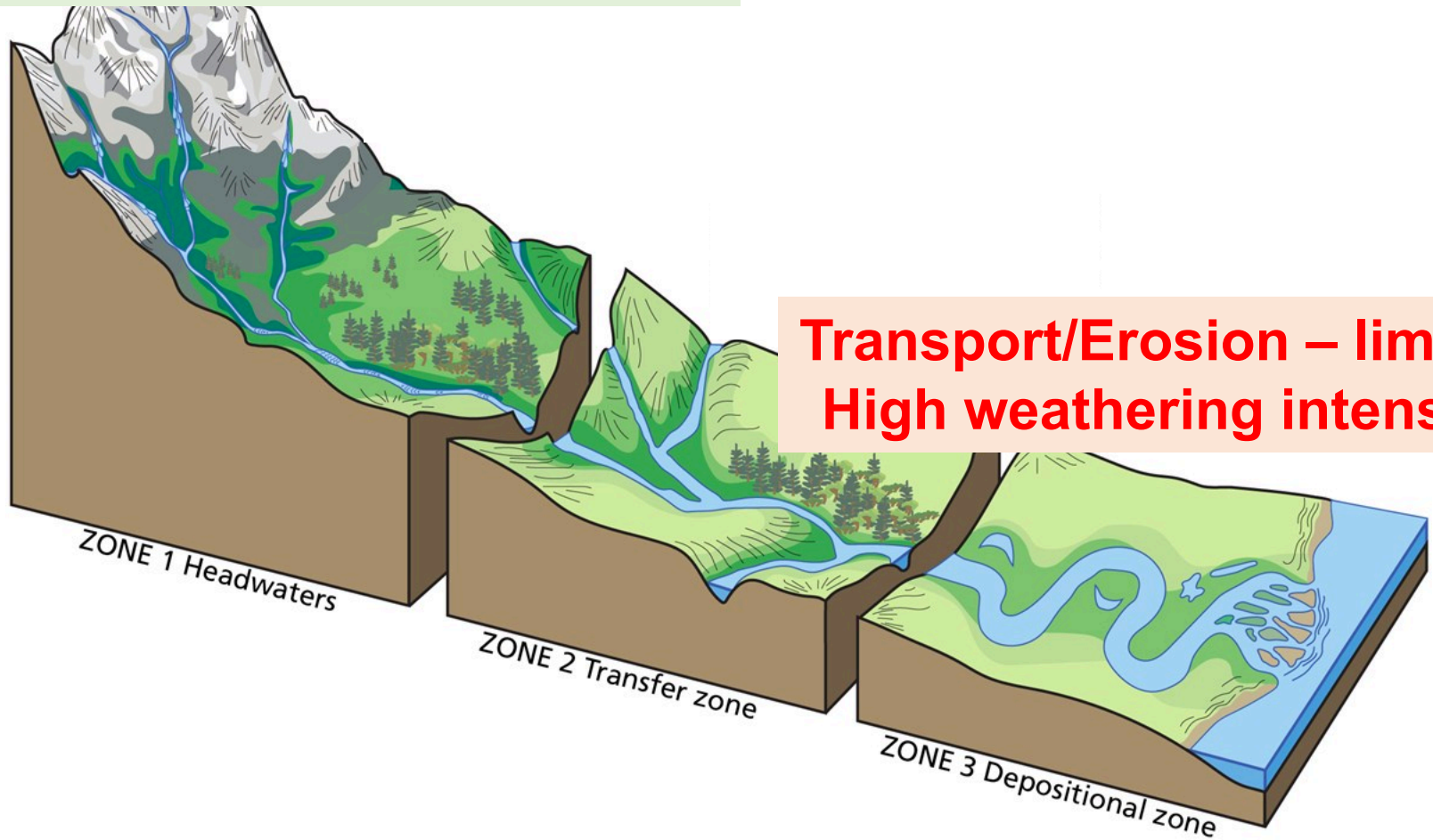
– Small streams



What controls $\delta^7\text{Li}$ in rivers?

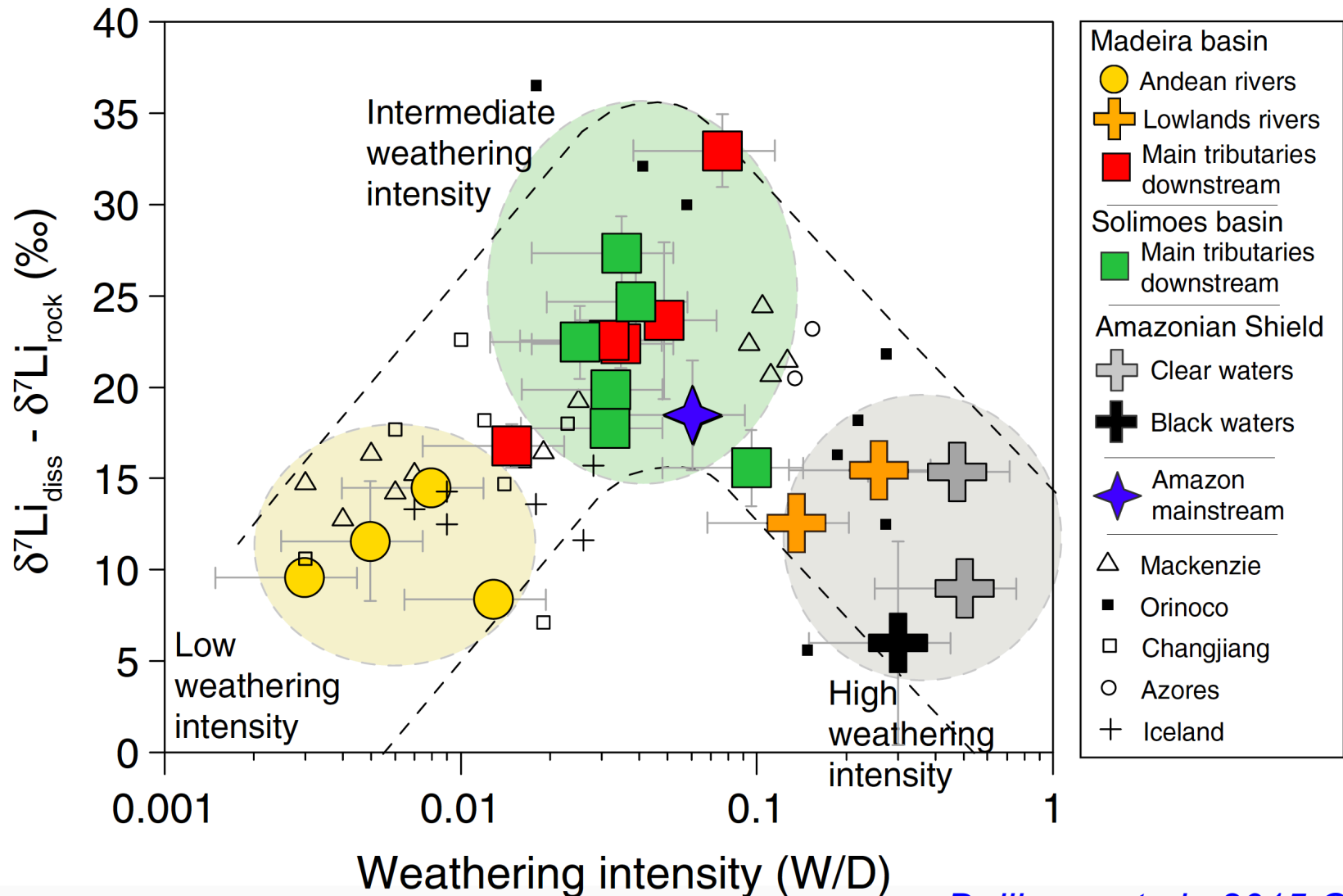
– Large rivers

Reaction/Weathering – limited
Low weathering intensity

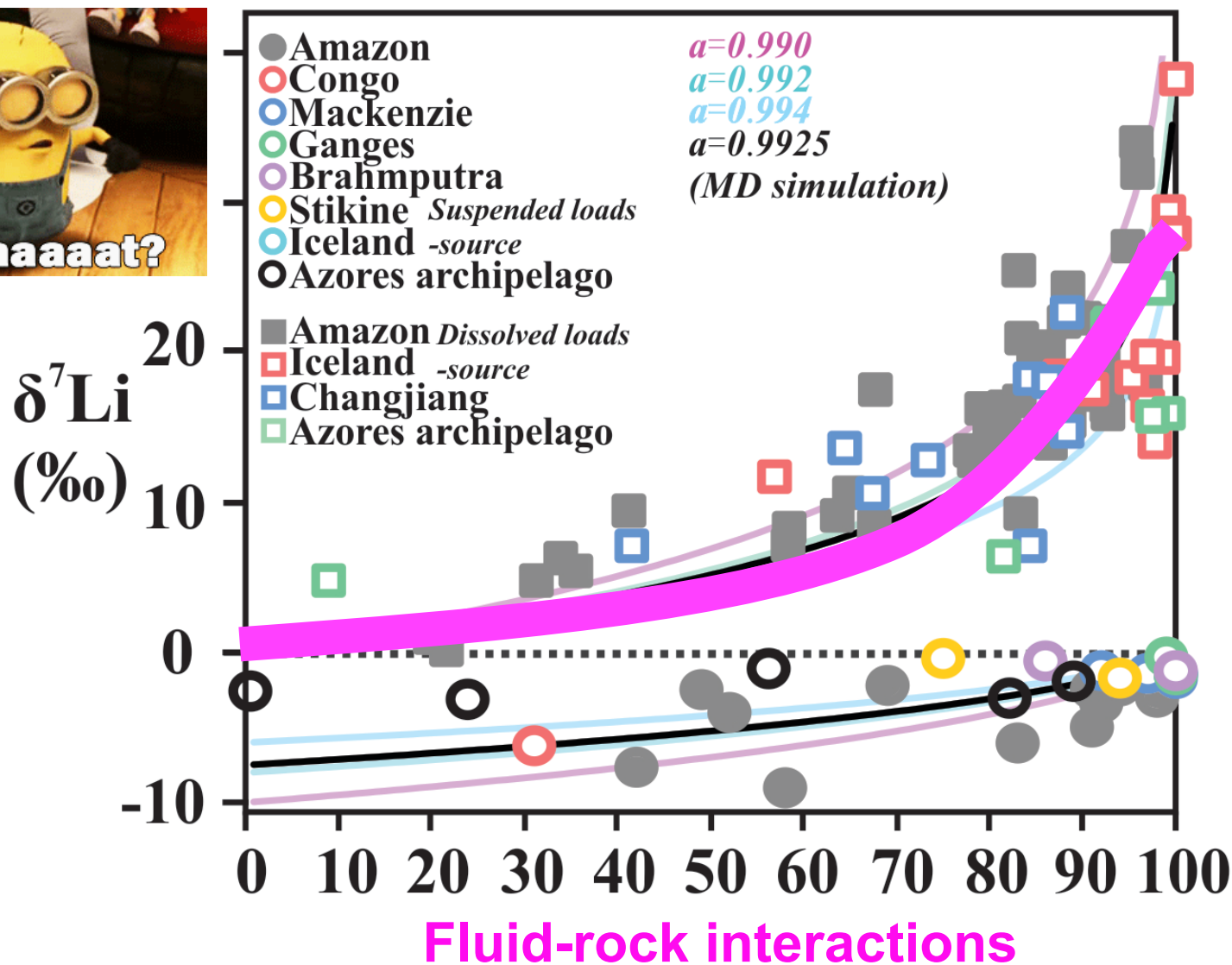
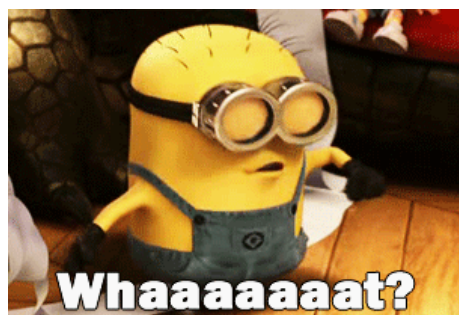


$\delta^7\text{Li}$ as a weathering intensity tracer?

– Large rivers



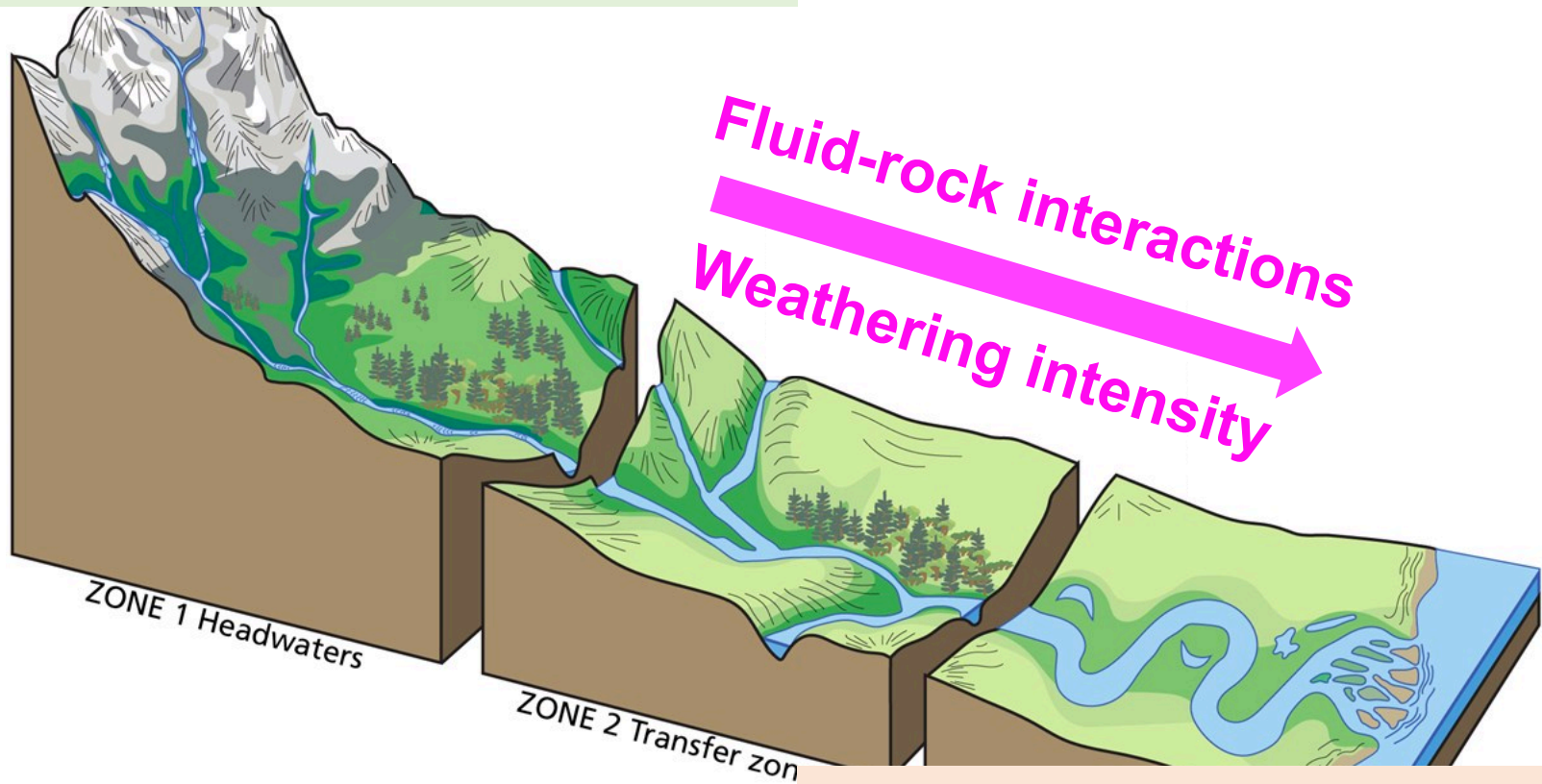
$\delta^7\text{Li}$ as a weathering intensity tracer?



Summary:

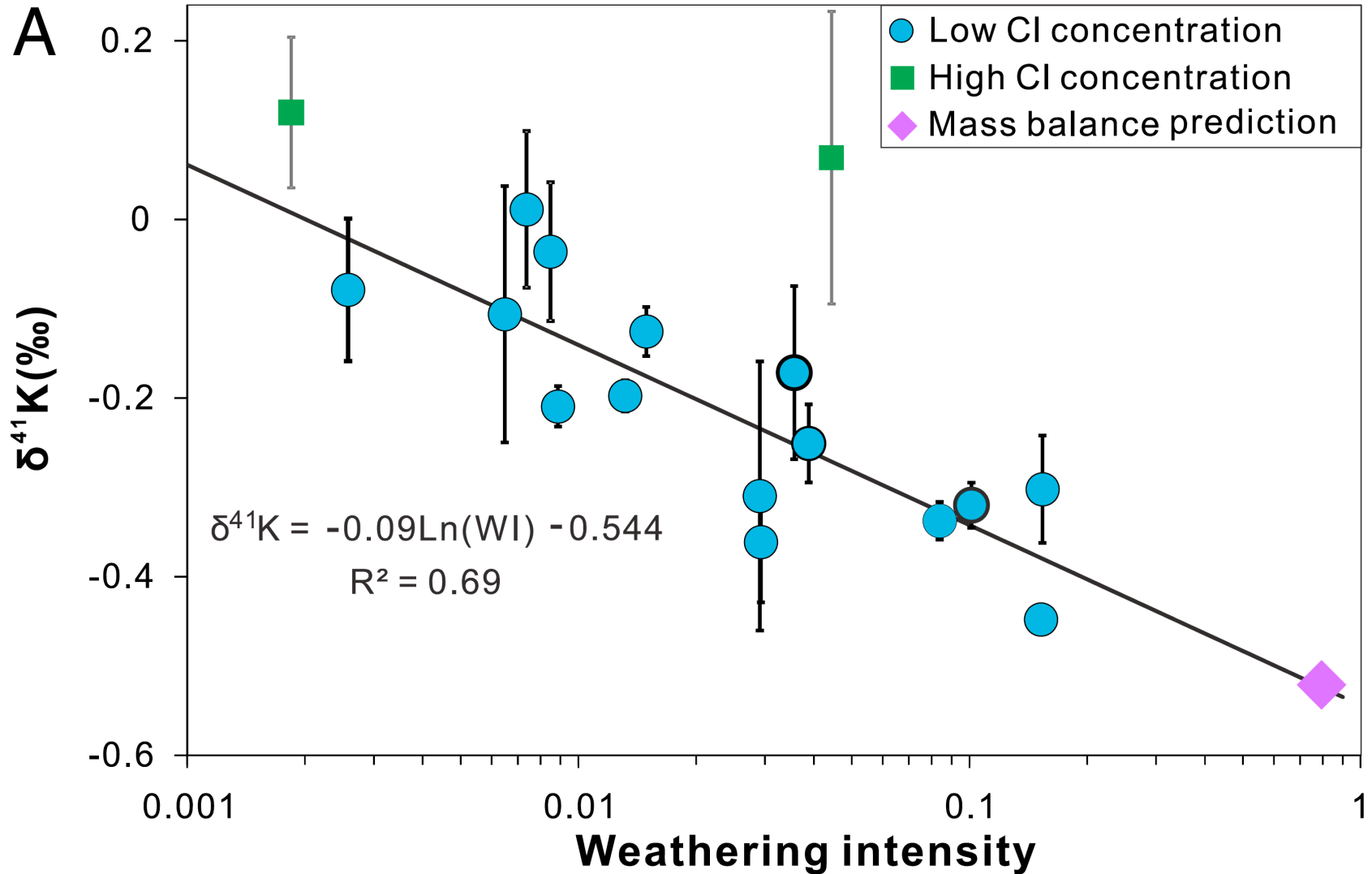
What controls $\delta^7\text{Li}$ in rivers?

Reaction/Weathering – limited
Low WI – Low $\delta^7\text{Li}$, high [Li]

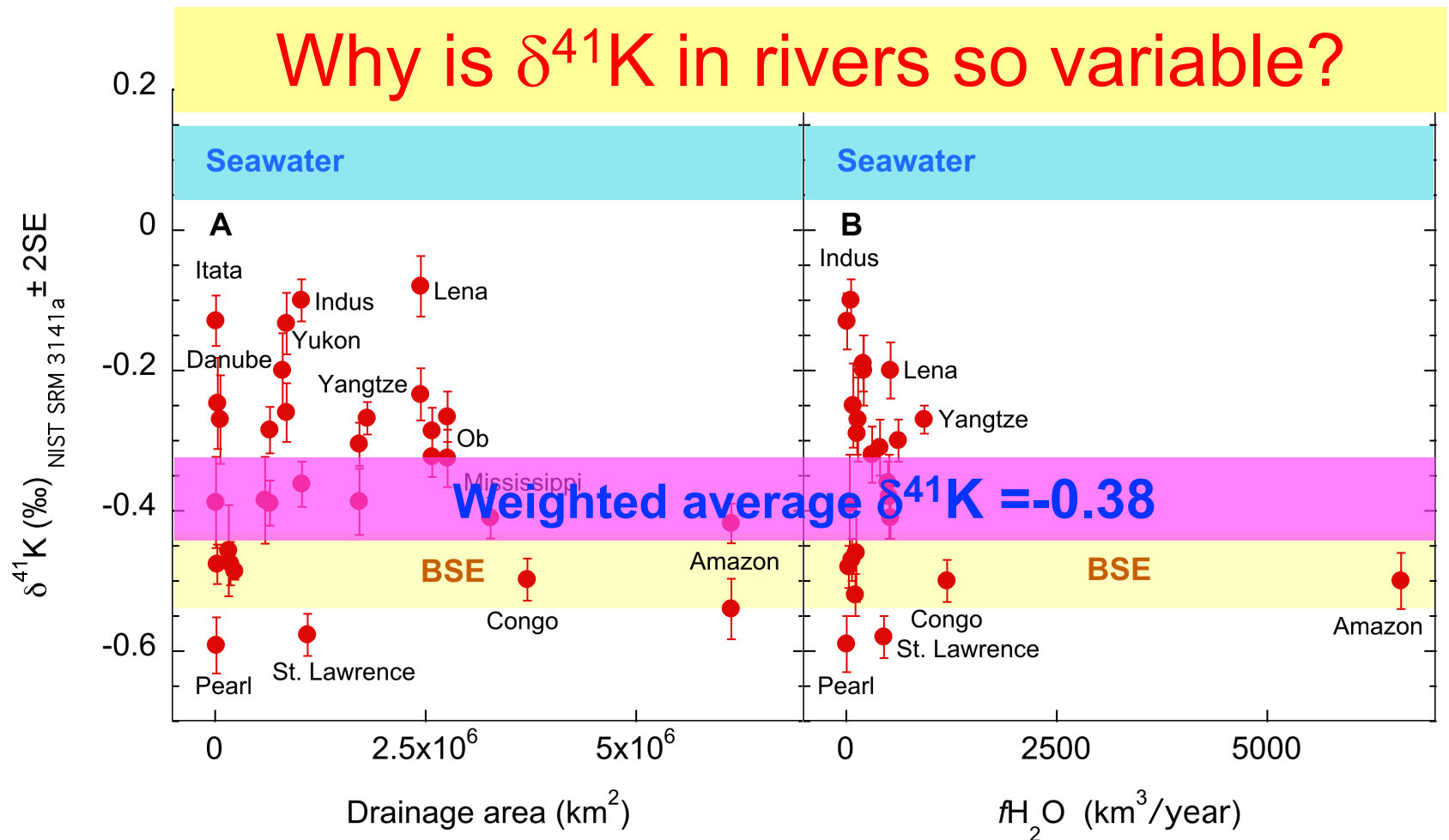


Transport/Erosion – limited
High WI – High $\delta^7\text{Li}$, low [Li]

$\delta^{41}\text{K}$ as a weathering intensity tracer?



Water – World rivers



Wang et al., in review



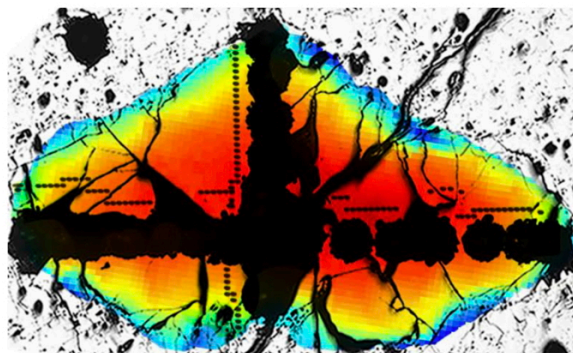
REVIEWS in
**MINERALOGY &
GEOCHEMISTRY**
Volume 82



NON-TRADITIONAL STABLE ISOTOPES

EDITORS:

Fang-Zhen Teng, James M. Watkins
and
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Lithium Isotope Geochemistry

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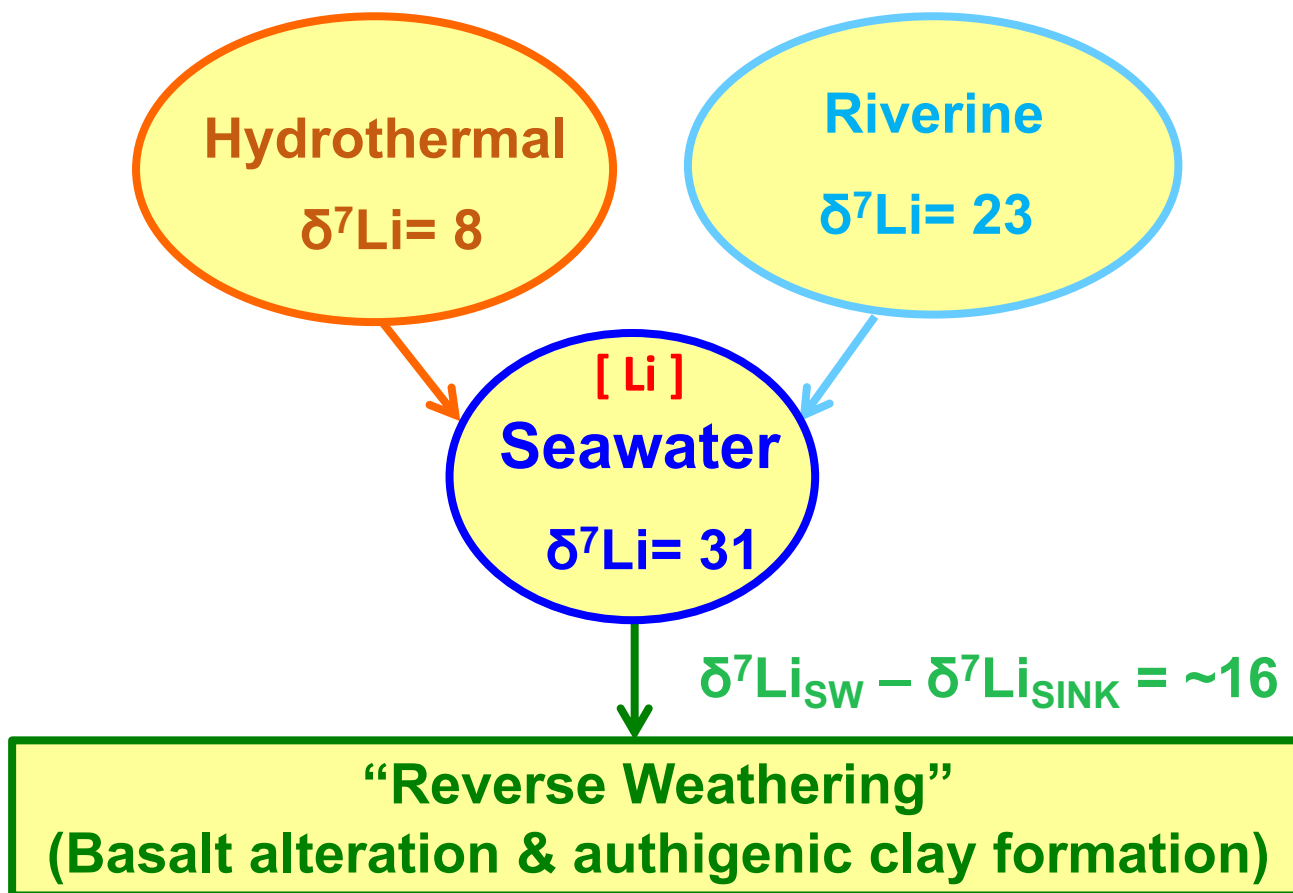
Roberta L. Rudnick^{1,2}

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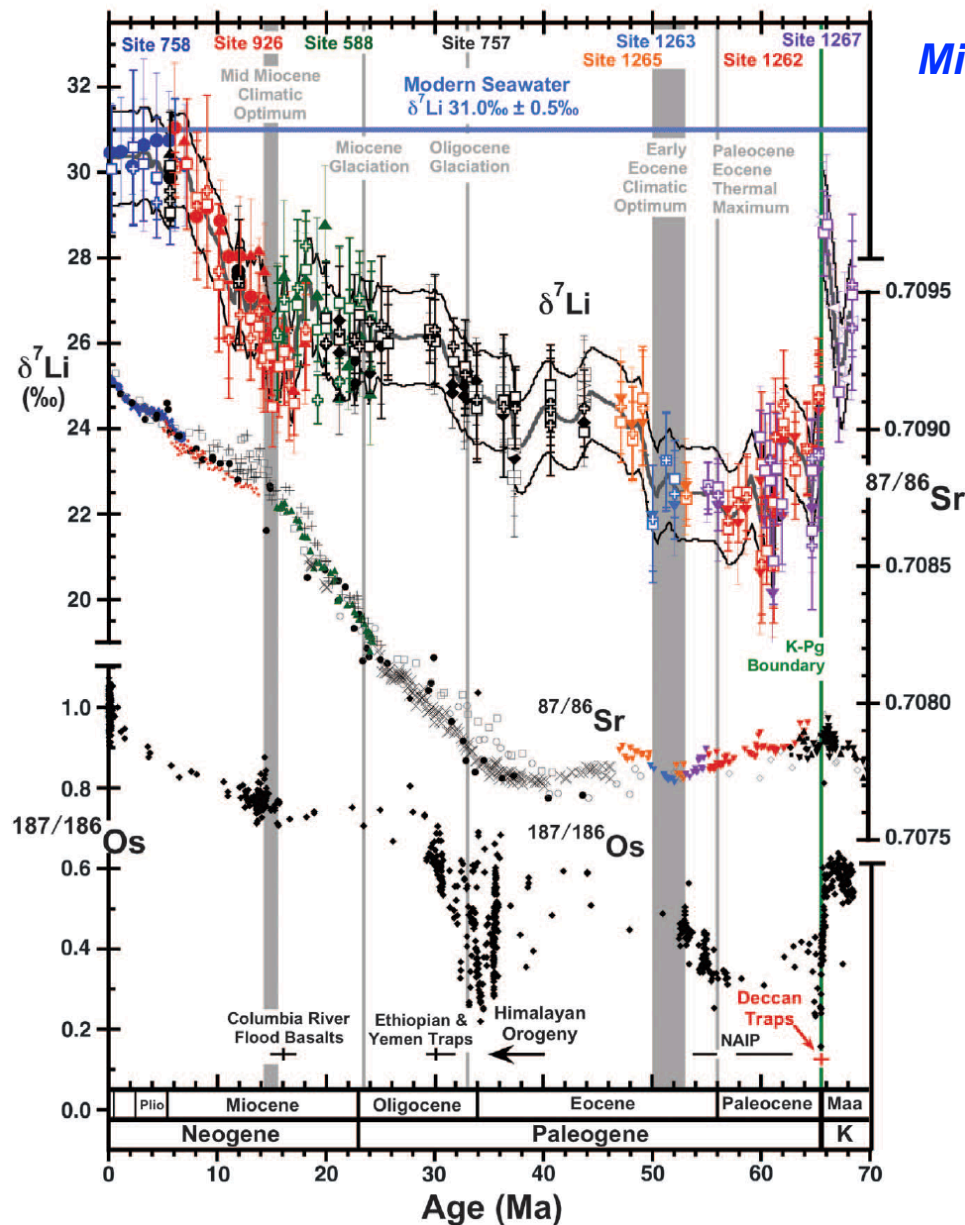
3. Weathering and global ocean cycle in Earth's history

Why does seawater have high $\delta^7\text{Li}$?

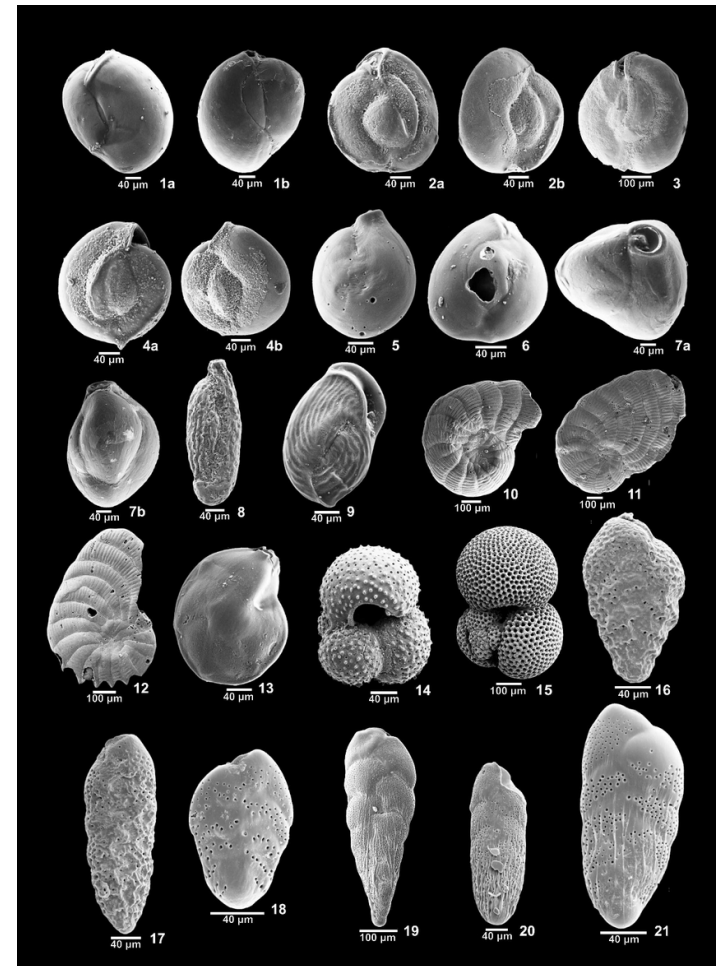


$\delta^7\text{Li}$ in forams: proxy for silicate weathering?

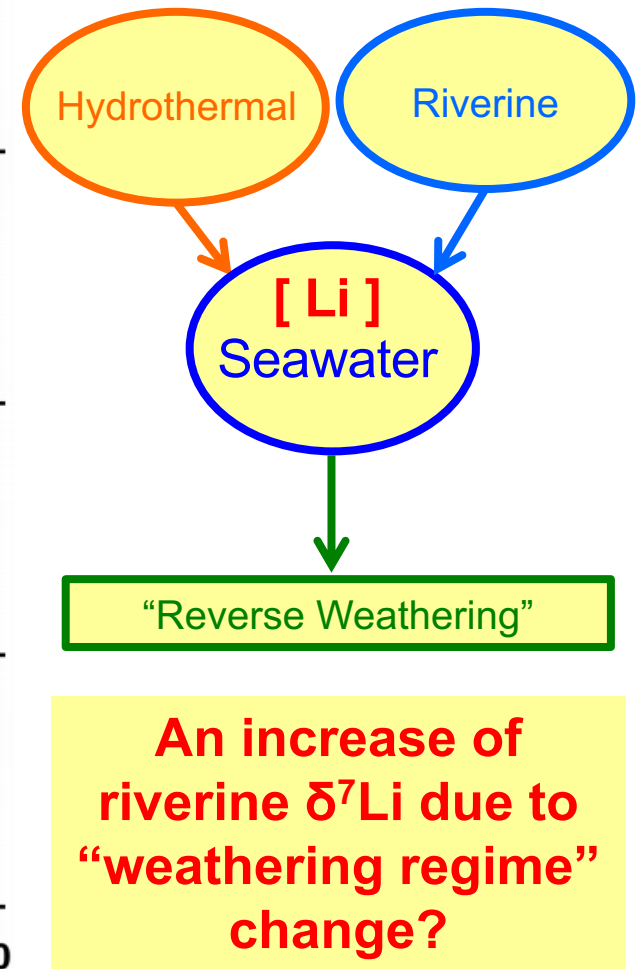
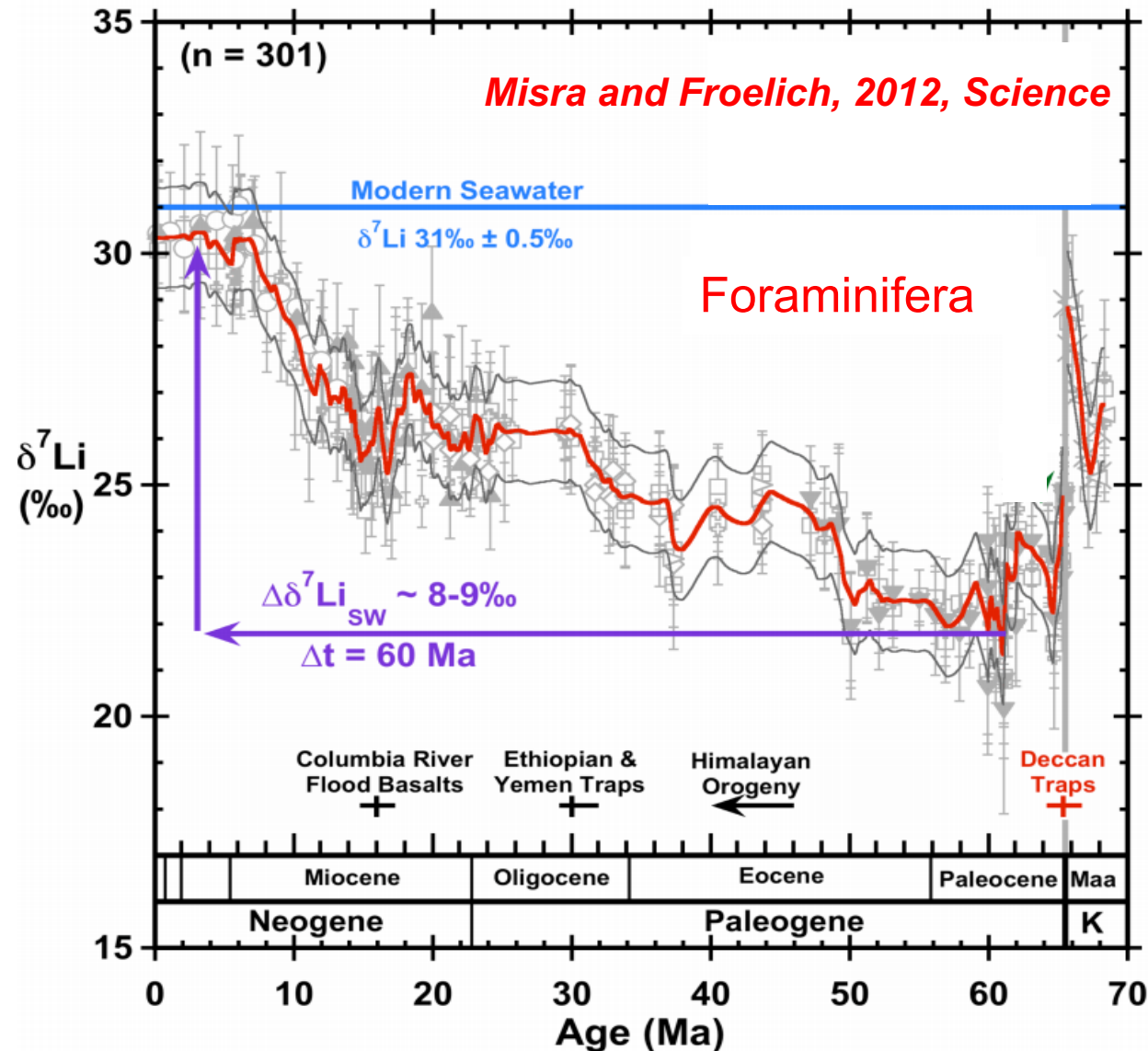
Misra and Froelich, 2012 Science



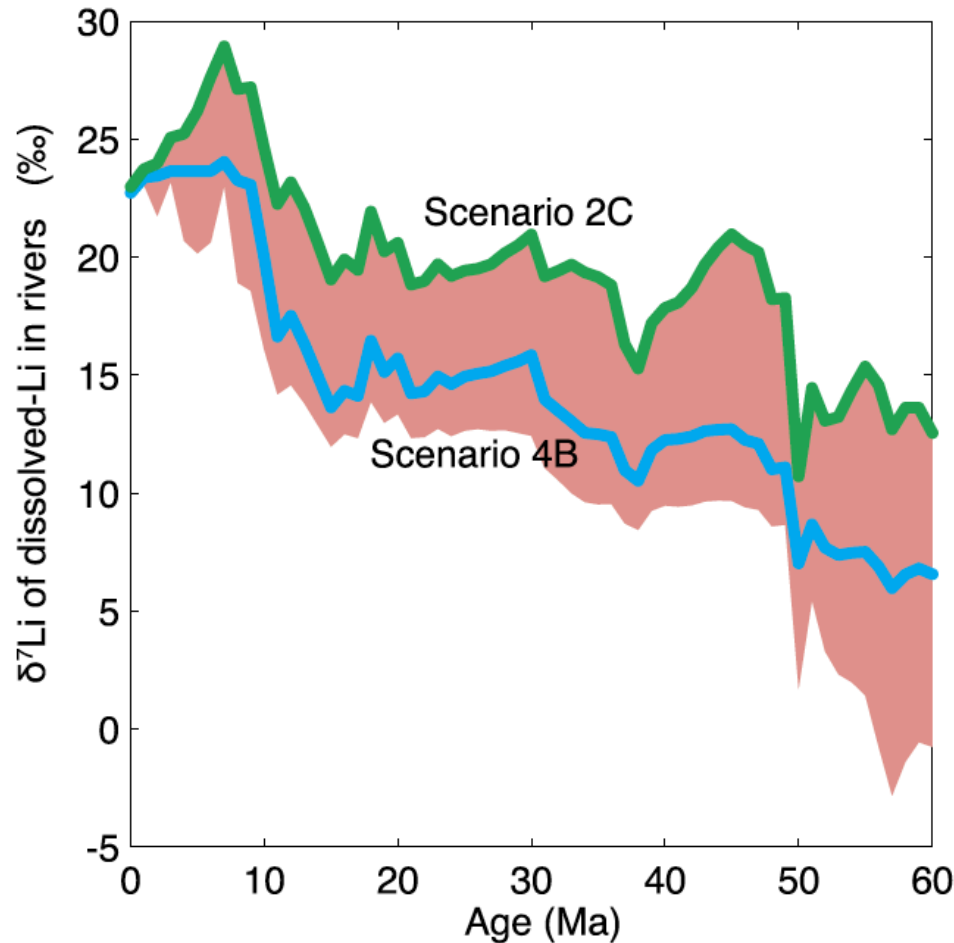
Foraminifera



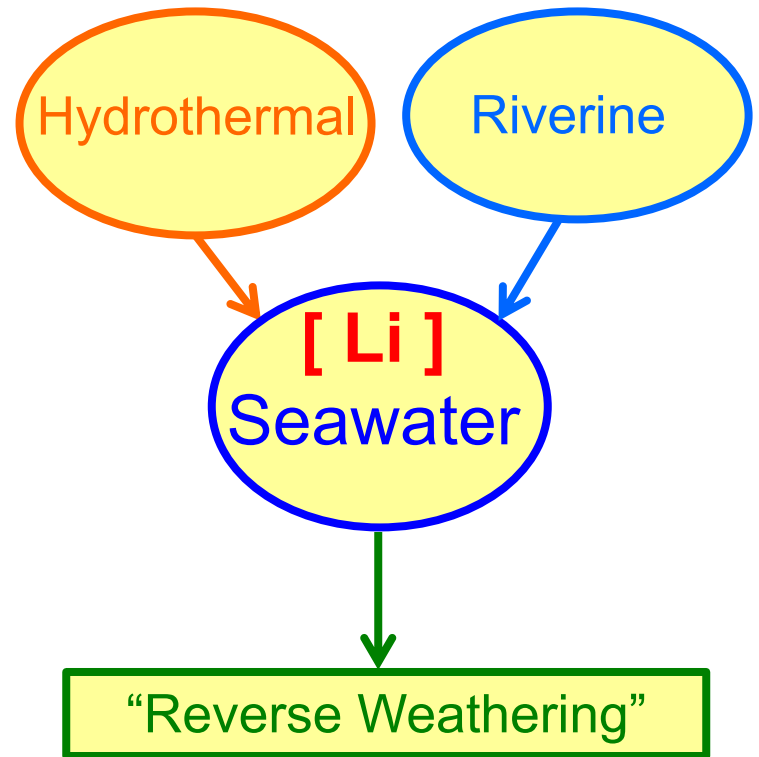
$\delta^7\text{Li}$ in forams: proxy for silicate weathering?



Other Interpretations

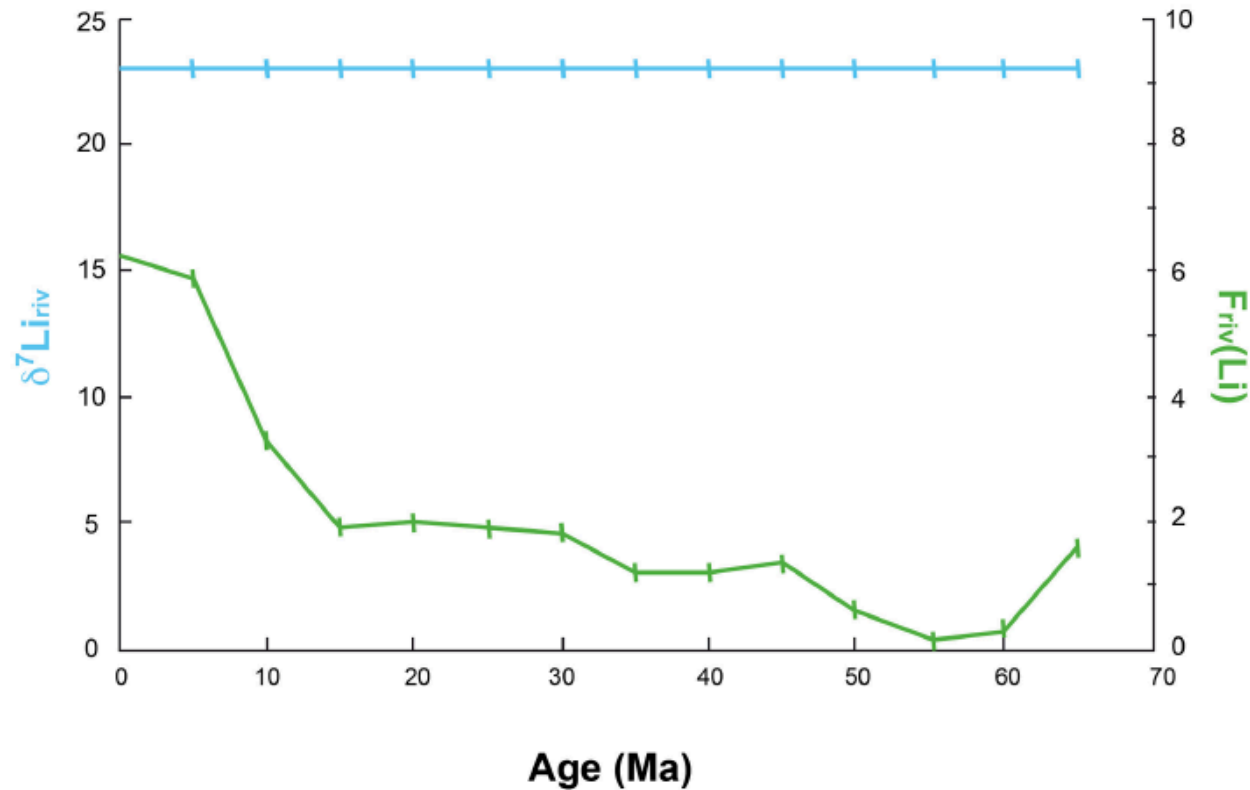


Requires a change in dissolved riverine $\delta^7\text{Li}$ (*Li and West, 2014 EPSL*)



**variations in
ocean sinks**

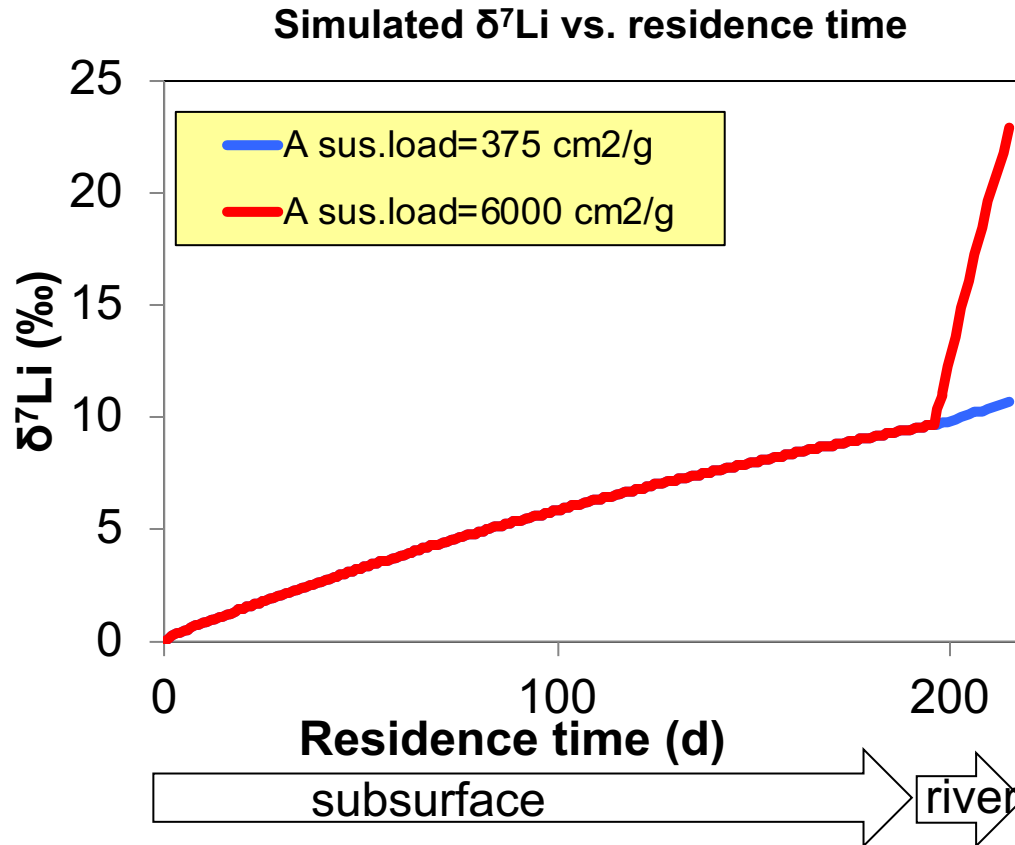
Other Interpretations



An increase in riverine Li flux

Vigier and Godderis, 2015 Clim. Past

Other Interpretations



$\delta^7\text{Li}$ increase due to increasing riverine suspended loads from erosion

$\delta^7\text{Li}$ in forams as proxy for silicate weathering in Cenozoic

Increased seawater $\delta^7\text{Li}$ is probably dominated by increased riverine/weathering input (either Li flux or $\delta^7\text{Li}$).

Seawater $\delta^7\text{Li}$ can be influenced by changes in other sinks like reverse weathering.

$\delta^7\text{Li}$ in marine carbonates as tracer of silicate weathering in the past

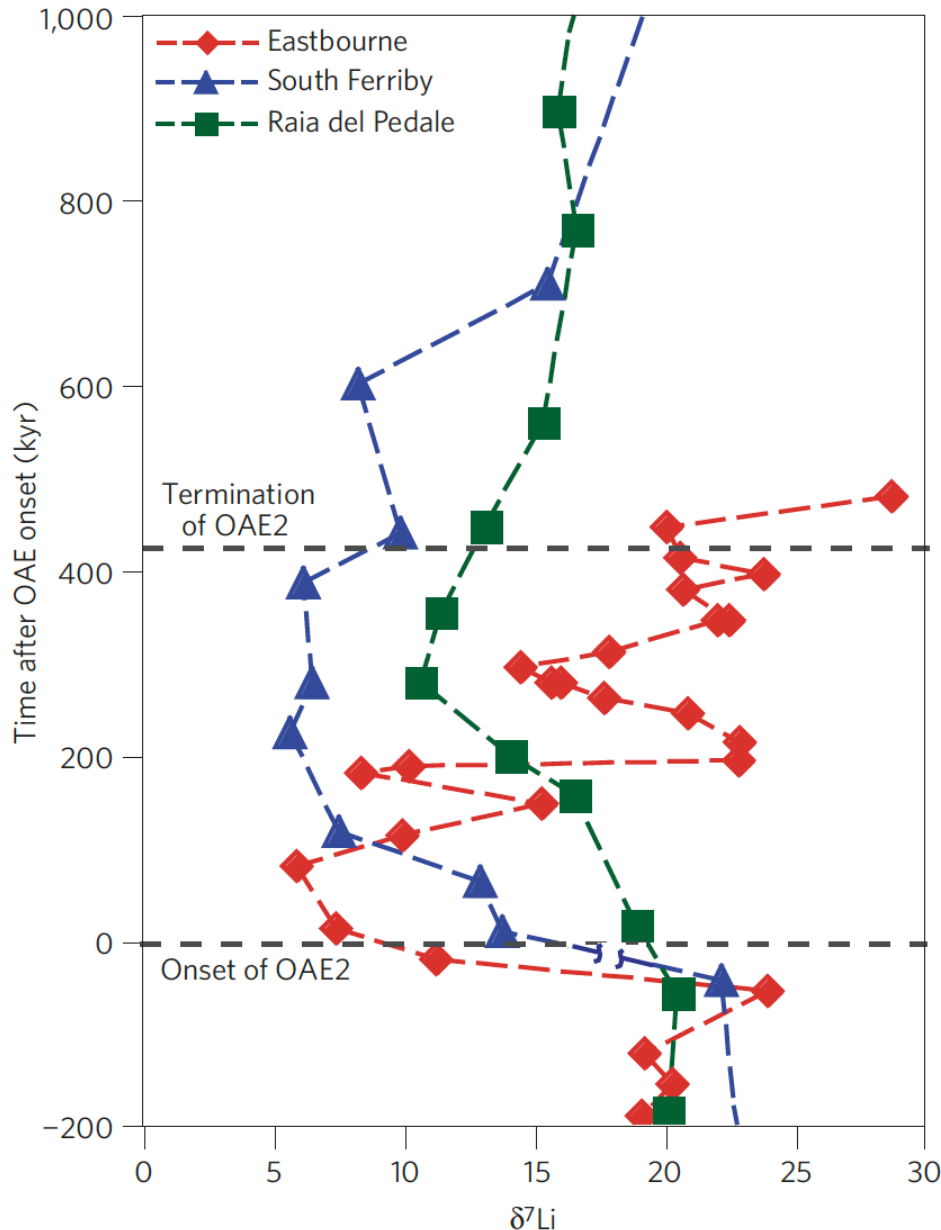
Assumptions:

1. Li is entirely controlled by weathering of silicates
2. We can extract marine signal from bulk carbonates

Hypothesis:

Increased $\delta^7\text{Li}$ in seawater is dominated by increased riverine input/weathering intensity (Li flux and/or $\delta^7\text{Li}$).

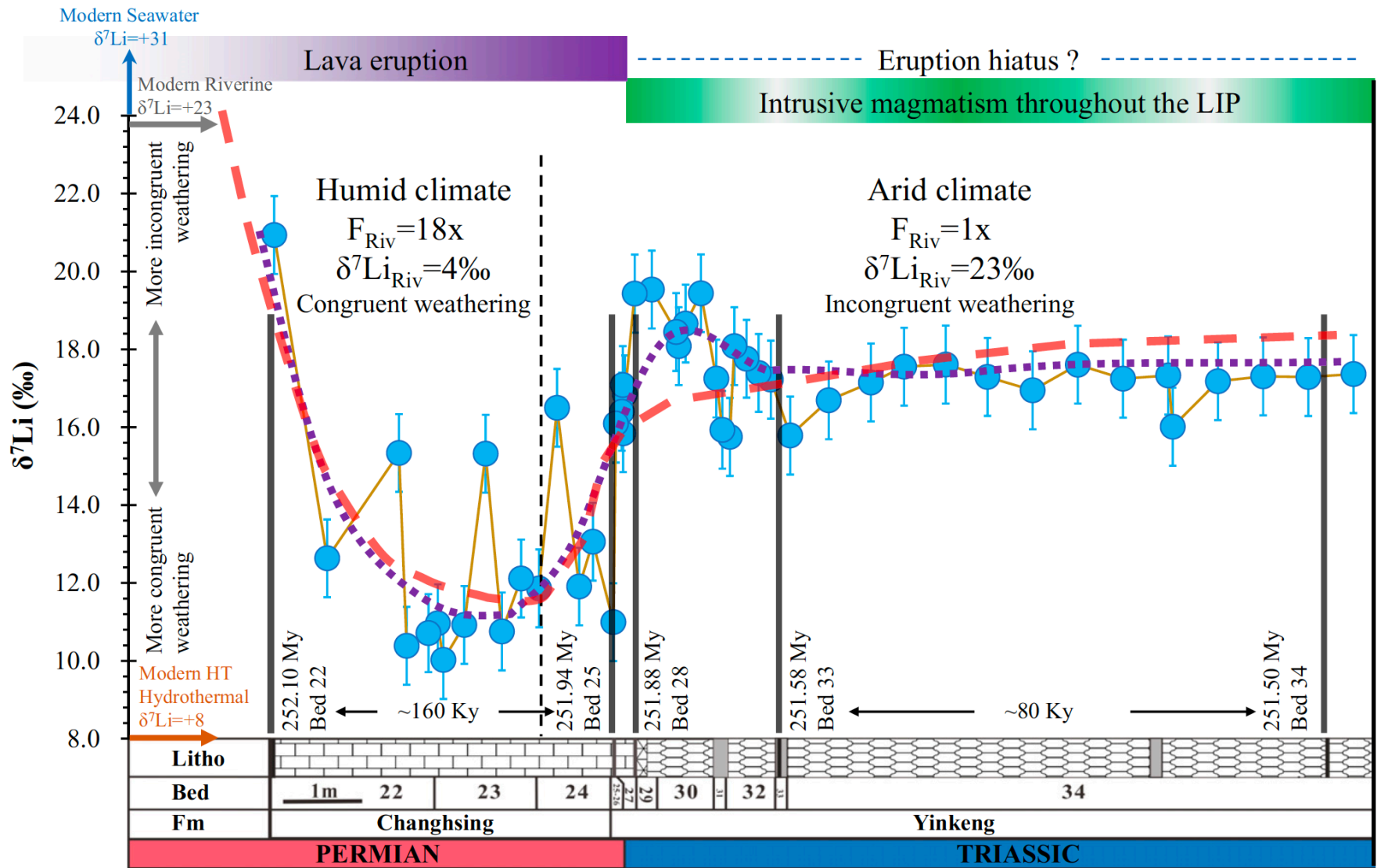
Case studies – OAE2



Eruption of a **large igneous province** led to high atmospheric **CO₂** and **rapid global warming**, which **initiated OAE2**. The warming was accompanied by a roughly **accelerated weathering of mafic silicate rocks**.

Pogge von Strandmann et al., 2013 Nat. Geo.

Case studies – P-T boundary

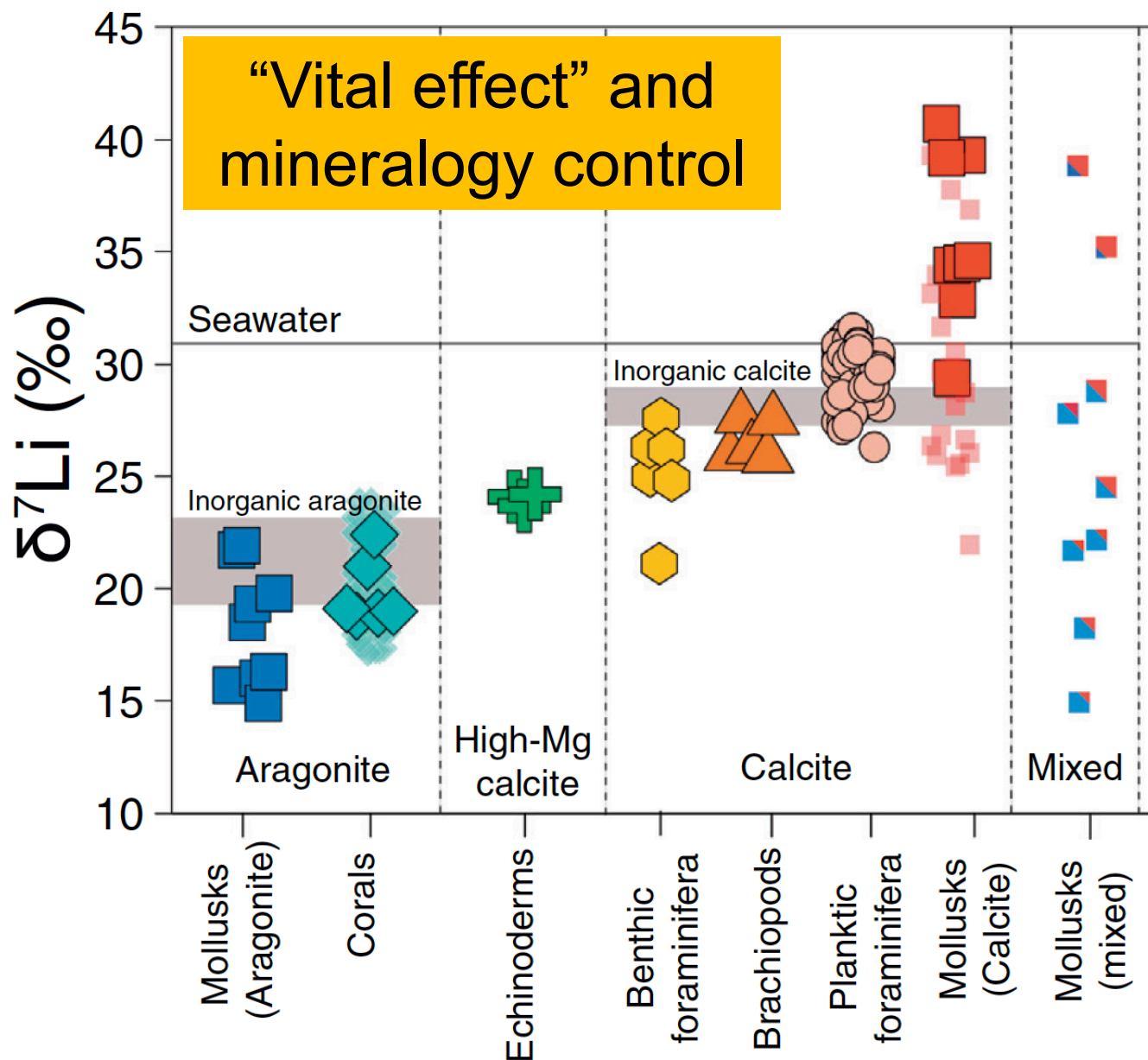


Extract marine signal from bulk carbonate rocks is nontrivial!



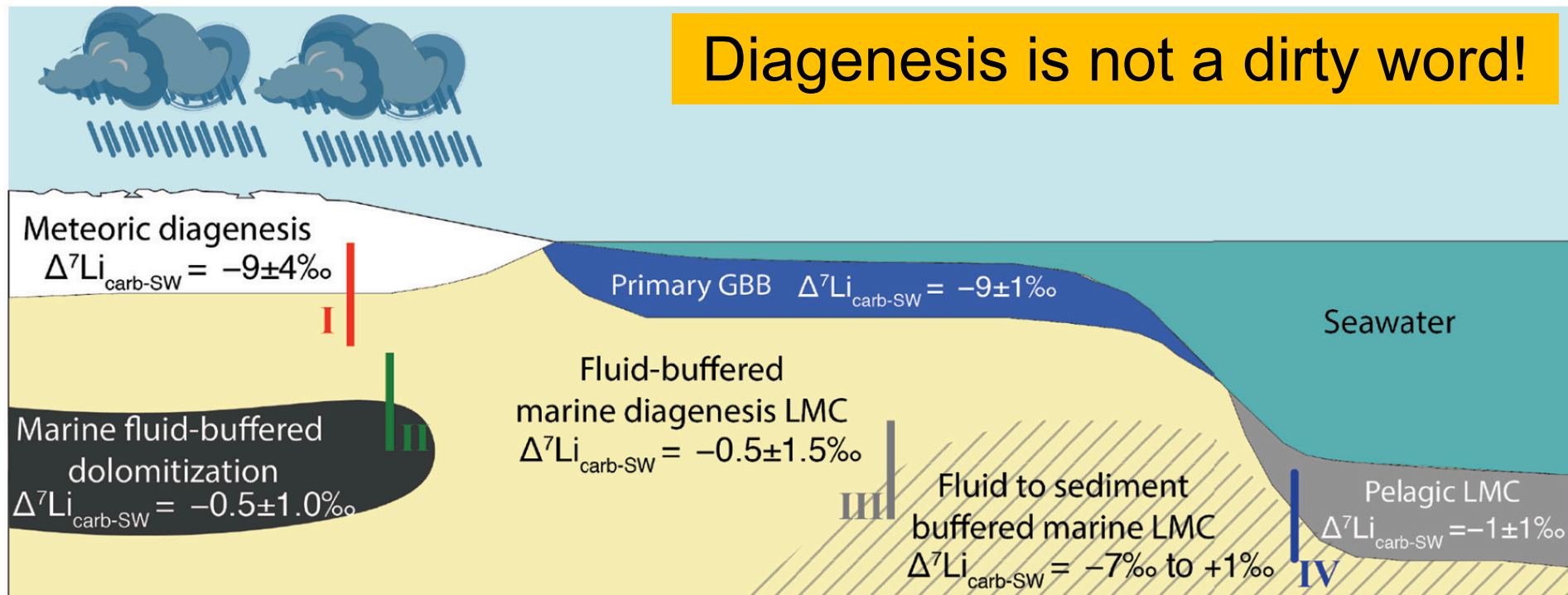
**“I suppose I’ll be the one
to mention the elephant in the room.”**

Marine carbonate = seawater?: **Nature**



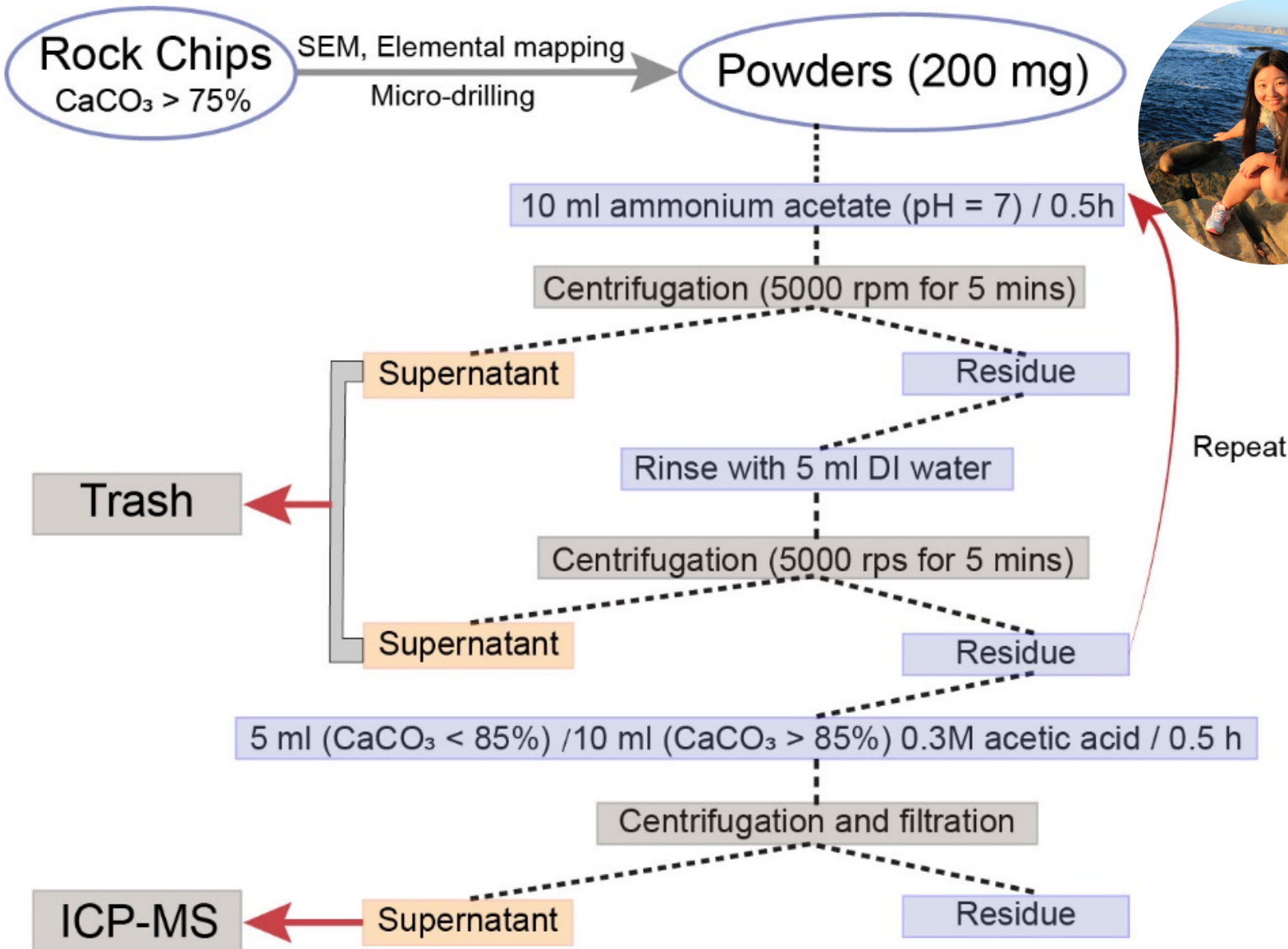
Marine carbonate = seawater?: Nature

Diagenesis is not a dirty word!

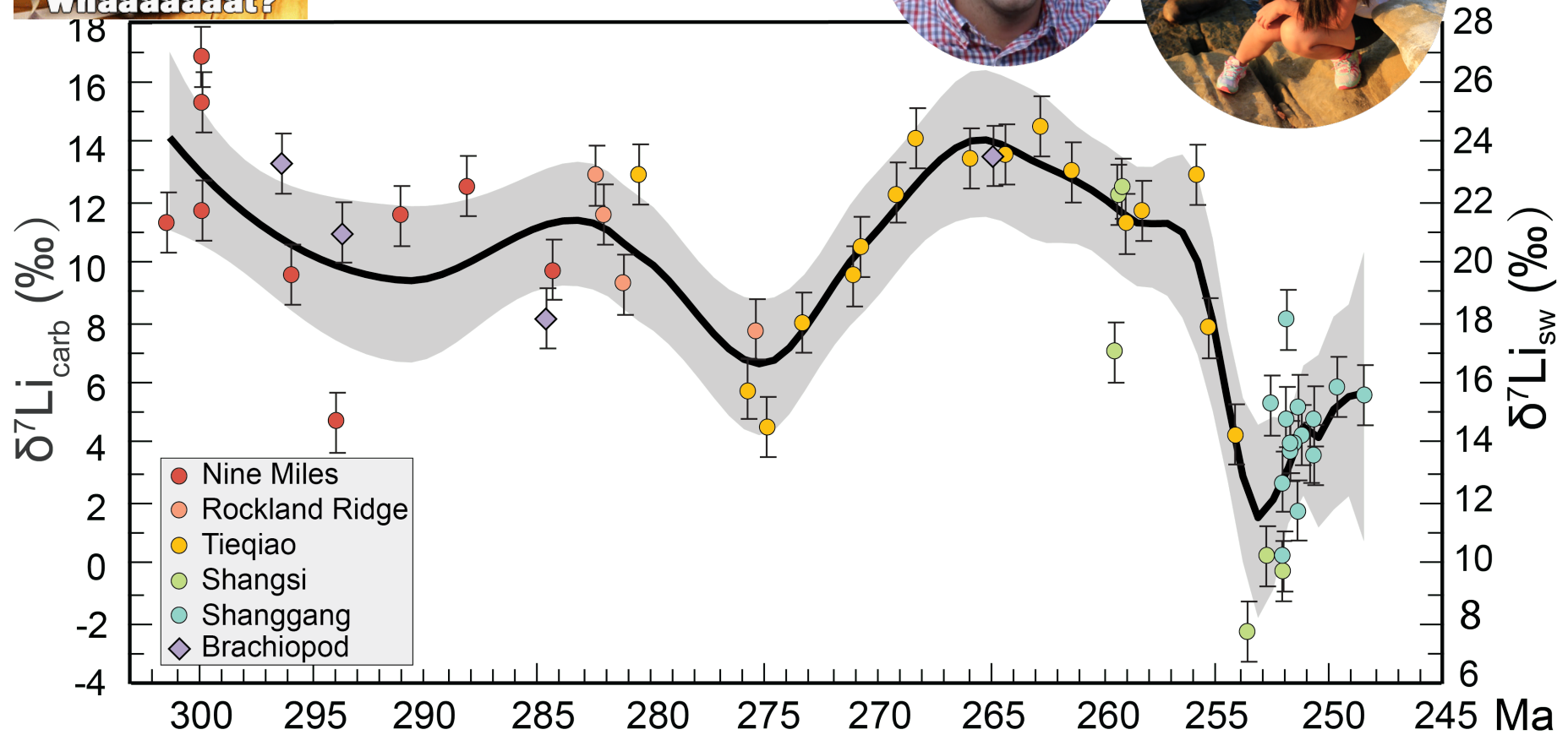
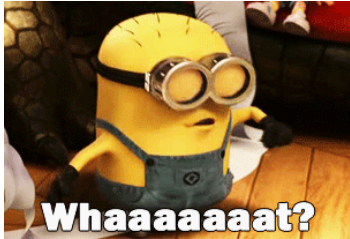


Dellinger et al., 2020 AJS

Marine carbonate = seawater?: Lab

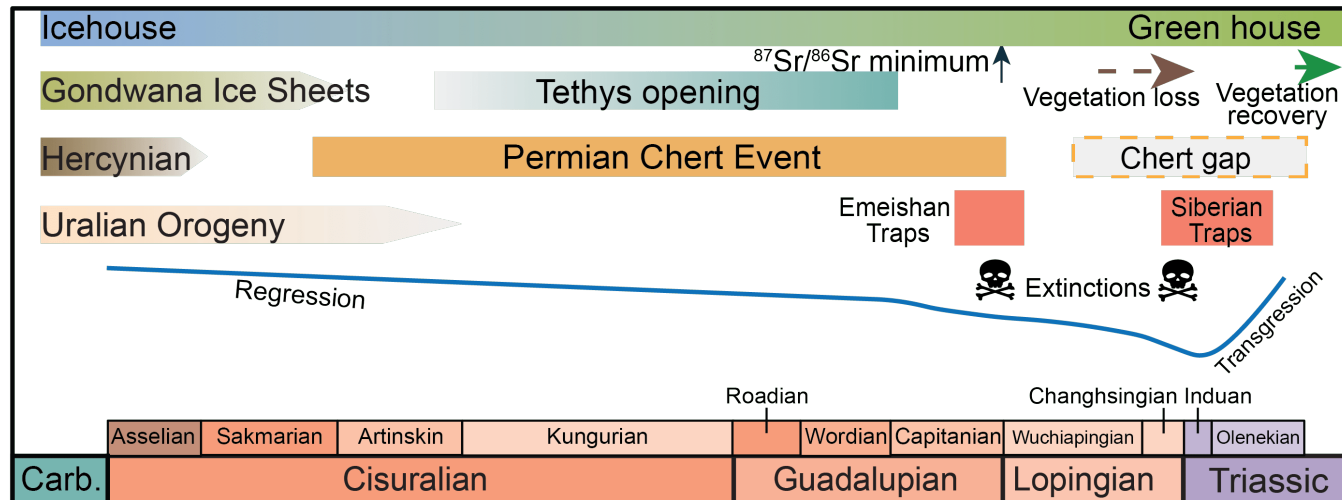
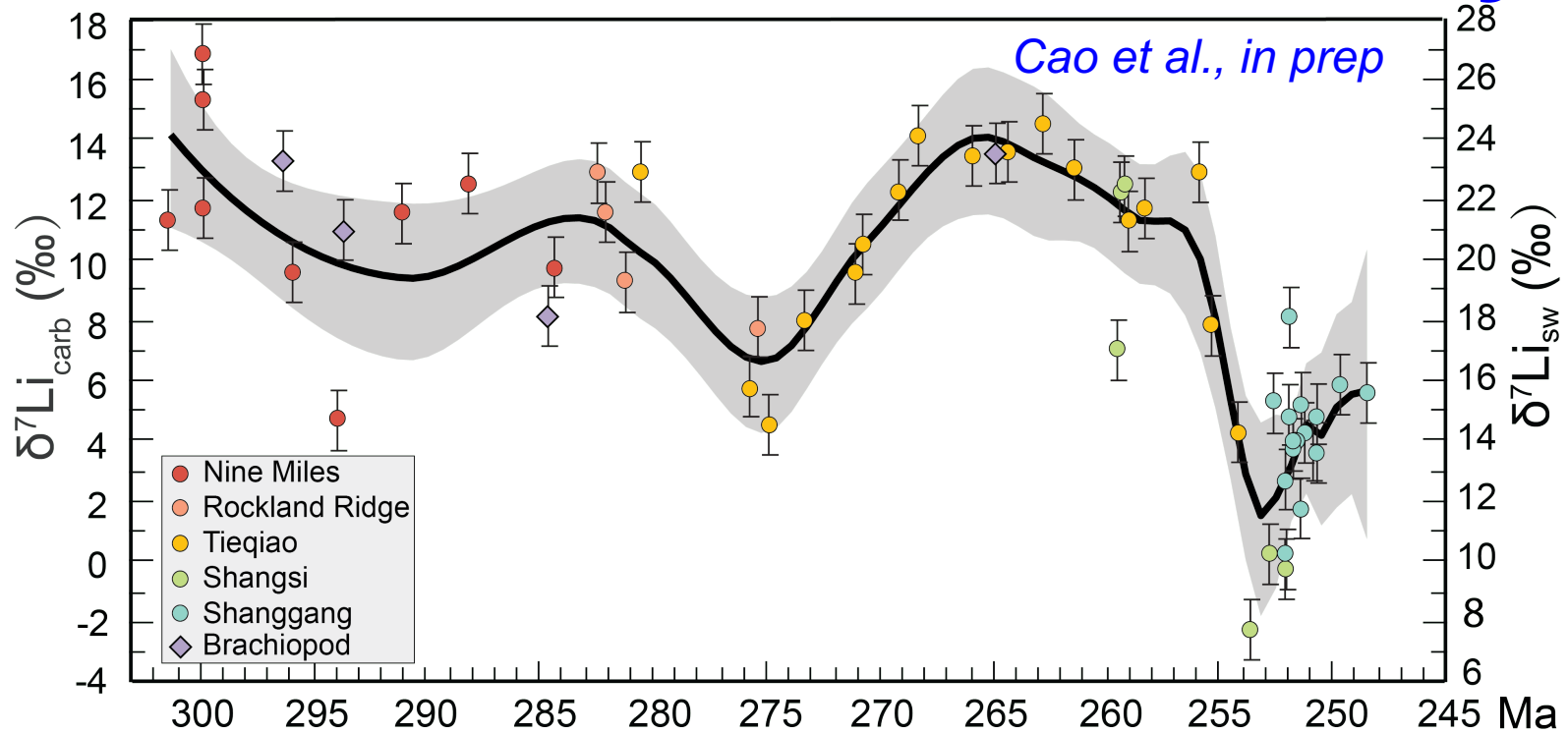


Case studies – P-T boundary



Cao et al., in prep

Case studies – P-T boundary



4. Conclusions and outlook

1. Li and K isotopes may be good proxy for continental silicate weathering
2. Li and K isotopes may have potential to trace weathering/reverse weathering and global ocean cycles in Earth's history
3. Need to understand Li and K isotope fractionation mechanisms in Earth's surface

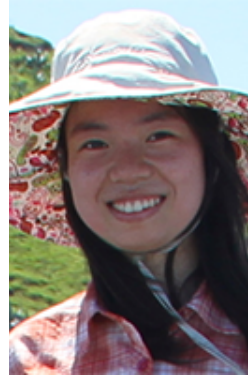
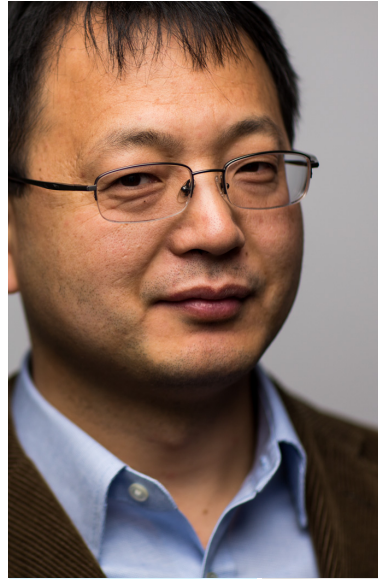


Thank you!



My postdoc and students
contributed to this talk

Collaborators





PMS is always looking for motivated students and scholars!

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Xikai Wang



Xiaoming Liu



wenshuai



Xiaofeng



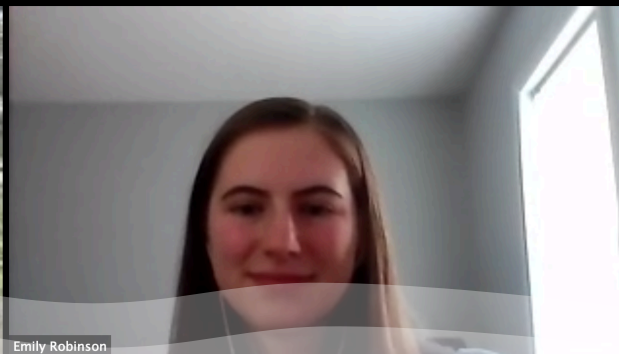
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Yiwen Cao



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<https://xiaomingliu-unc.wixsite.com/xiaomingliu-site>