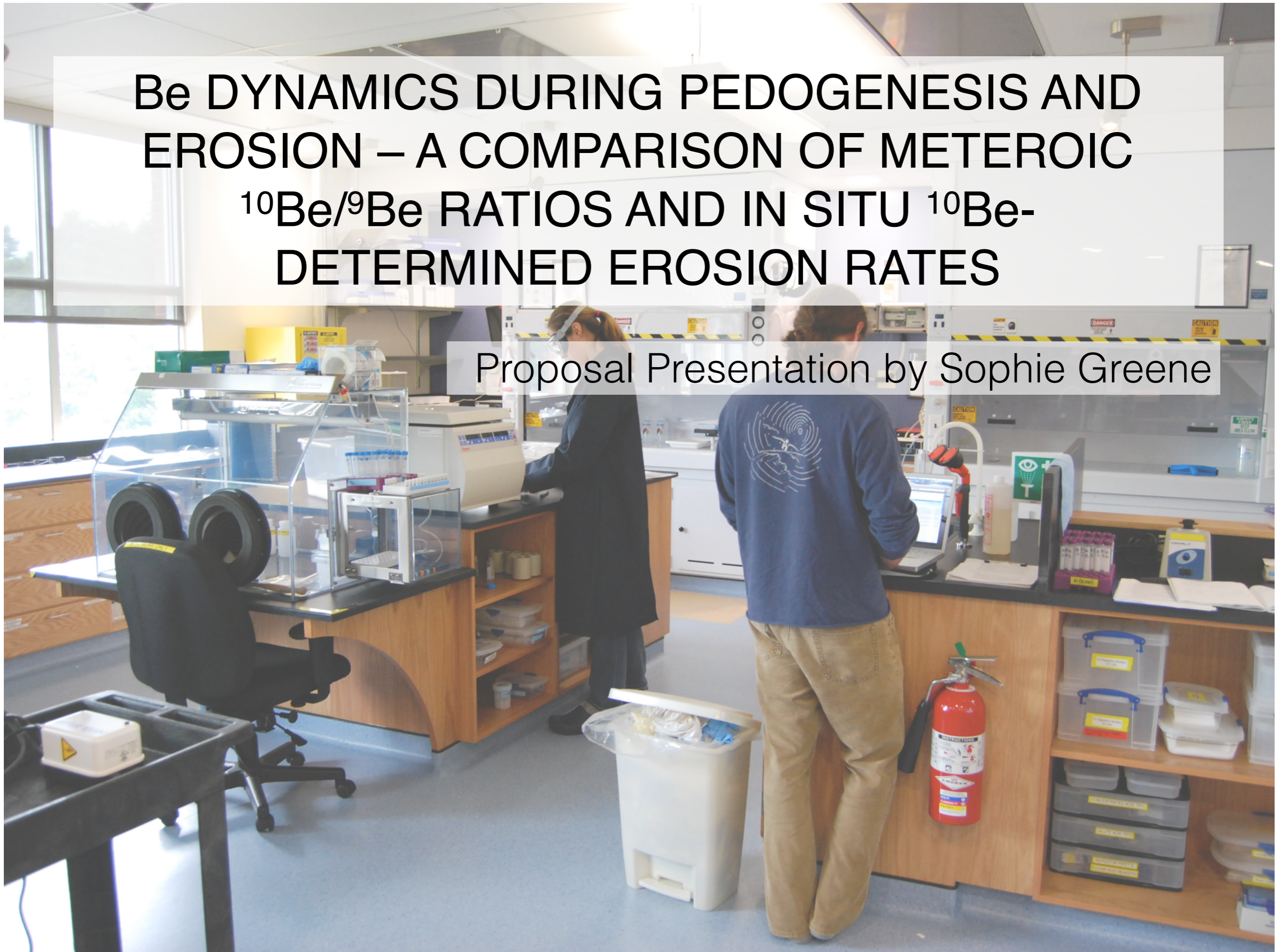










Be DYNAMICS DURING PEDOGENESIS AND EROSION – A COMPARISON OF METEOROIC $^{10}\text{Be}/^9\text{Be}$ RATIOS AND IN SITU ^{10}Be - DETERMINED EROSION RATES

Proposal Presentation by Sophie Greene



In a nutshell...

	“meteoric-10” $^{10}\text{Be}_{\text{met}}$	“9” ^9Be	“in situ -10” $^{10}\text{Be}_{\text{is}}$	“meteoric:9 ratio” $\frac{^{10}\text{Be}_{\text{met}}}{^9\text{Be}}$
Ease of measurement				(Hopefully) 
Ease of interpretation				(Hopefully) 

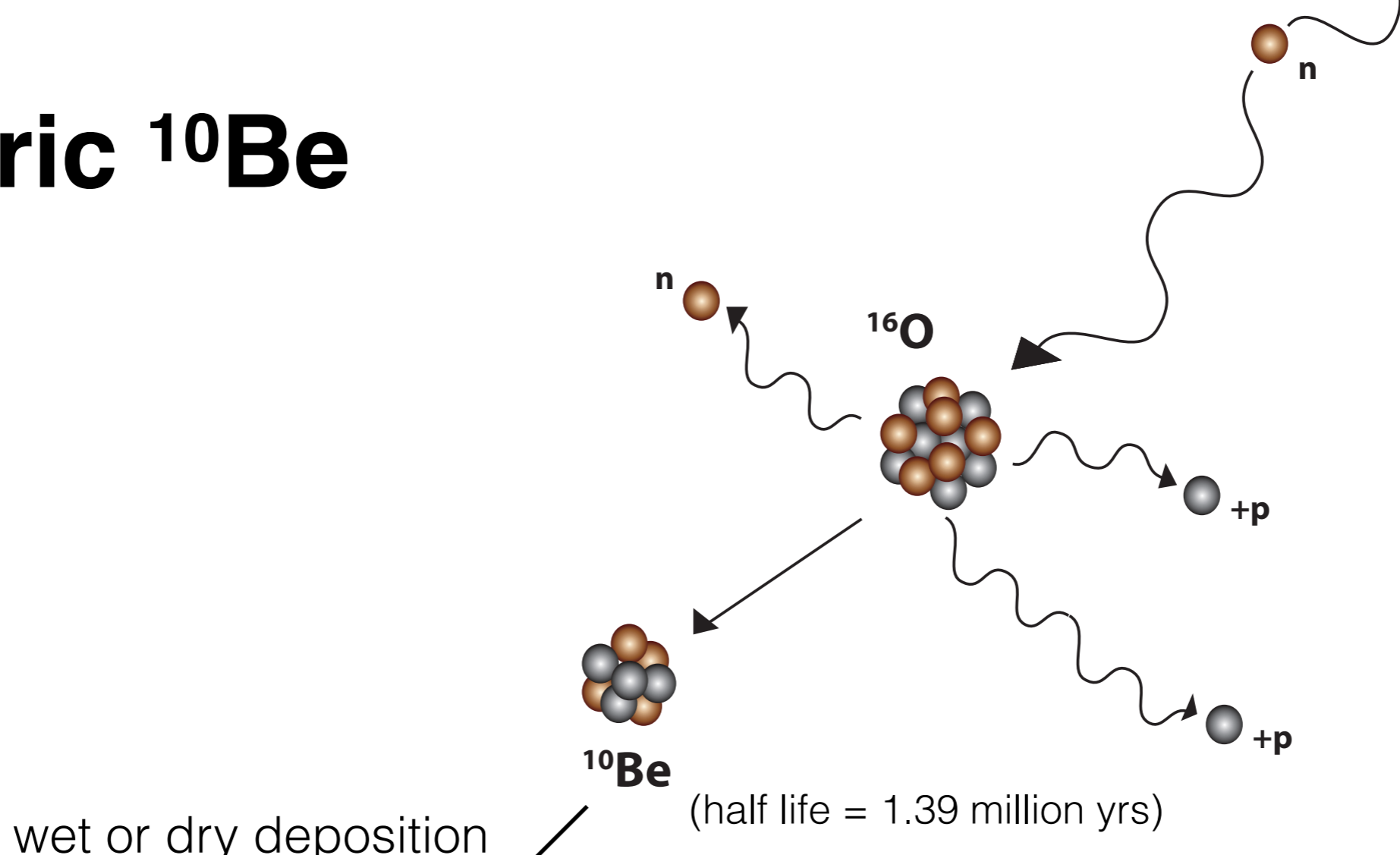
Types of questions Be isotope data could address:

- Do tropical environments erode faster than arid environments? By how much?
- How are trace metals transported during soil formation?
- How long does it take for soils to redevelop after a historic glaciation?

Outline

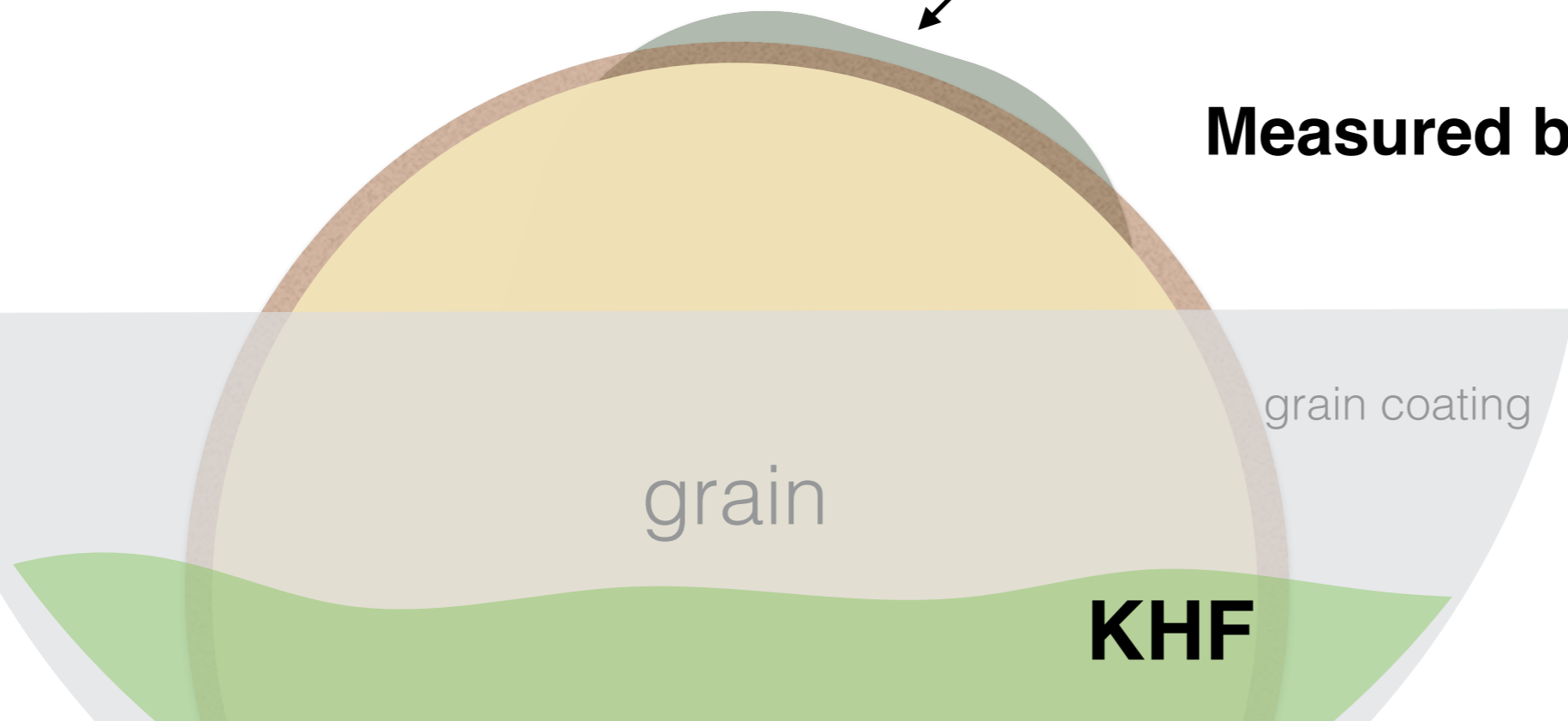
- Meteoric ^{10}Be
 - formation, measurement, erosion rate proxy?
- In situ ^{10}Be
 - formation, measurement, erosion rate proxy?
- ^9Be
 - distribution, measurement, tool for improving meteoric interpretations?
- Overview of initial sample sets
- Project logistics

Meteoric ^{10}Be



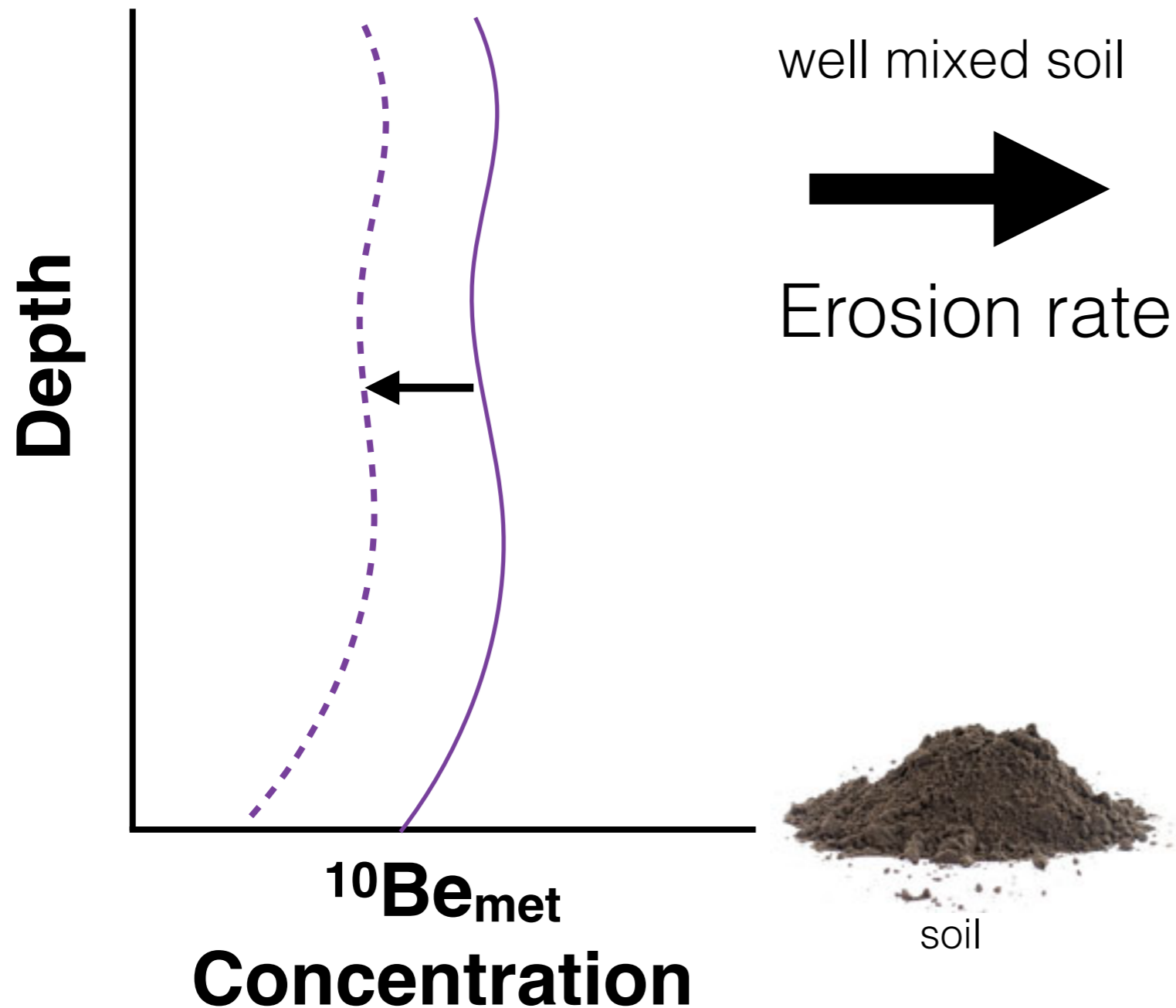
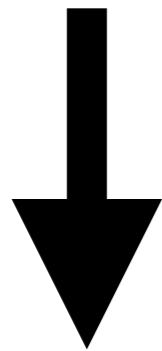
wet or dry deposition

Measured by digesting total grain



A perfect world: soil profiles of $^{10}\text{Be}_{\text{met}}$

Known meteoric
 ^{10}Be Flux



soil



fluvial sands



lake sediments

Measured Meteoric ^{10}Be in soil profiles

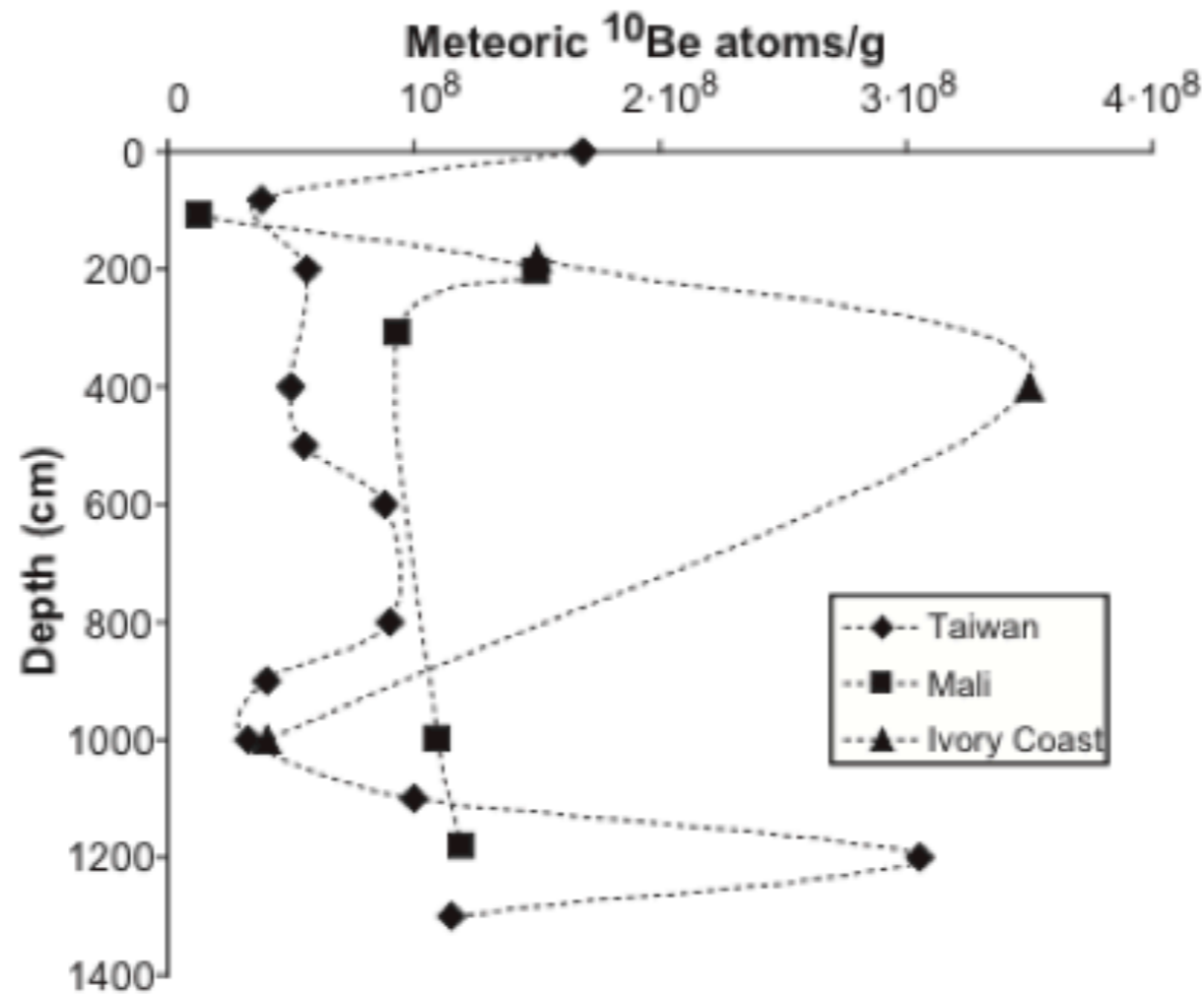
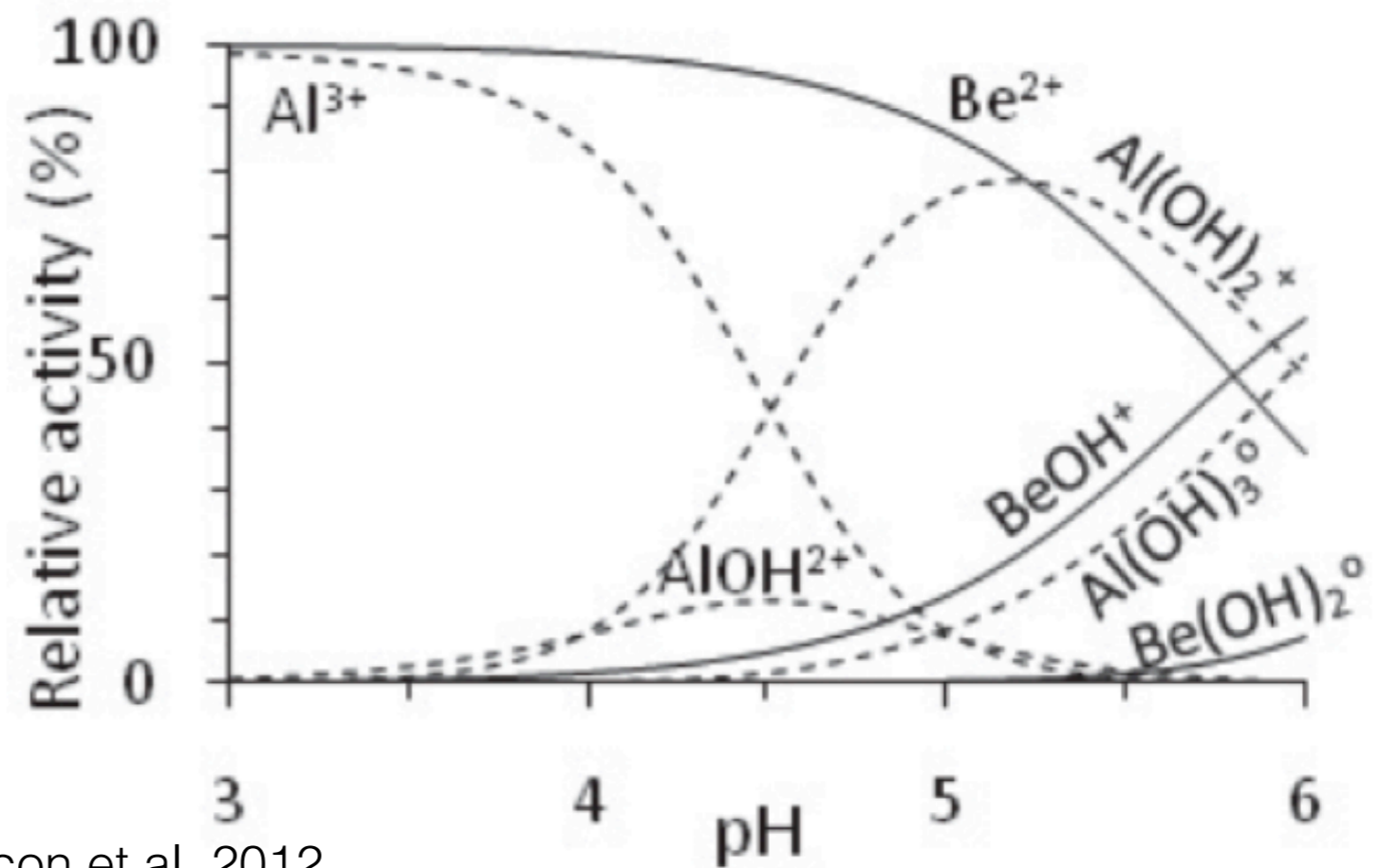


Fig. 9. Tropical and subtropical oxic soils (Barg et al., 1997; You et al., 1989) showing deeper infiltration of meteoric ^{10}Be and different profile shape dynamics than temperate soil profiles. Dashed lines indicate interpolation between point-sampled measurements.

Remobilization of $^{10}\text{Be}_{\text{met}}$



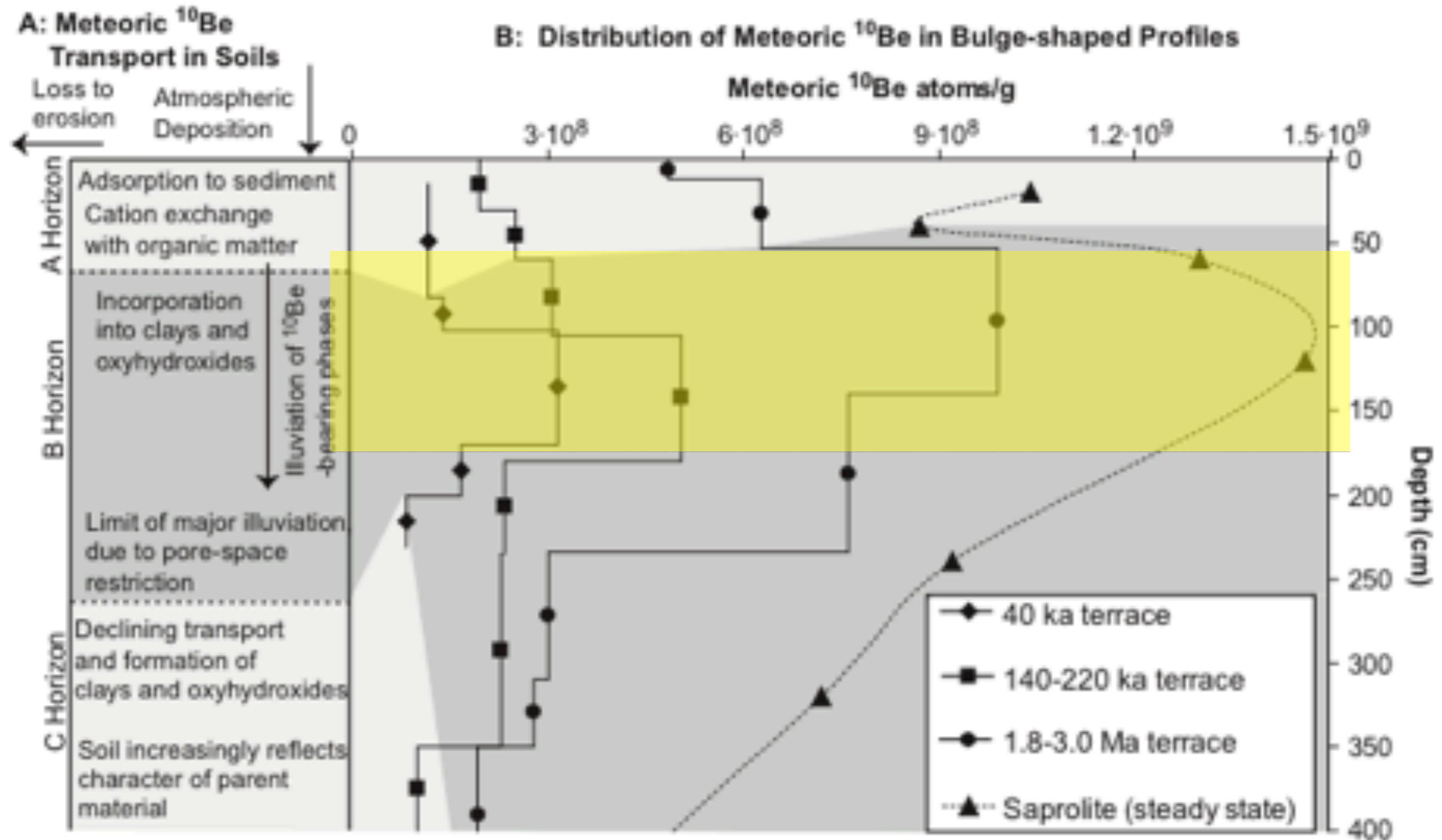
Be^{2+} = soluble in water



Bacon et al. 2012

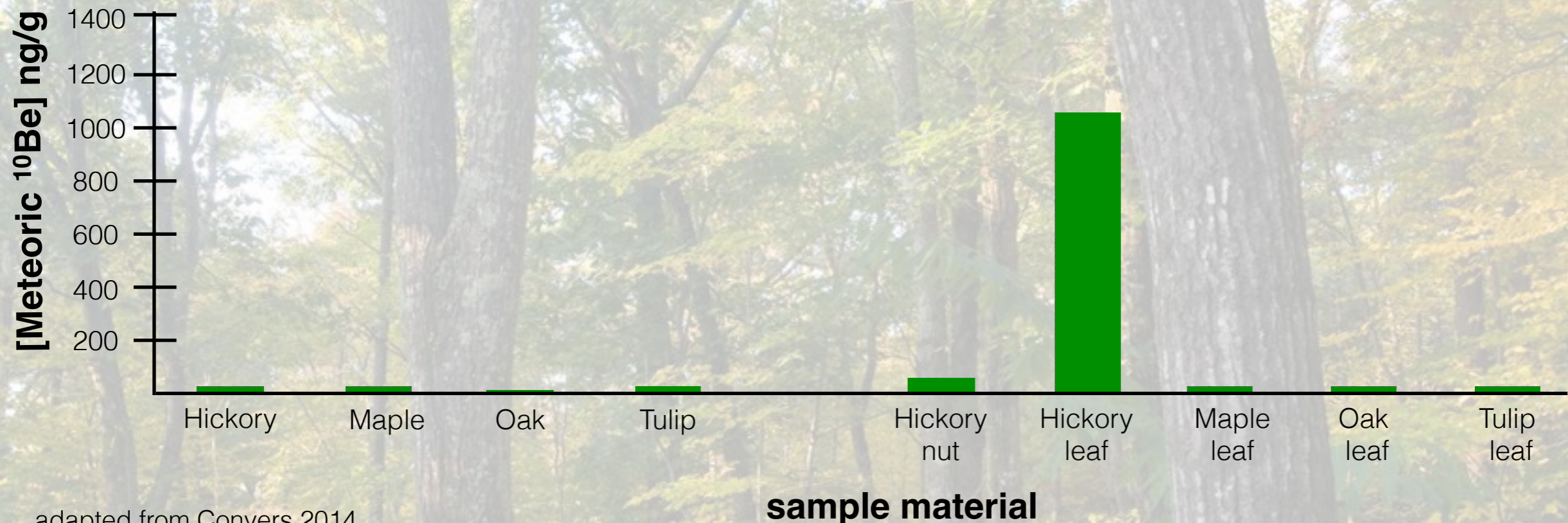
Meteoric ^{10}Be concentration is grain size dependent

$^{10}\text{Be}_{\text{met}}$ concentrations $\sim 1 \times 10^8$ **atoms/gram**



Does meteoric ^{10}Be bioaccumulate?

schematic: Meteoric ^{10}Be in samples by dry oven weight



adapted from Conyers 2014

Several orders of magnitude difference between ^{10}Be in Hickory and surrounding soils

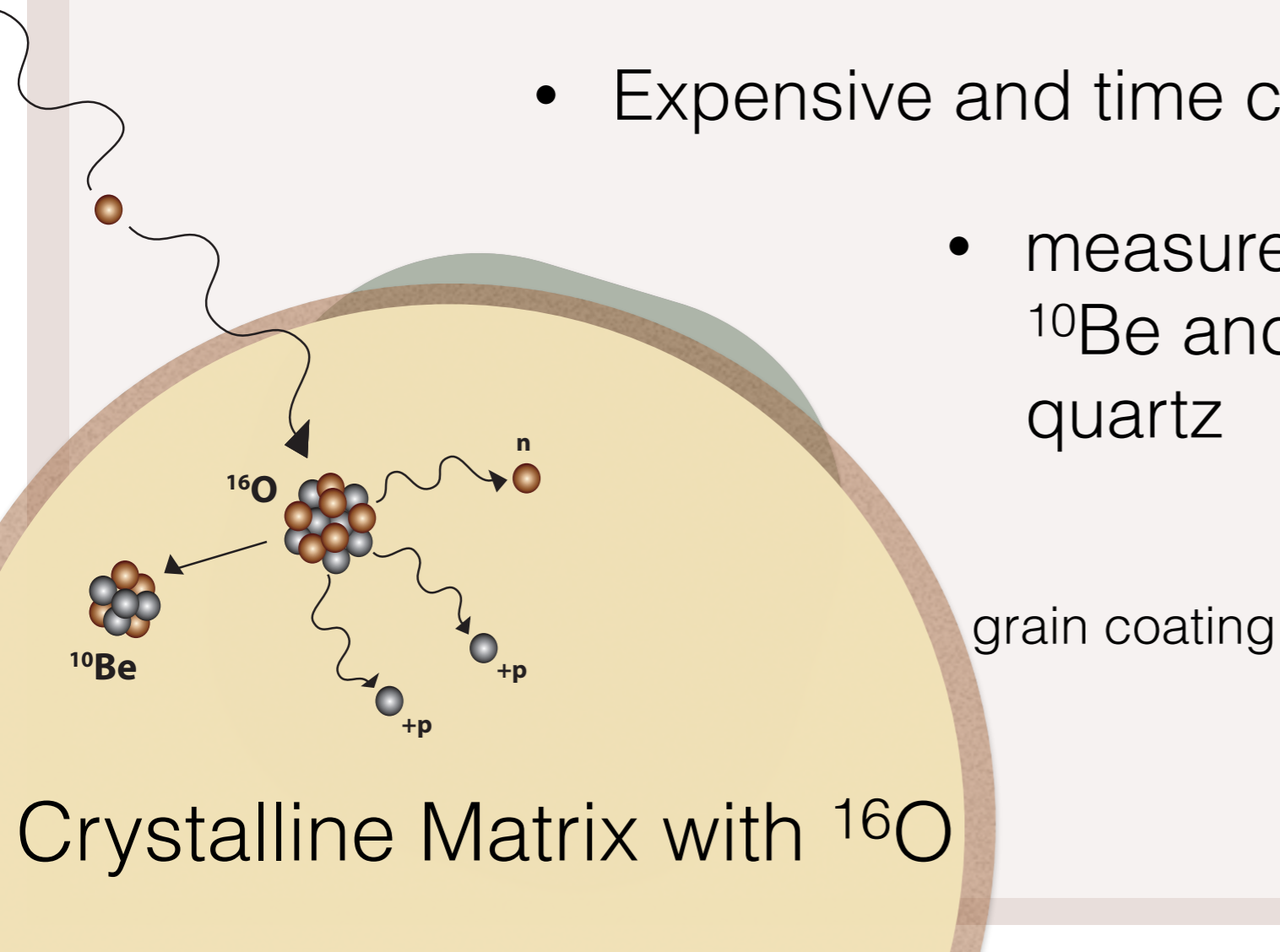
In Summary: Difficulties in $^{10}\text{Be}_{\text{met}}$ interpretations

- Could be leached from soils in acidic environments
- Has grain size dependent concentrations
- Bioaccumulates in some species

Remobilizes in unpredictable ways

in situ ^{10}Be

- concentrations many orders of magnitude lower than meteoric ^{10}Be
- Can only measure in sand-sized quartz
- Expensive and time consuming
- measured by stripping off meteoric ^{10}Be and dissolving the residual quartz

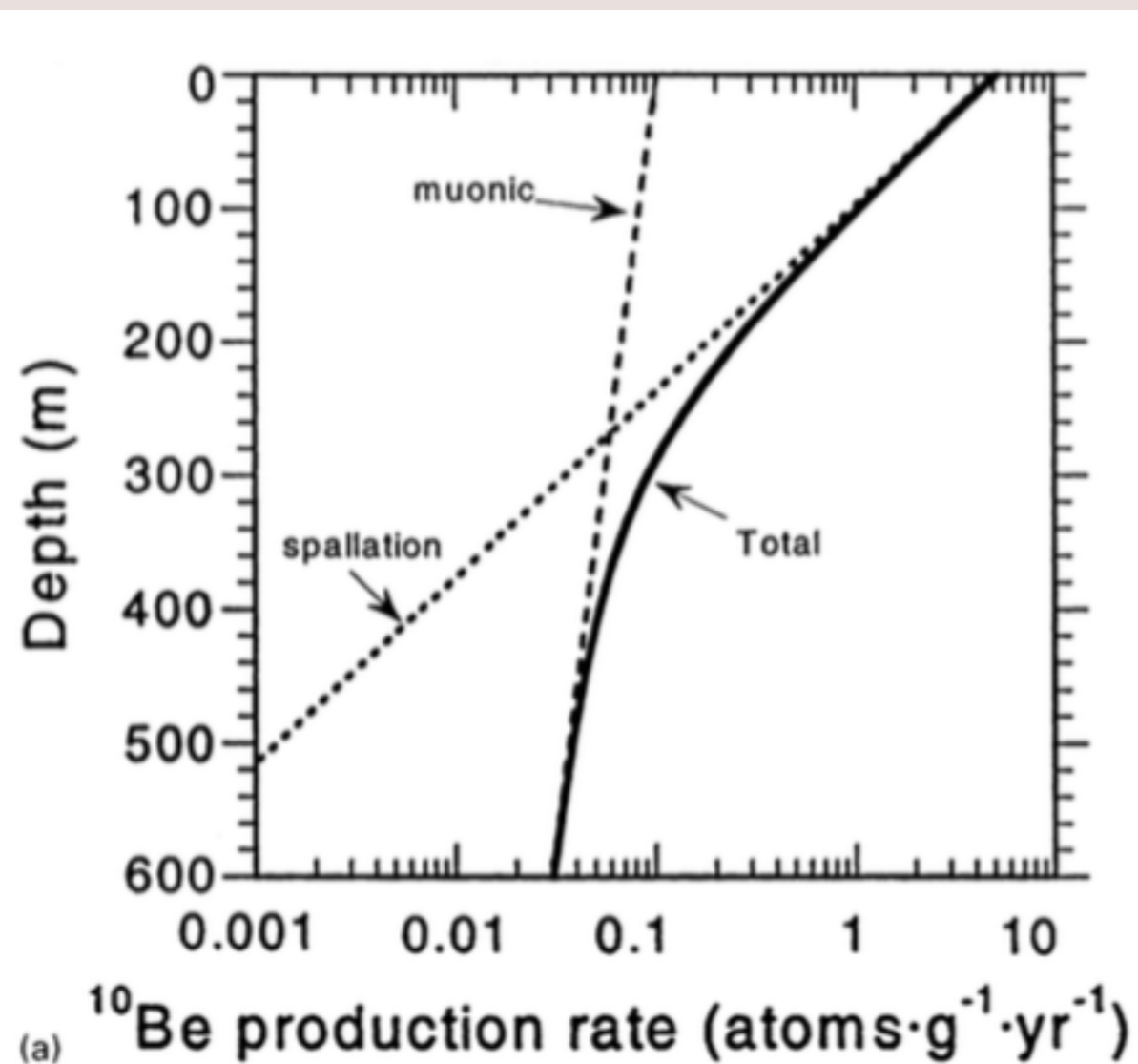


Crystalline Matrix with ^{16}O

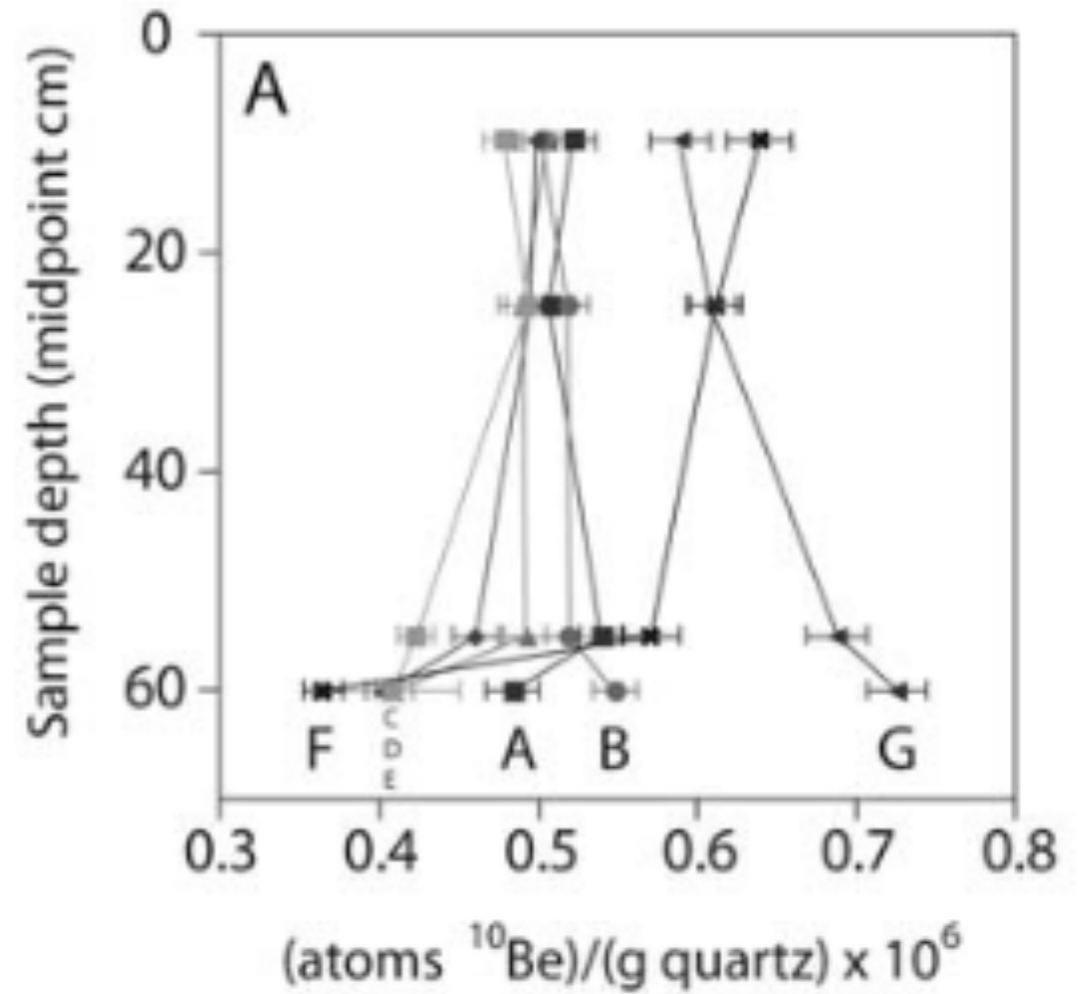
Benefits of in situ ^{10}Be

Known production rates with depth

No remobilization



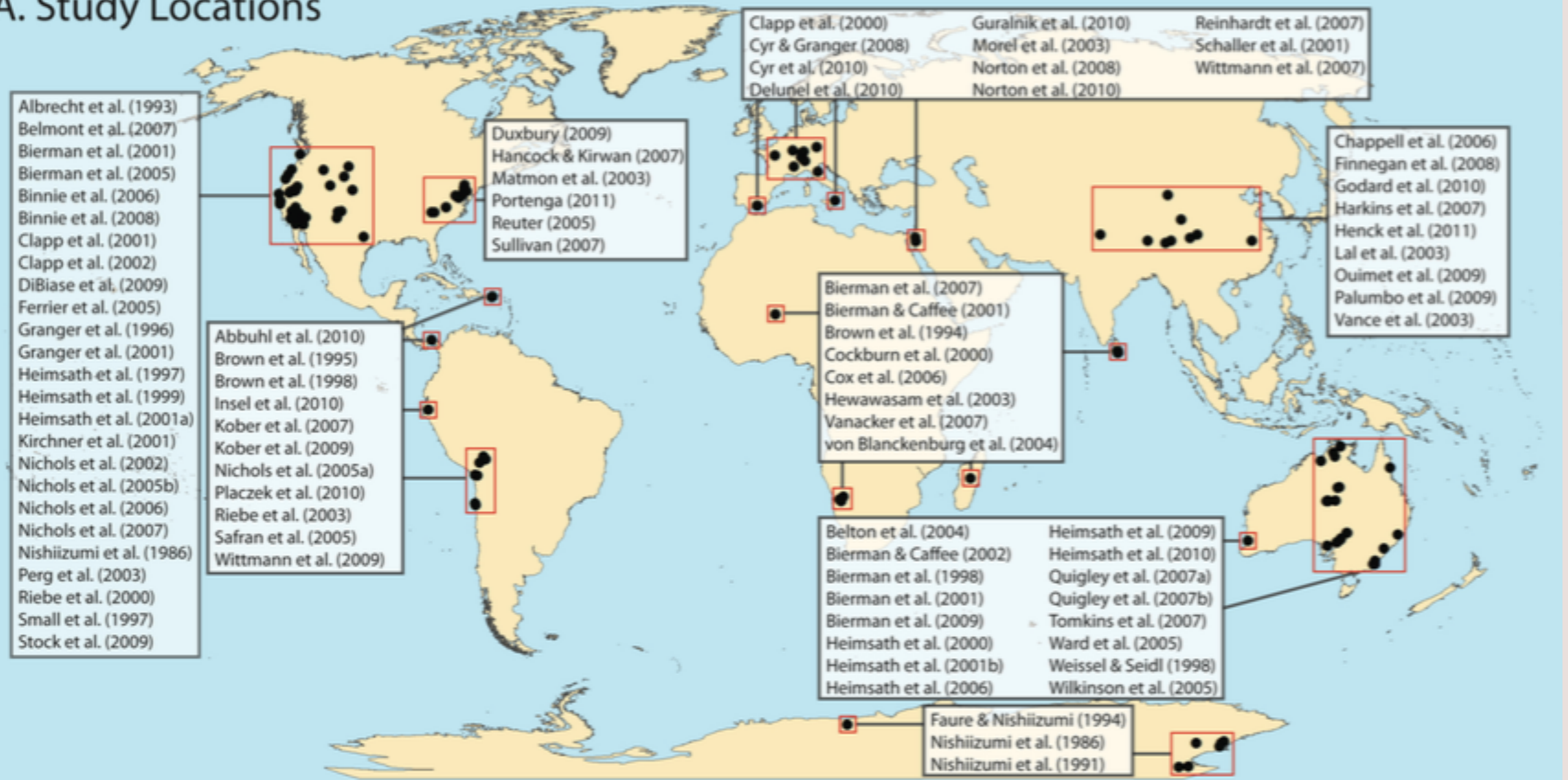
Gosse and Phillips 2011



Jungers et al. 2009

Sites around the world with known in situ-derived erosion rates

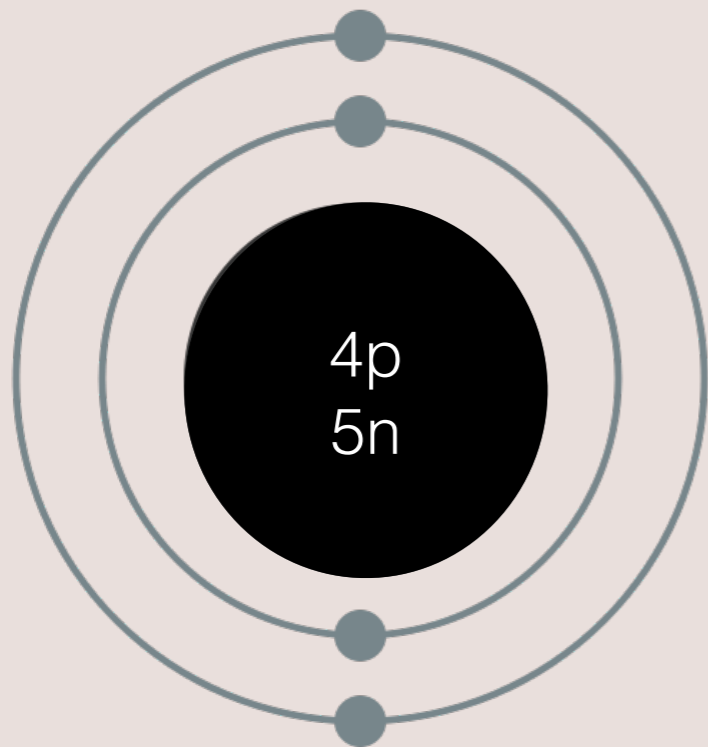
A. Study Locations



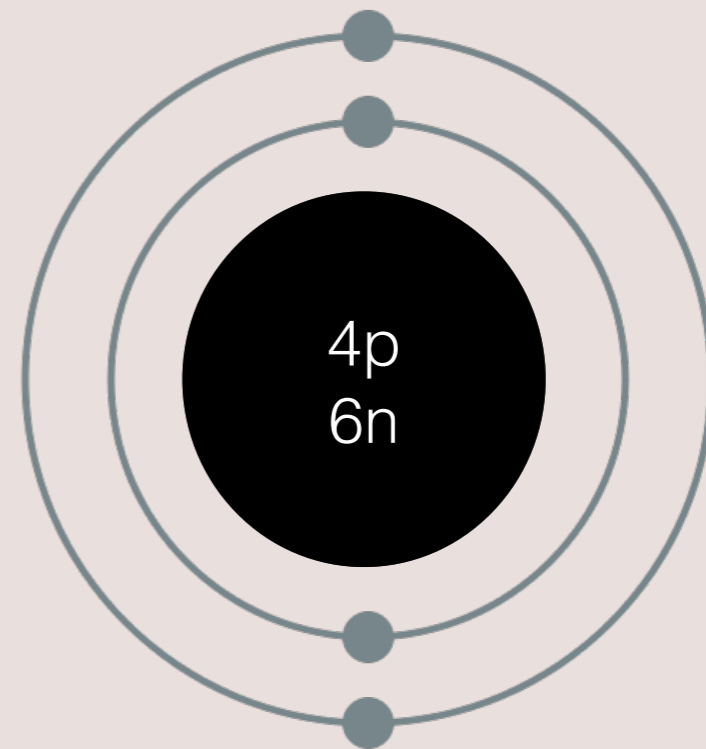
Portenga and Bierman 2011

The best of both worlds?

- Measuring meteoric ^{10}Be , but normalizing for grain size and remobilization
- What has a similar reactivity as meteoric ^{10}Be that is also present in surficial materials?



^9Be



^{10}Be

^9Be

- Weathers out of bedrock
- Not limited to sand-sized quartz grains
 - ^9Be present in grains and grain coatings, but only the grain coating should relate to meteoric ^{10}Be

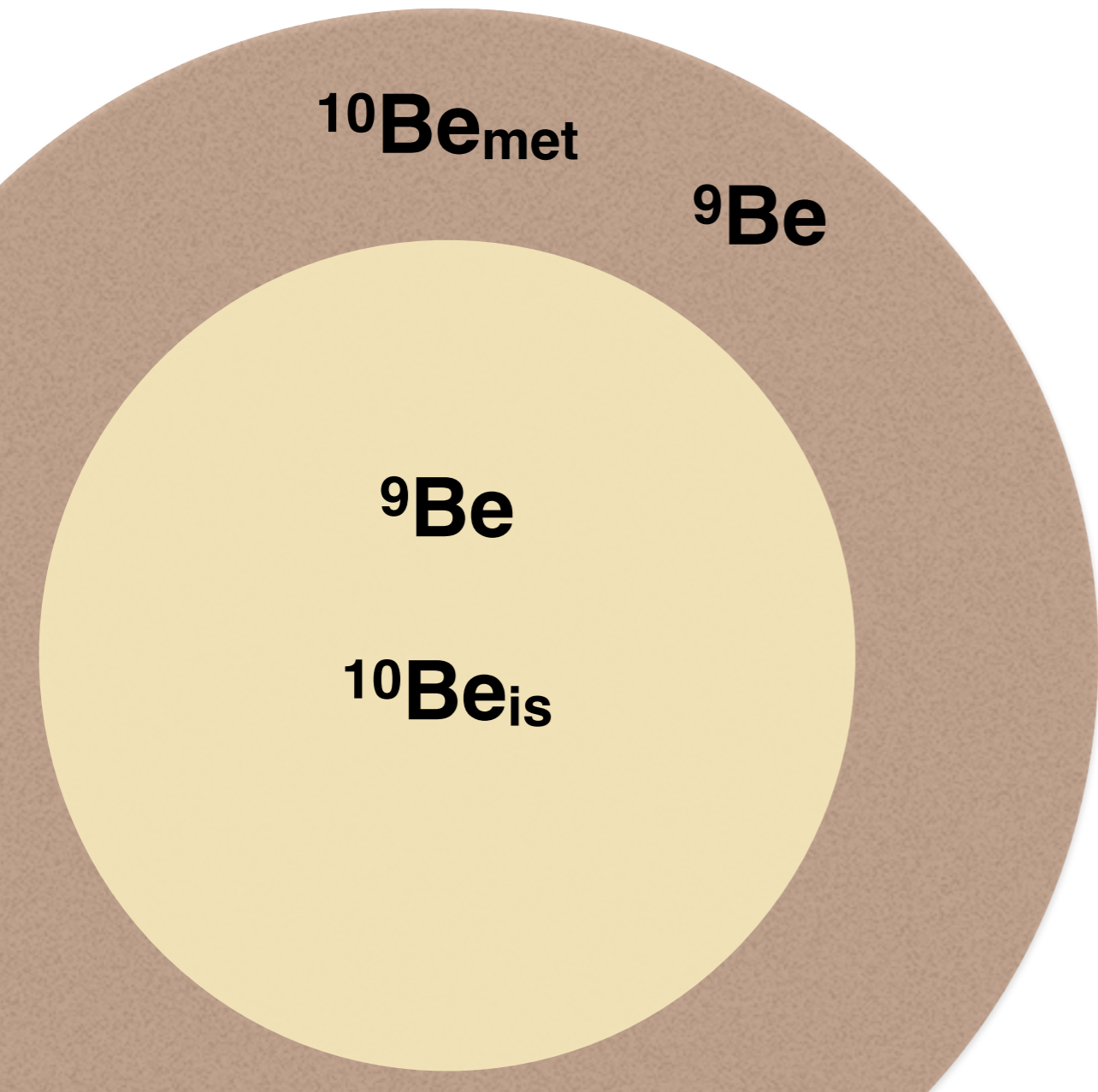
A diagram showing a cross-section of a grain. The inner part is a large yellow semi-circle labeled 'Crystalline Matrix with some ^9Be '. It is surrounded by a thin brown layer labeled 'grain coating with "mobile" ^9Be '. Above the brown layer is a thin green layer.

grain coating with "mobile" ^9Be

Crystalline Matrix with some ^9Be

In Review:

$$\frac{{}^{10}\text{Be}_{\text{met}}}{{}^9\text{Be}} \propto {}^{10}\text{Be}_{\text{is}}$$



Research questions:

- Are $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratios useful as a proxy for $^{10}\text{Be}_{\text{is}}$ derived erosion rates?
- In soil profiles, are $^{10}\text{Be}_{\text{met}}/{}^9\text{Be}$ ratios similar to $^{10}\text{Be}_{\text{is}}$ trends?
- Overall, what does the concentration and location of ${}^9\text{Be}$ in grain coatings tell us about Be during pedogenesis?

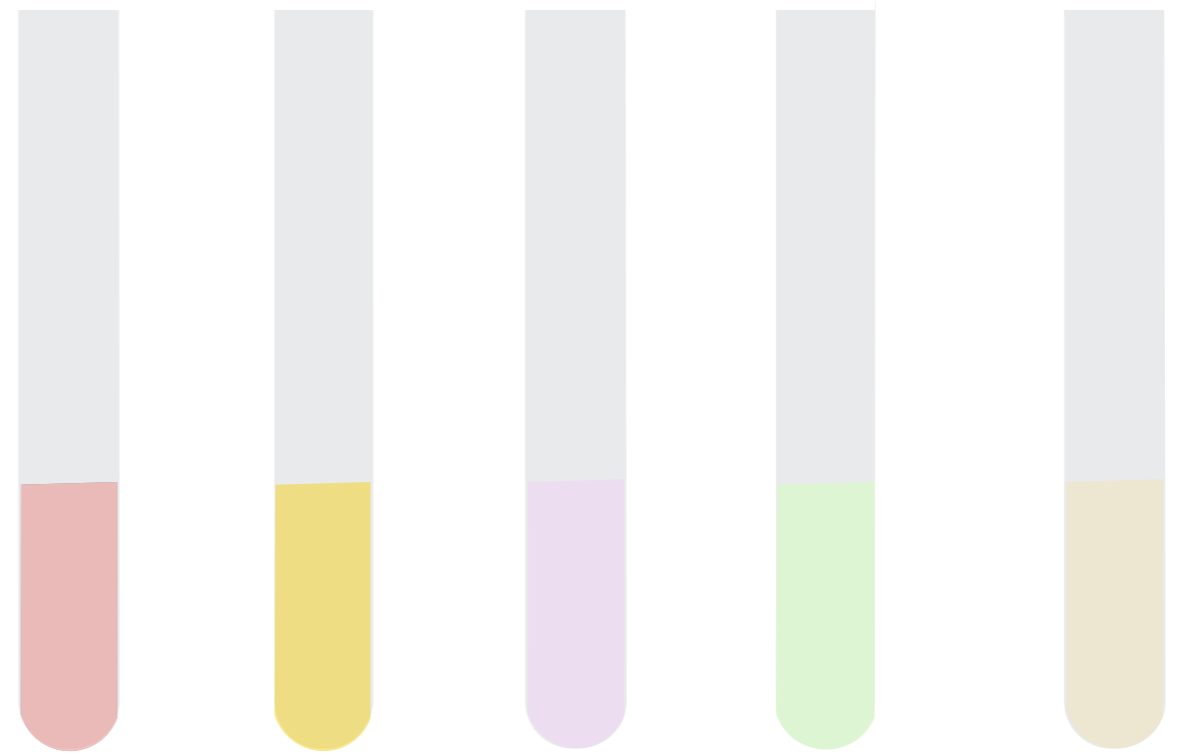
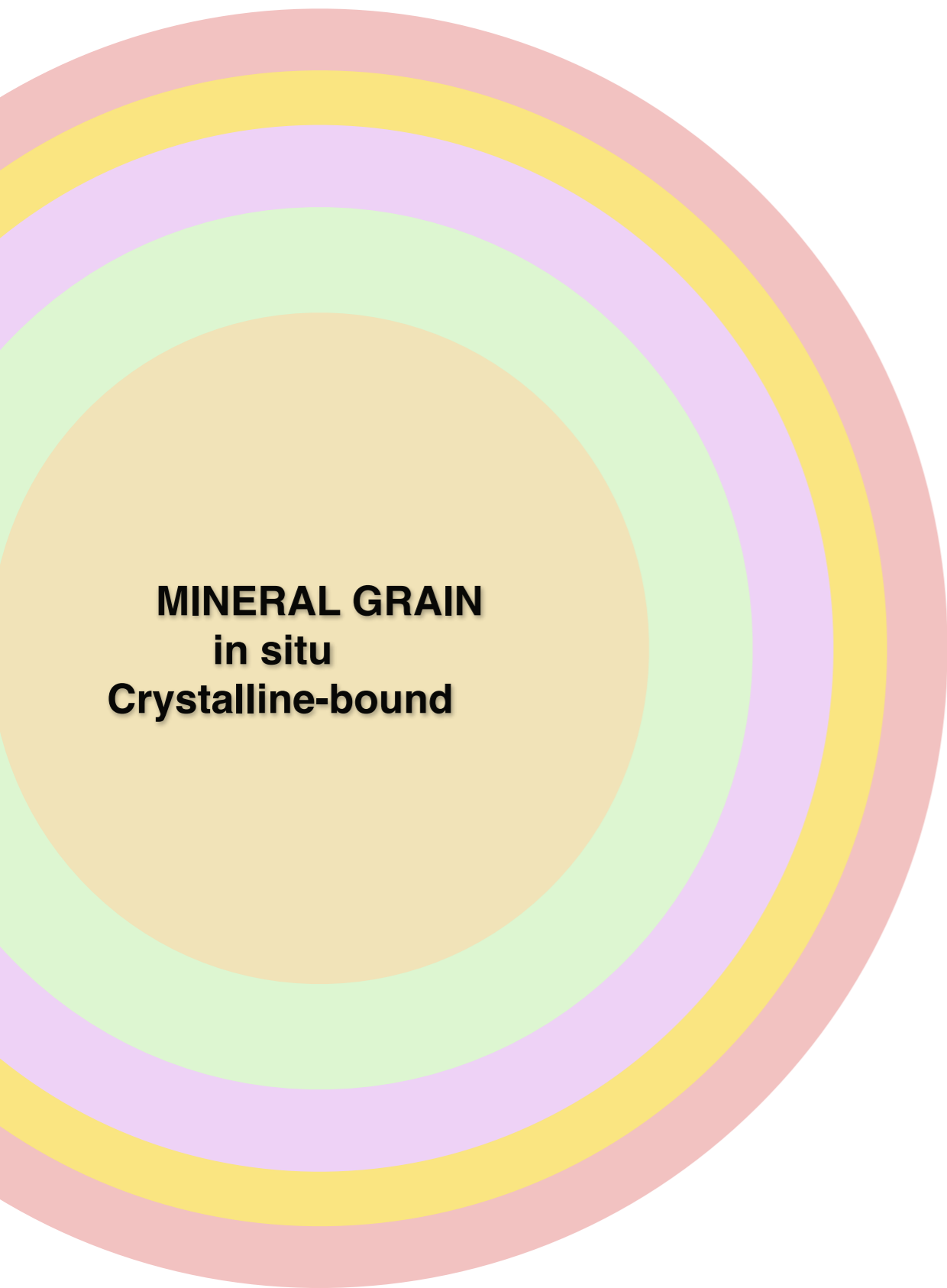
What I have:

- Access to 10 sample sets that have already be analyzed for $^{10}\text{Be}_{\text{met}}$ and $^{10}\text{Be}_{\text{is}}$

What I have to do:

- Extract ^9Be from those samples both by stripping the entire grain coating and extracting from the grain sequentially.
- Compare $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios to existing erosion rate data to determine if correlations exist.
- Use ^9Be sequential extraction results to determine if the nature of the Be-grain association corresponds to Be mobility.

Sequential Extractions of ^9Be



Exchangeable — BaCl_2

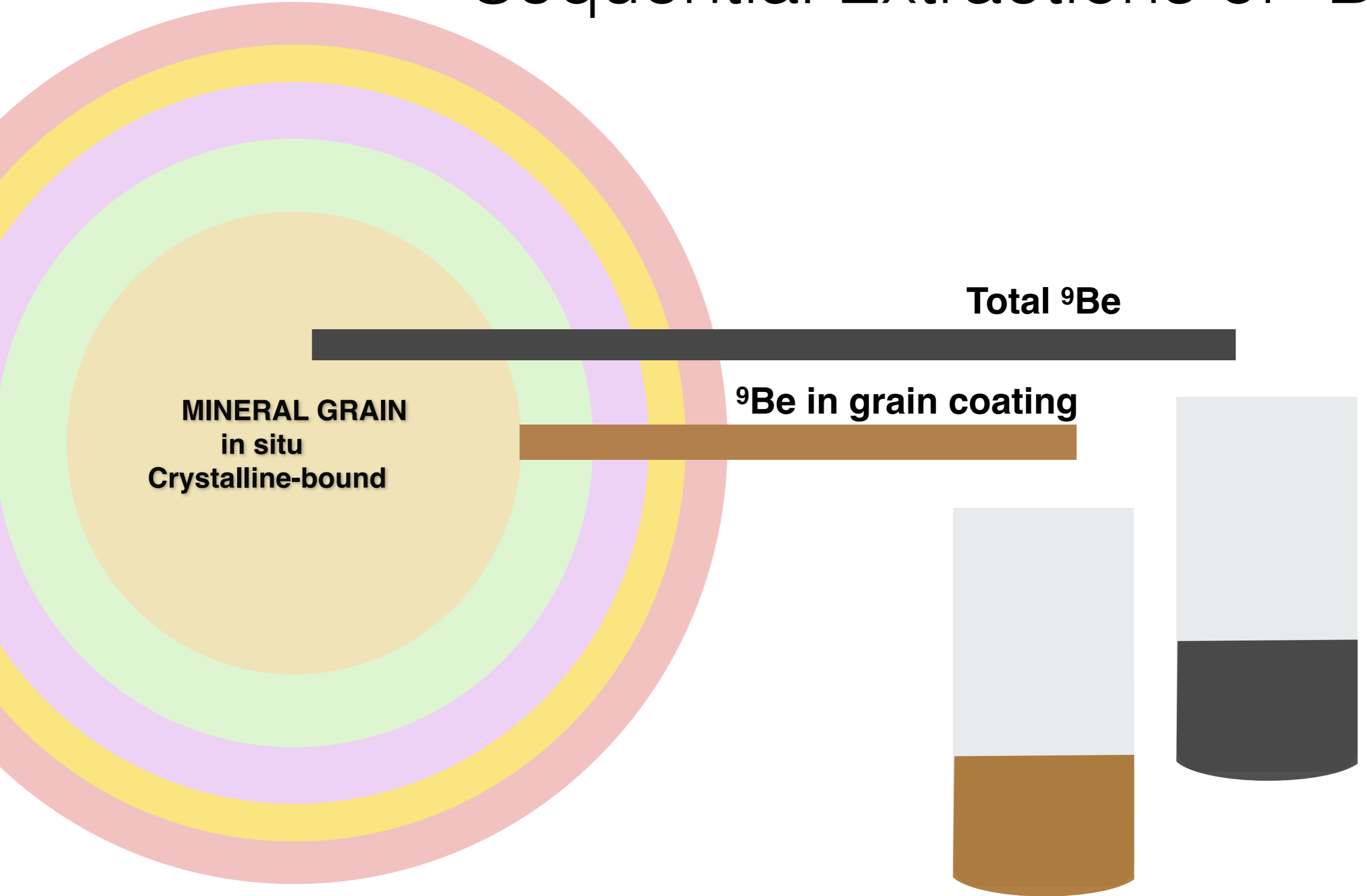
Amorphous Oxide-Bound — HCl

Crystalline Oxide-Bound — HH

Organic-Bound — HNO_3 and H_2O_2

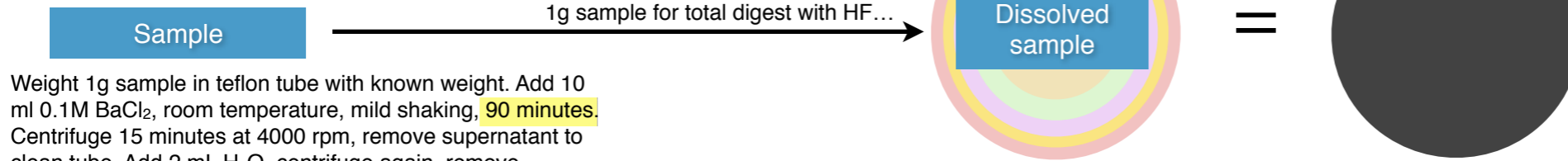
Residual — Total Digest

Sequential Extractions of ^9Be

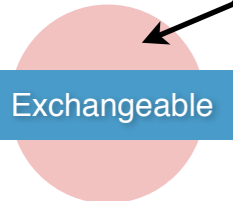


Sequential Extractions Method (modified from Wittmann et al. 2012)

If possible, check to see the grain size of powdered sample

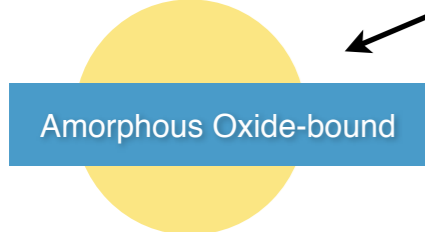


Weight 1g sample in teflon tube with known weight. Add 10 ml 0.1M BaCl₂, room temperature, mild shaking, 90 minutes. Centrifuge 15 minutes at 4000 rpm, remove supernatant to clean tube. Add 2 mL H₂O, centrifuge again, remove supernatant and add to the new tube. Weigh remaining material.



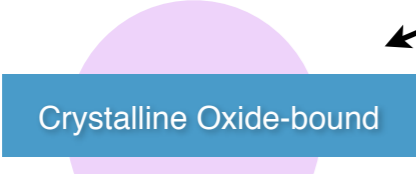
R

Add 10 ml 0.5M HCl, more if carbonates are present, and mix well to dissipate pellet from centrifuge. Agitate gently for 24 hours C (on shaking hotplate), centrifuge, rinse and weigh as in 1st step.



R

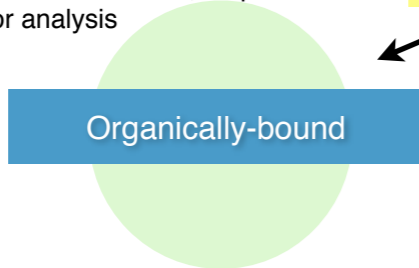
Add 10 ml 1M HH in 1 M HCl and mix well. Heat at 90 C for 4 hrs on shaking hotplate, centrifuge, rinse and weigh.



R

(If HH is a problem on the ICP OES) remove HH by adding mixture of concentrated HNO₃ and H₂O₂, dry at 70 C, (repeat if solution not clear), dissolve in 10 ml 3 M HNO₃, aliquots for major and minor analysis

Add 2 ml of 0.01M HNO₃ and 10 M H₂O₂, place on hotplate at 80 C for 2 hrs, add 1 ml H₂O₂ and leave for another hour, add 2 ml 0.01M HNO₃ and leave another hour, centrifuge, rinse, and weigh.

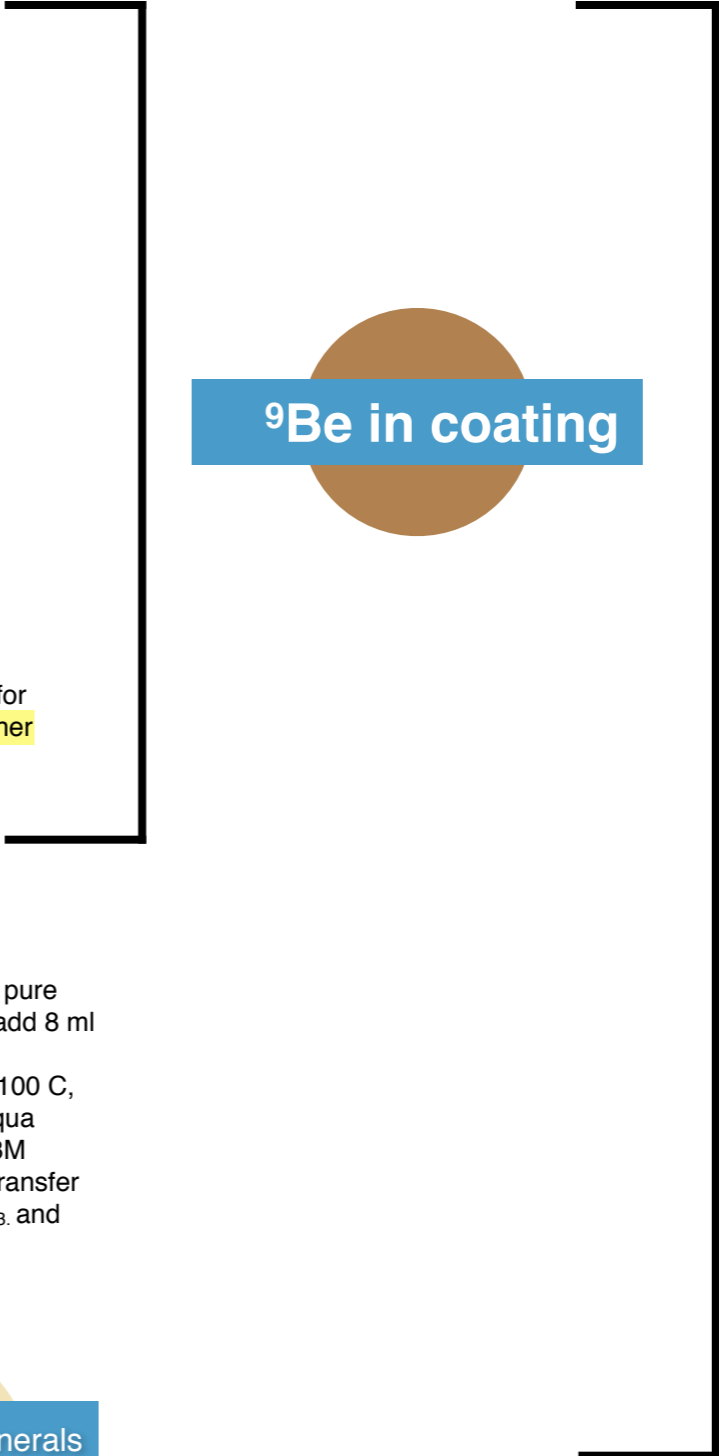


R

Wash remaining sediment with ultra pure H₂O, transfer to microwave vessel, add 8 ml HNO₃, 5 ml HCl, and 5 ml HF, run microwave. Dry close to dryness at 100 C, run microwave reactor again with Aqua Regia, dry again at 70 C. Add 1 ml 3M HNO₃ and heat at 80 C for 1 hour. Transfer to new tube, add 8-9 ml or 3M HNO₃. and take aliquots for analysis.



Compare the sum of all fractions to the total digest of the untreated sample



Measuring concentrations on the ICP-OES

- Installing the ultrasonic nebulizer to decrease detection limits



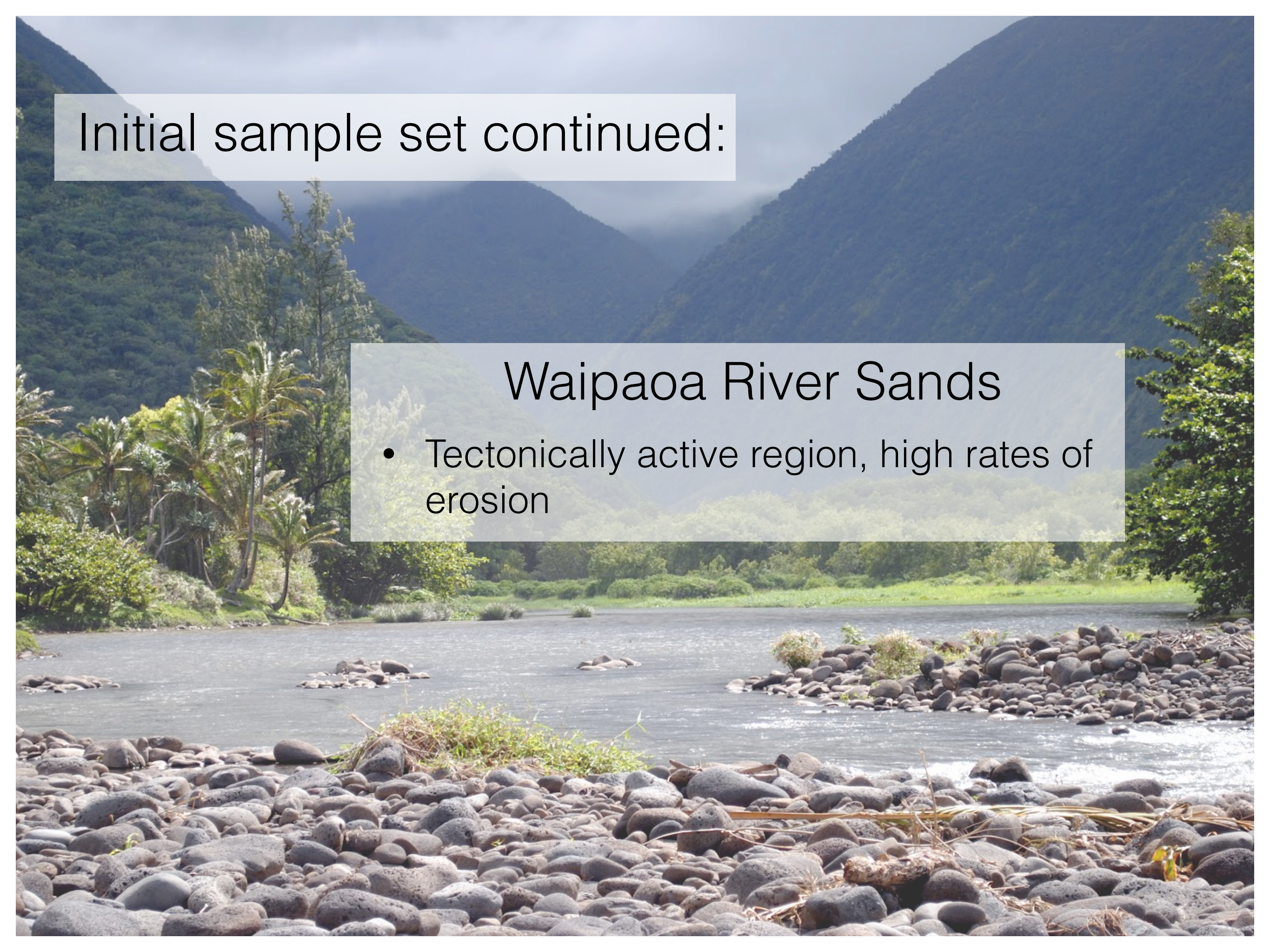
- Monitor Si content



Initial sample sets: phase 1

Scottish Peat Soil Pit

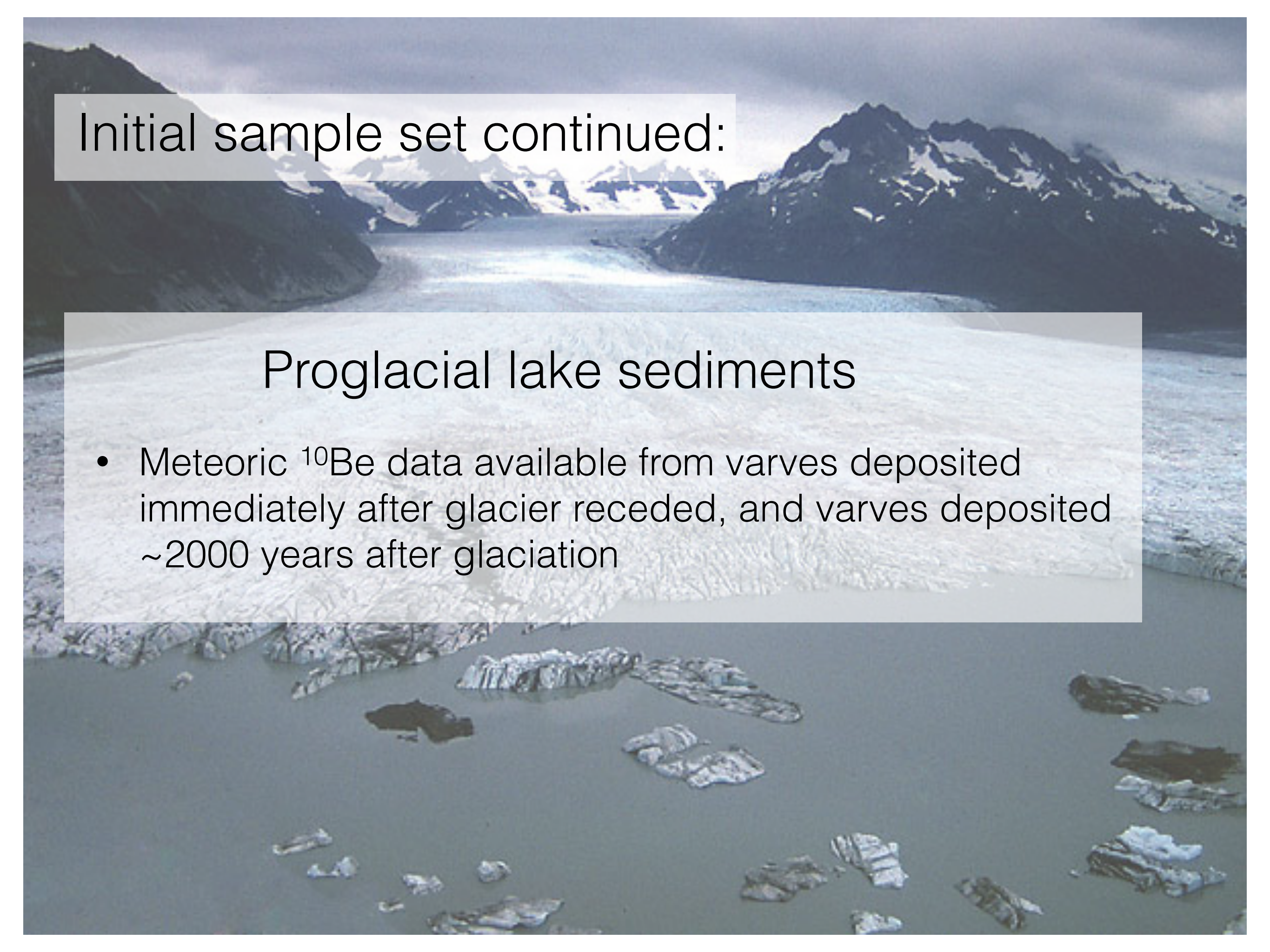
- Acidic conditions, lots of organic material, tephra



Initial sample set continued:

Waipaoa River Sands

- Tectonically active region, high rates of erosion



Initial sample set continued:

Proglacial lake sediments

- Meteoric ^{10}Be data available from varves deposited immediately after glacier receded, and varves deposited ~2000 years after glaciation

Phase 2: testing ratio across climatic and tectonic regimes

sample	climate	soil type	tectonic setting	rock type/parent material	precip (mm/yr)	pub sources	in situ met sample pairs	sediment yield data?
Susquehanna River Sands	humid temperate, glaciated	n/a	passive margin	deformed metamorphic rocks, fold and thrust belt with sandstone, shale, and carbonate, far N and W sandstone and shale	800-1300	Joanna Reuter, UVM thesis	17 paired	yes
NAVC varves	glacial and immediately post glacial	n/a	passive margin	metamorphic and igneous intrusive (granites)	no data	NAVC proposal	200+ met only	sort of...varve thickness
Scottish soil profile	humid temperate, glaciated	blanket bog peat over glacial till	passive margin	metamorphic and igneous intrusive	~1100	Fuklop et al. 2015	18 paired	n/a
Potomac River Sands	humid temperate, never glaciated	n/a	passive margin	deformed metamorphic rocks, sandstone, shale, and carbonate	890-1320	Trodick 2011	62 met, 8 paired	yes
Barron River Sands (NE Australia)	humid, tropical, never glaciated	n/a	passive margin	granitic and biogenetic carbonate	900-2500	Nichols et al. 2014	15 paired	modeled
Georges River Sands (SE Australia)	humid temperate, never glaciated	n/a	passive margin	triassic sandstone, granodiorite	800-1300	not published	9 paired	modeled
China, 3 Rivers Region Sands	tropical, never glaciated	n/a	tectonically active	lightly metamorphosed granite and sedimentary	500-1000	not published	>120 paired	some
Nambian River Sands	sub-humid to hyperarid, tropical, never glaciated	n/a	passive margin	granitic and gneissic	25-400	Some in Bierman and Caffee, 2001	12 paired	no
Waipoia River Sands	temperate, humid, never glaciated	n/a	tectonically active	carbonate bearing silt and sandstone	1000-1500	Reusser and Bierman 2010, not all data published	90 met; 18 paired	yes
Waipoia River Soil Pit	temperate, humid, never glaciated	pumice and podzol	tectonically active	river terrace sand and silt derived from carbonate bearing silt and sandstone	1000-1500	Reusser et al. 2010	13 met only	n/a
Great Smokey Mountains soil profiles	temperate, never glaciated	Inceptisols	passive margin	meta-siltstone, metamorphosed conglomeratic sandstone, carbonates and gneiss	1400-2300	Jungers et al., 2009	59 paired	n/a

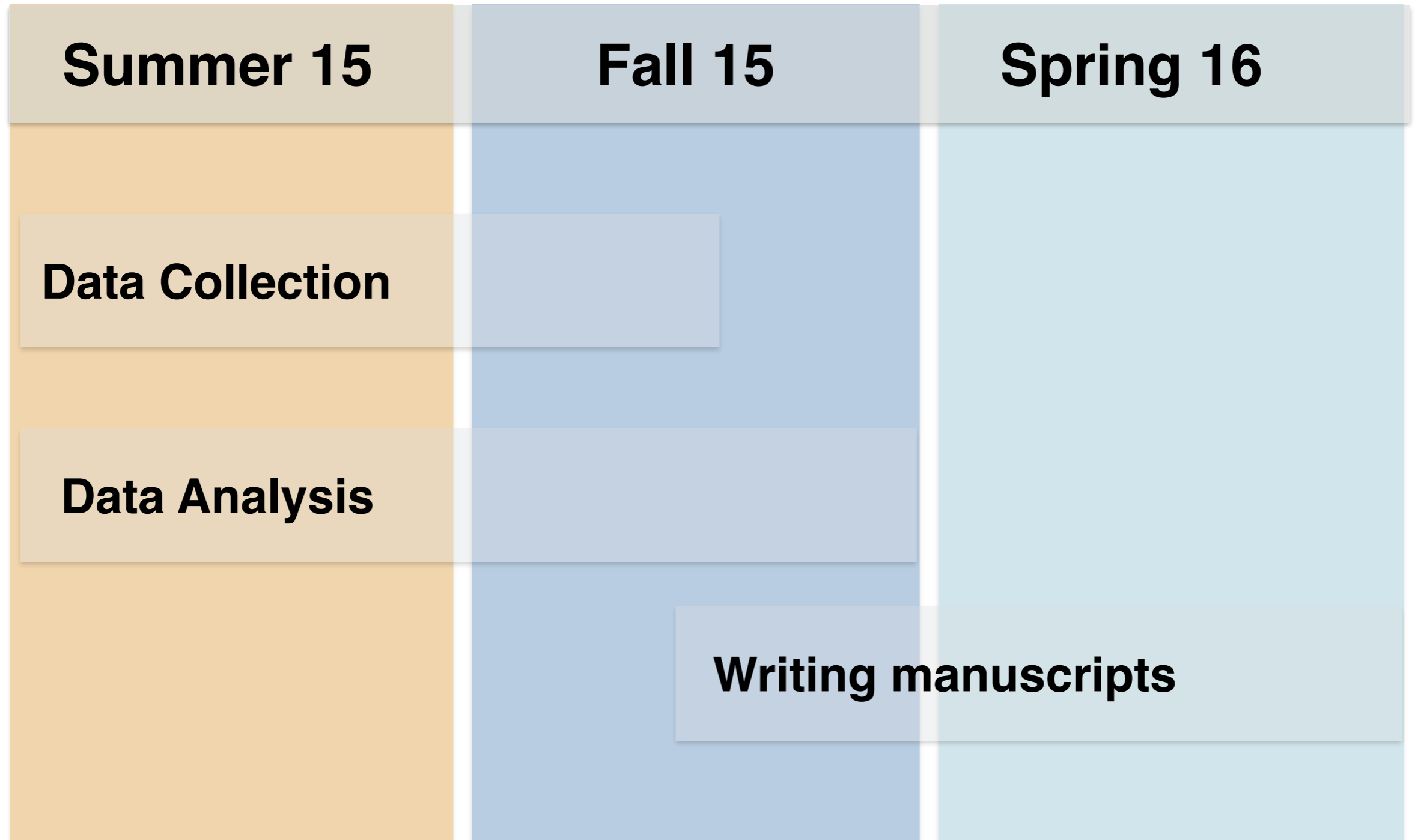


Potential problem:

^9Be concentrations tend to be between 10 and 300 ppm in coal, but 2000 ppm has been measured.

For samples in coal rich areas, coal could provide additional ^9Be to our samples

Timeline

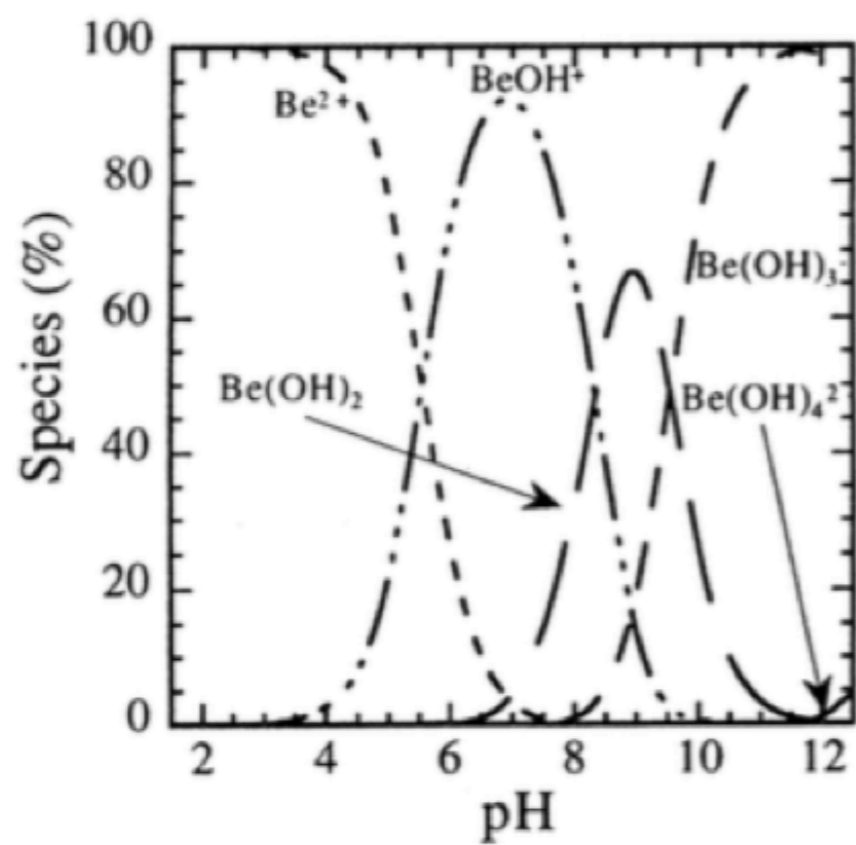


Thanks! Any Questions?

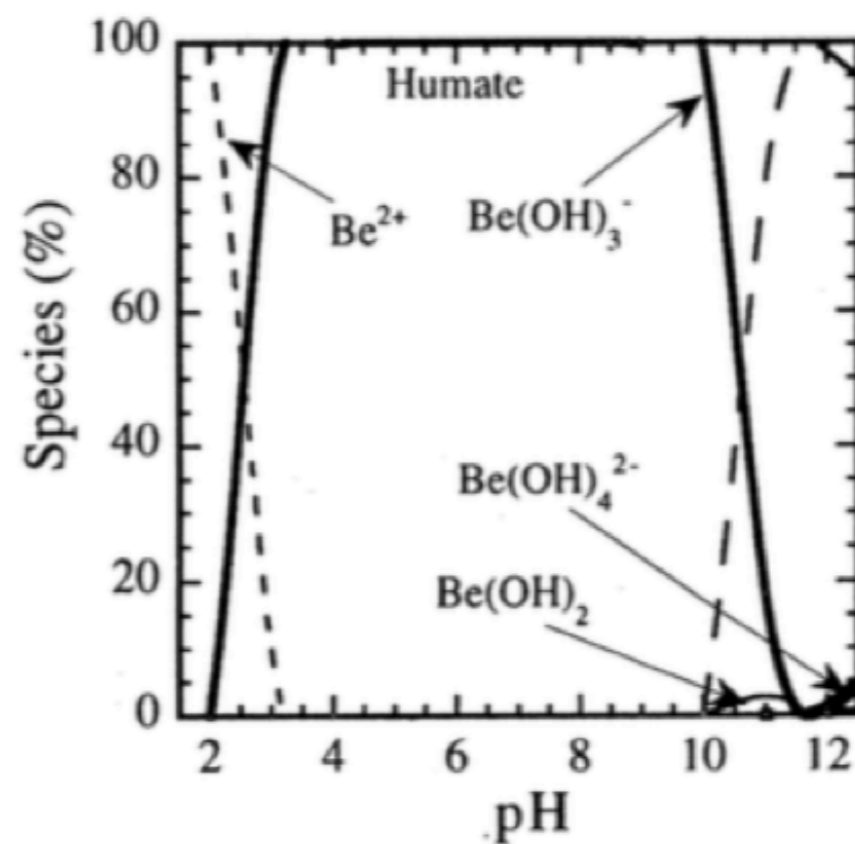


(A) In the absence of humic acid

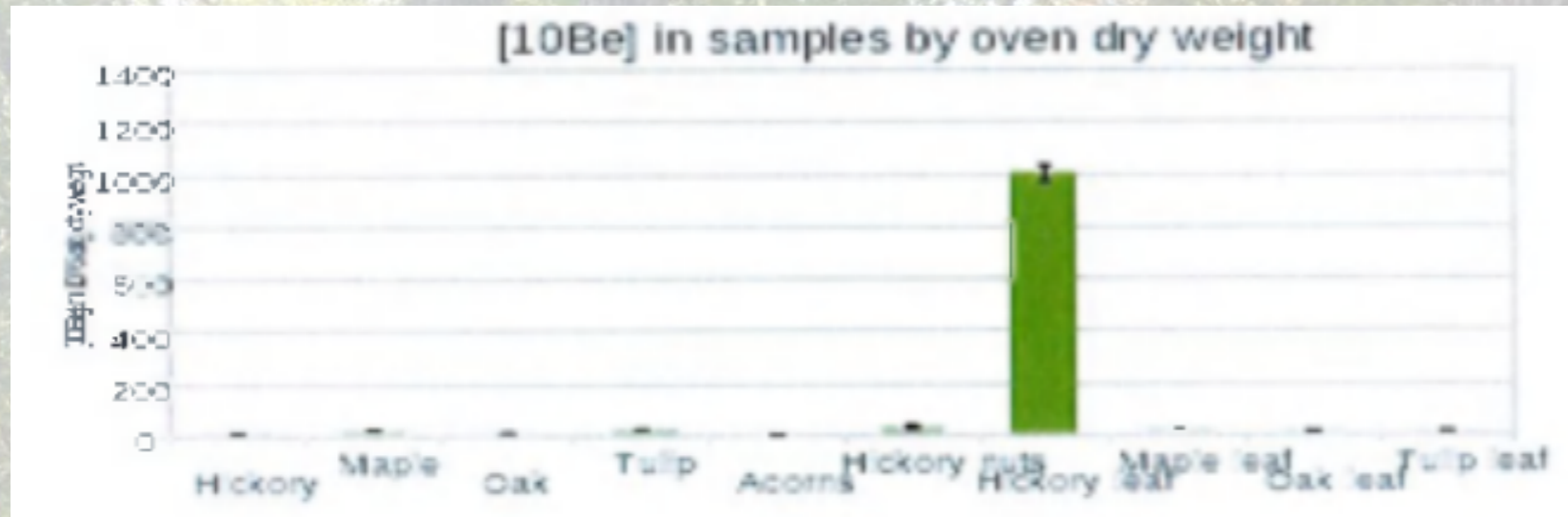
Be



In the presence of humic acid



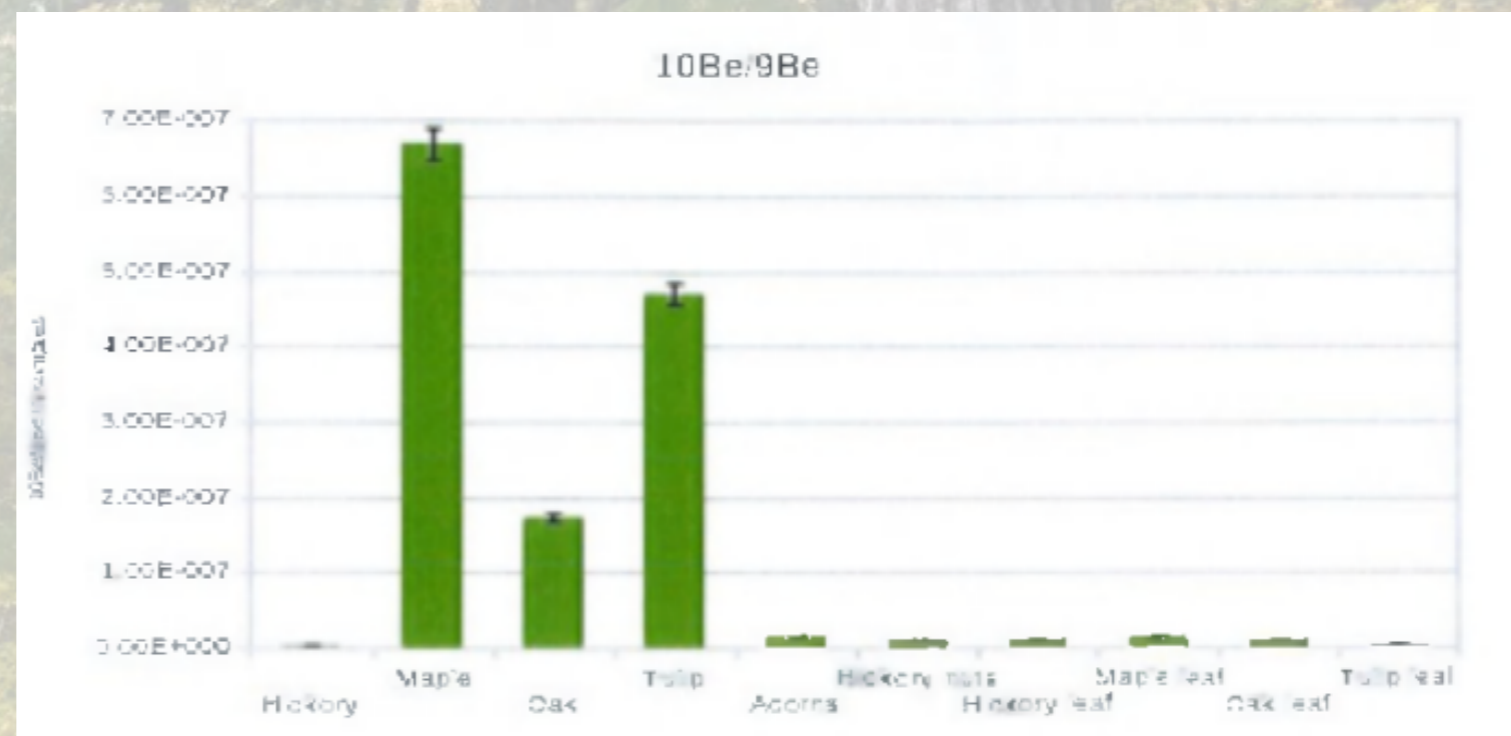
Does meteoric ^{10}Be bioaccumulate?



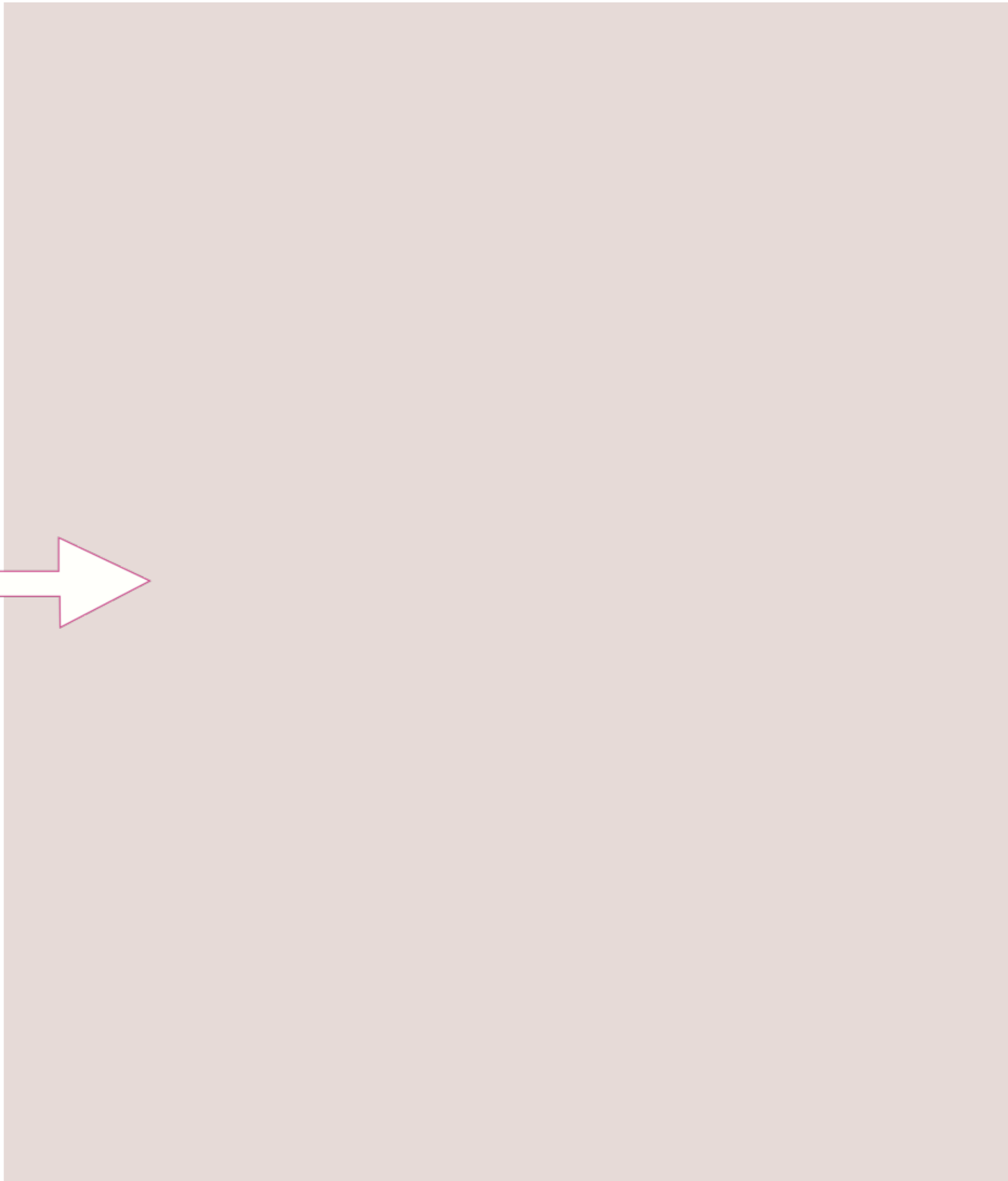
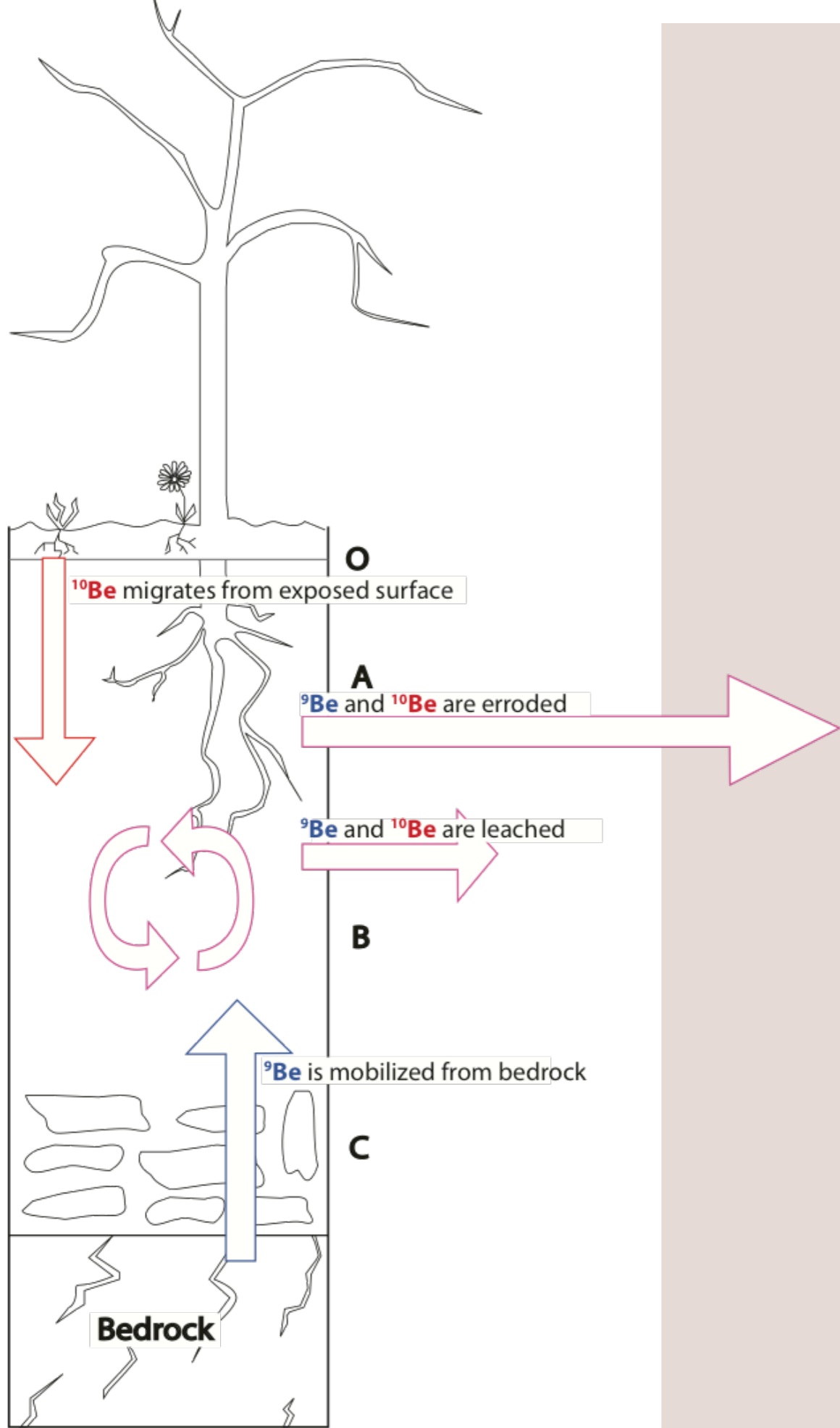
3 orders of magnitude difference between ^{10}Be in Hickory and other trees measured and surrounding soils

Conyers 2014

All samples, biomass and soil, within an order of magnitude



Conyers 2014



<u>Horizon</u>	<u>Characteristics</u>
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O	organic rich
A	organic rich, permeable and leached
B	Clayey, Al + Fe oxyhydroxides
C	Region of active alteration of parent material
Bedrock	



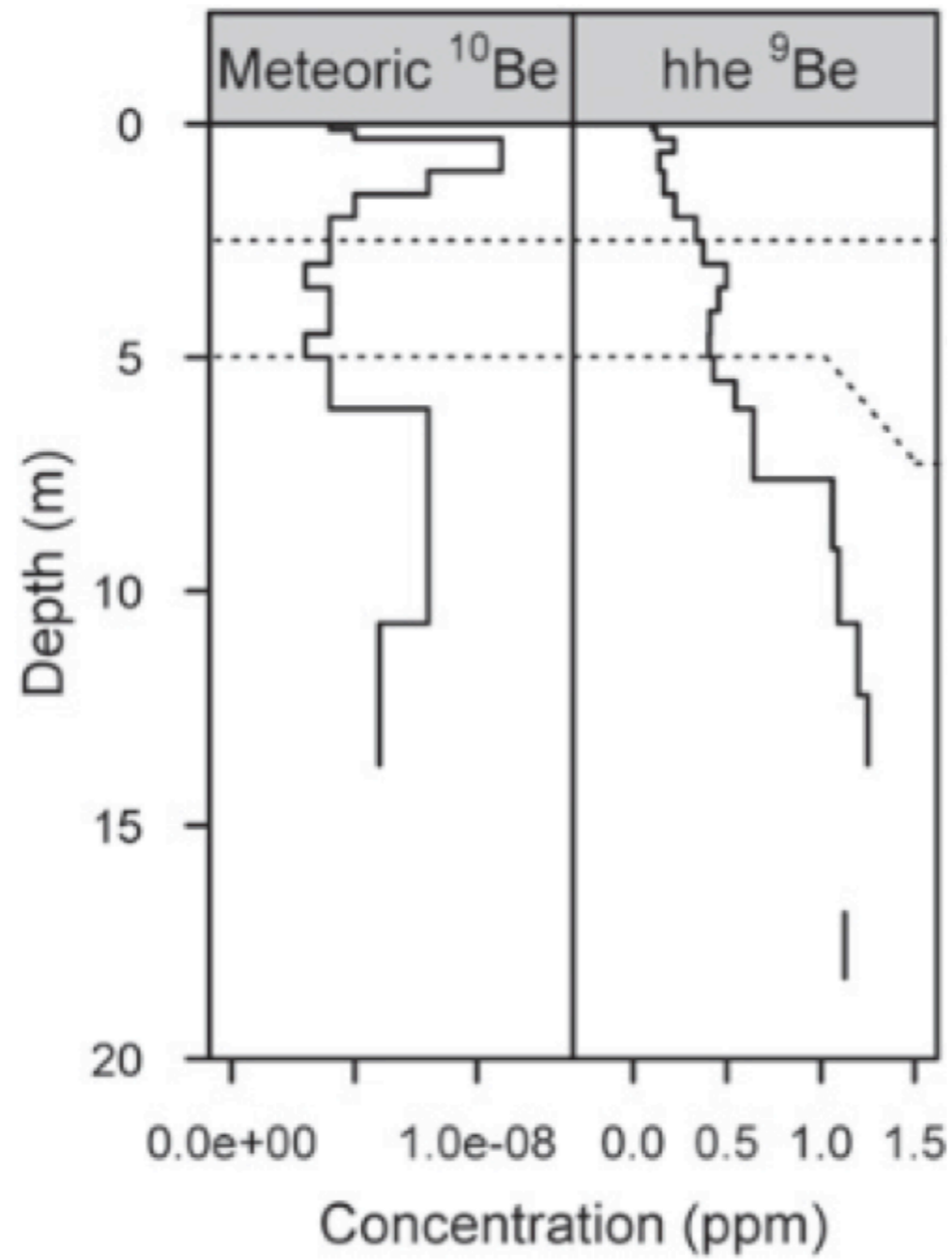
First equilibration of Be and ^9Be in solution and in absorbed phases

Partial dissolution of authigenic minerals (?) and release of ^{10}Be and ^9Be in dissolved phases

Percolation of acidic solutions
Principal zone for weathering and formation of clay minerals

Direction of Weathering Front

Barg et al. 1992



Hypotheses

Relatively few studies of ^9Be sequential extractions from soils and sediments have been performed (Barg et al. 1997, Bacon et al. 2012, Wittmann et al. 2012), so it is difficult to predict which fractions of sequential Be extraction will have the highest ^9Be concentrations. Barg et al. (1997) and Wittmann et al. (2012) show that Be accumulates in organic-rich and clay-rich layers of soils. I therefore hypothesize that the sequential extraction fractions that selectively dissolve organic and exchangeable phases will liberate the largest quantity of Be. However, in samples with significant amounts of humic acids, I hypothesize that the crystalline oxide and amorphous oxide-bound fractions will contain significant amount of ^9Be (Taskahashi et al. 1998). Because the total grain coating is extracted for $^{10}\text{Be}_{\text{met}}$ analysis, I hypothesize that the ^9Be from the total grain coating will result in the most meaningful relationship between ^9Be , $^{10}\text{Be}_{\text{met}}$, and long-term erosion rates. I hypothesize that there will be an increased concentration of ^9Be in grain coatings in the distal glacial lake sediments than the proximal sediments because ^9Be will have become more mobile during pedogenesis in the time after glaciation.

Many published reports show results that indicate the $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratio normalizes $^{10}\text{Be}_{\text{met}}$ data to account for grain size effects, $^{10}\text{Be}_{\text{met}}$ remobilizing and/or $^{10}\text{Be}_{\text{met}}$ leaching (Merrill et al. 1959, Barg et al. 1997, Bacon et al. 2012, Conyers 2014, Von Blanckenburg et al. 2012, Wittmann et al. 2010, Willenbring and von Blanckenburg 2010). Because publications indicate that $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratios could be meaningful indicators of erosion, I hypothesize that a $^{10}\text{Be}_{\text{met}}/^9\text{Be}$ ratio that includes the total ^9Be in the outside coating of grains will correlate with erosion rates calculated using $^{10}\text{Be}_{\text{is}}$ data.