Non-Traditional Isotope Laboratory

Potassium Isotope Geochemistry

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滕方振

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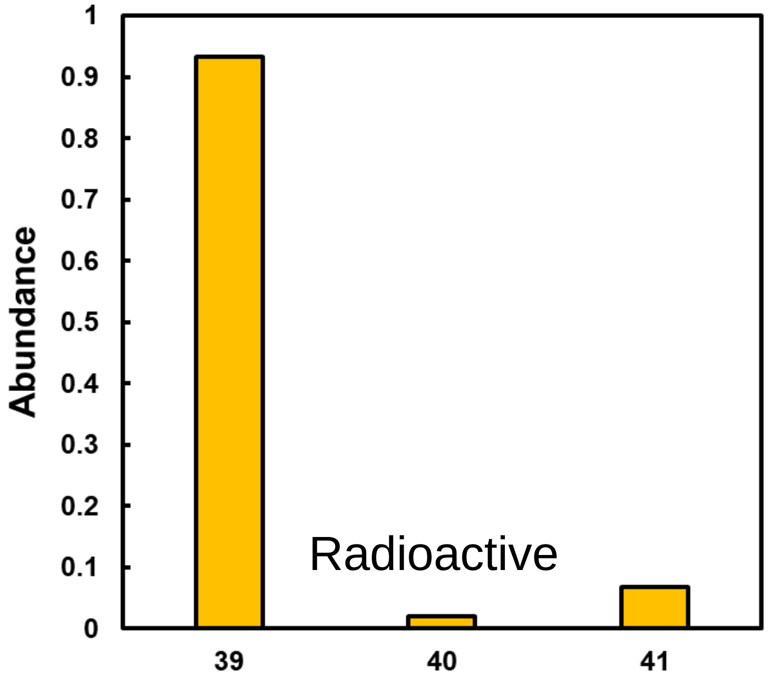
Outline

- ❑ K Isotope Analysis
- ❑ Moon-Forming Giant Impact
- ❑ Crust-Mantle Interactions
- ❑ Continental Weathering
- ❑ Biological/Medical/Others

Potassium isotope geochemistry

→ Over 5% mass difference between ^{39}K and ^{41}K

→ Large mass-dependent isotope fractionation?



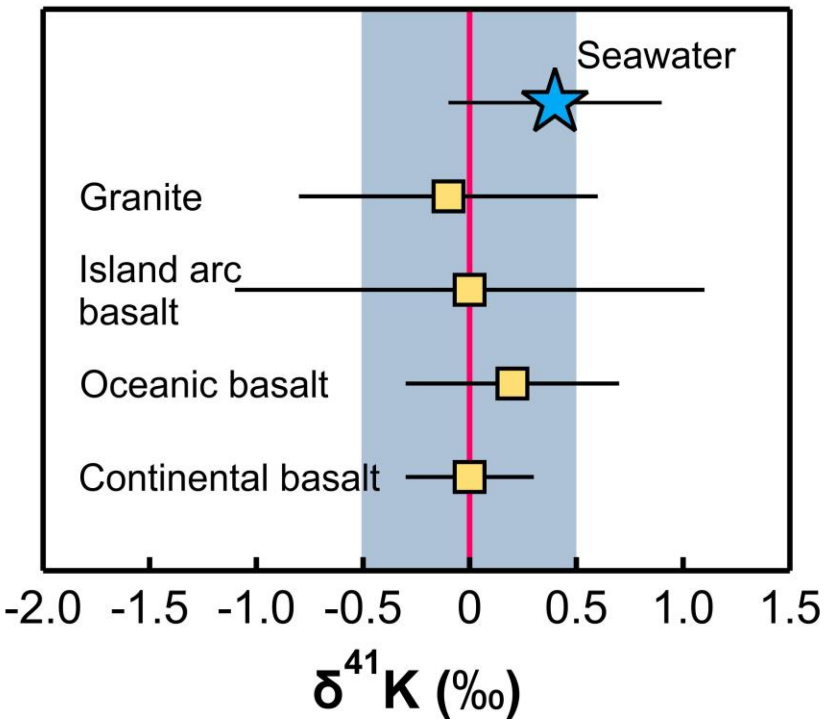
$$\delta^{41}K\ (‰) = \left[\frac{(^{41}K/^{39}K)_{sample}}{(^{41}K/^{39}K)_{std}} - 1\right] \times 10^3, \quad std = \text{NIST SRM 3141a}$$

Potassium isotope geochemistry

Large mass-dependent isotope fractionation?

Previous methods
Precision 0.5 ~ 1‰

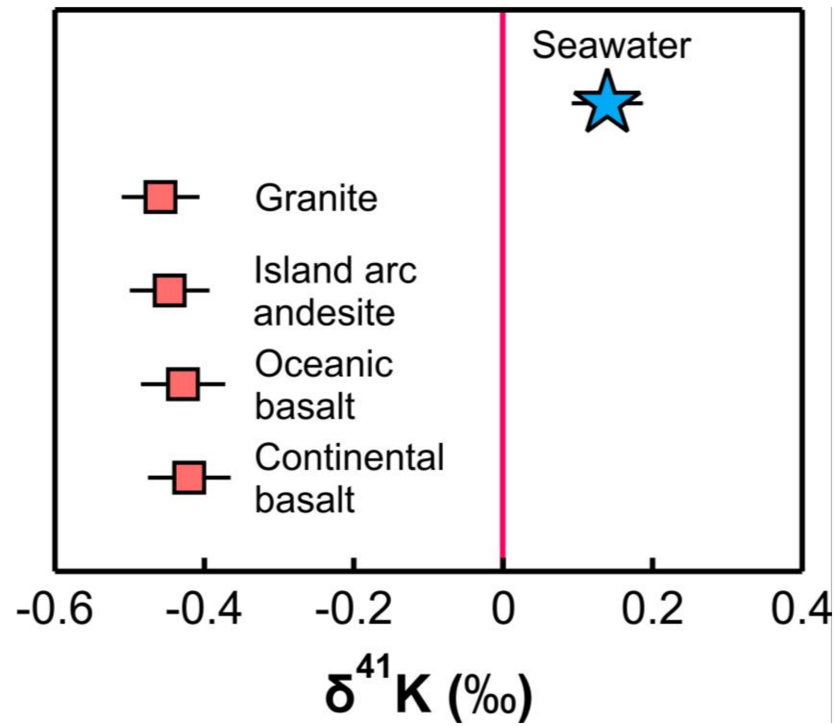
$\delta^{41}K_{Earth} = 0 \pm 0.5‰$



Humayun & Clayton, 1995

New methods (since 2016)
Precision < 0.06‰

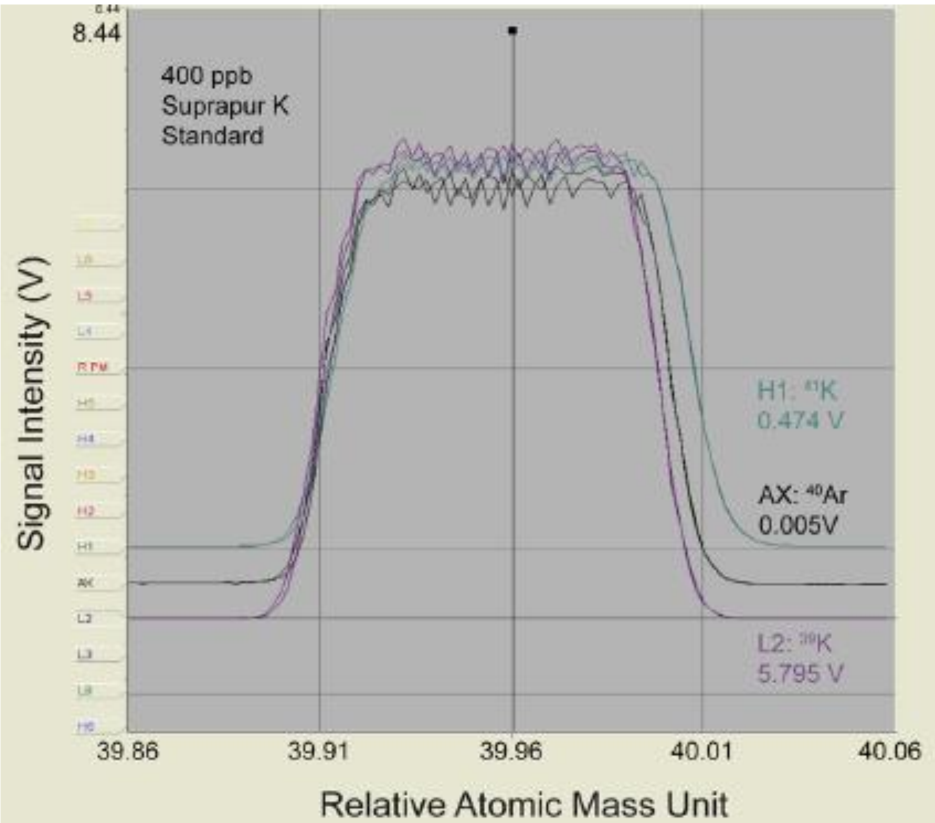
$\delta^{41}K_{Seawater} - \delta^{41}K_{Rock} = 0.6‰$



Hu et al., 2018

High-precision K isotope analysis

IsoProbe MC-ICPMS



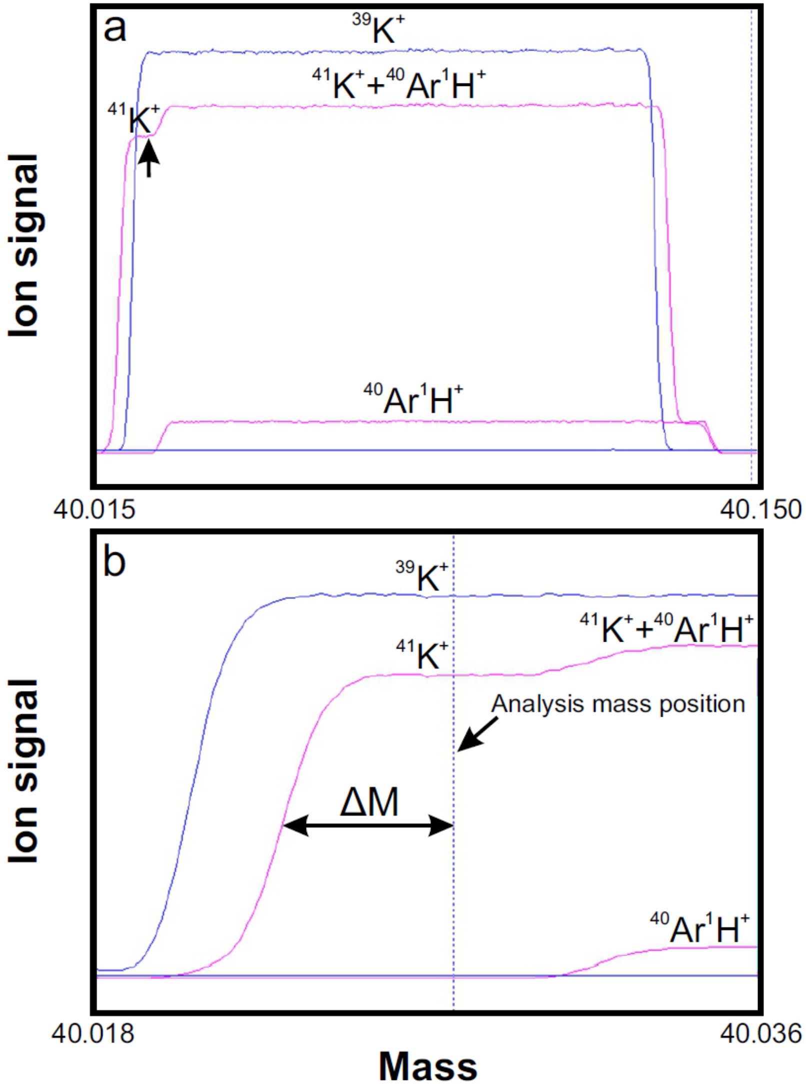
Collision cell → No HAr interference

Precision 0.05‰ (2 SE)

Wang and Jacobsen 2016 GCA

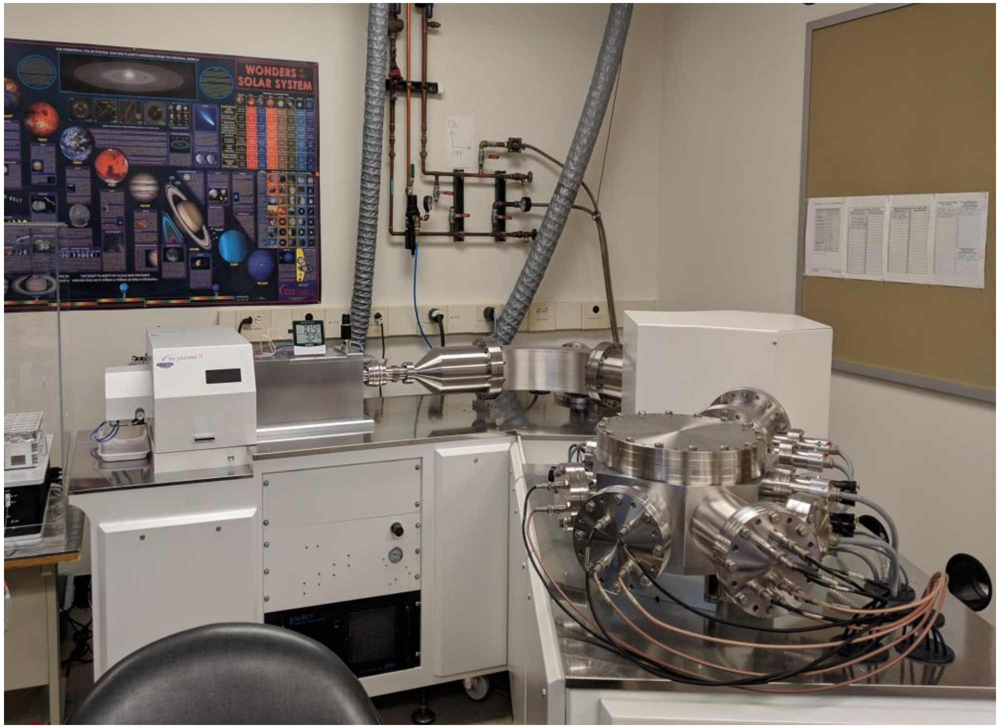
High-precision K isotope analysis

Nu Plasma II High-resolution MC-ICPMS



Major challenge: ArH interference

External precision < 0.06‰ (95% C.I.)



Hu et al., 2018 CG
Xu et al., 2019 CG

Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 178 (2016) 223–232
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

2016 IsoProbe

An estimate of the Bulk Silicate Earth potassium isotopic composition based on MC-ICPMS measurements of basalts

Kun Wang (王昆)*, Stein B. Jacobsen

Department of Earth and Planetary Sciences, Harvard University, 20 Oxford Street, Cambridge, MA 02138, USA

Received 7 September 2015; accepted in revised form 31 December 2015; Available online 3 February 2016

JAAS

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Cite this: *J. Anal. At. Spectrom.*, 2016, **31**, 1023

2016 IsoProbe

Precise measurement of stable potassium isotope ratios using a single focusing collision cell multi-collector ICP-MS†

Weiqiang Li,*[ab] Brian L. Beard[cd] and Shilei Li[e]

Chemical Geology 493 (2018) 100–108

Contents lists available at ScienceDirect

Chemical Geology

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

2018 Nu Plasma II

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,*]

[a] Isotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195-1310, USA
[b] Lunar and Planetary Science Research Center, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, Guizhou 550081, China

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High-precision $^{41}K/^{39}K$ measurements by MC-ICP-MS indicate terrestrial variability of $\delta^{41}K$†

Leah E. Morgan, [*a] Danielle P. Santiago Ramos, [b] Brett Davidheiser-Kroll, [c] John Faithfull, [d] Nicholas S. Lloyd, [e] Rob M. Ellam[f] and John A. Higgins[b]

2018 Neptune Plus

Chemical Geology 513 (2019) 101–107

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CHEMICAL GEOLOGY
ISOTOPE GEOSCIENCE

2019 Nu Plasma II

Potassium isotopic compositions of international geological reference materials

Check for updates

Ying-Kui Xu[a,b,c], Yan Hu[b,*], Xin-Yang Chen[b], Tian-Yi Huang[b], Ronald S. Sletten[d], Dan Zhu[e,c], Fang-Zhen Teng[b,*]

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c8ja00303c

2019 Neptune Plus

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 *

ARTICLE

2020 Nu Plasma 3

Optimal separation method for high-precision K isotope analysis by using MC-ICP-MS with a dummy bucket

Received 00th January 20xx,

Xiaoqiang Li, [a] Guilin Han, *[a] Qian Zhang [a, b] and Zhuang Miao [c]

Multi-Collector- Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS)

Company	*Brand*	*Year*
• VG Elemental:	*Plasma 54*	*1992*
• Micromass:	*Iso-Plasmatrace*	*1996*
• **Nu Instruments:**	***Nu Plasma***	***1997***
• GV Micromass:	*IsoProbe*	*199?*
• VG Elemental:	*Axiom*	*1998*
• **Nu Instruments**	***Nu 1700***	**1999**
• **Thermal-Fisher:**	***Neptune***	***2000***
• **Thermal-Fisher:**	***Proteaus****	***2015***
• **Nu Instruments**	***Sapphire****	**2018**

How to assure high accuracy during high-precision analysis?

数据要精确，更要准确

How to assure high accuracy during high-precision analysis

Step-by-step instructions

Step 1. analysis of pure standard by standard-bracketing method
You will get the highest precision (internal)

Step 2. put pure standards through column chemistry and analyse the column cut. – test column chemistry. In theory, you should get similar precision as step 1.

Step 3. doping experiments. Add matrix elements to pure standard to check the maximum tolerance of matrix elements – know how efficient your column chemistry needs to be.

How to assure high accuracy during high-precision analysis

Step 4. make synthetic solutions by mixing pure standard with matrix elements that match natural samples; put synthetic solutions through column chemistry. – test column chemistry for “natural samples” for precision and accuracy

Step 5. put a rock/mineral sample through column chemistry many times. – test column chemistry for “natural samples” with large amount of matrix elements that needs additional times of column chemistry

Step 6. put the same rock sample through many columns simultaneously – external precision

How to assure high accuracy during high-precision analysis

Step 7. always process at least one standard together with unknown samples. – Long-term external precision based on this standard

Step 8. Analyses of standard materials

- USGS standard materials (rock/mineral)
- IRMM standard materials (rock/mineral)
- Seawater
- Others

How to assure high accuracy during high-precision analysis

朋友圈不被封
微信号不被封
公众号不被封
微信群不被封
微博不被封
抖音不被封

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《不被拒经》

Outline

- ❑ K Isotop
- ❑ Moon-F
- ❑ Crust-M
- ❑ Contine
- ❑ Biologic

The Moon - Satellite of the Earth

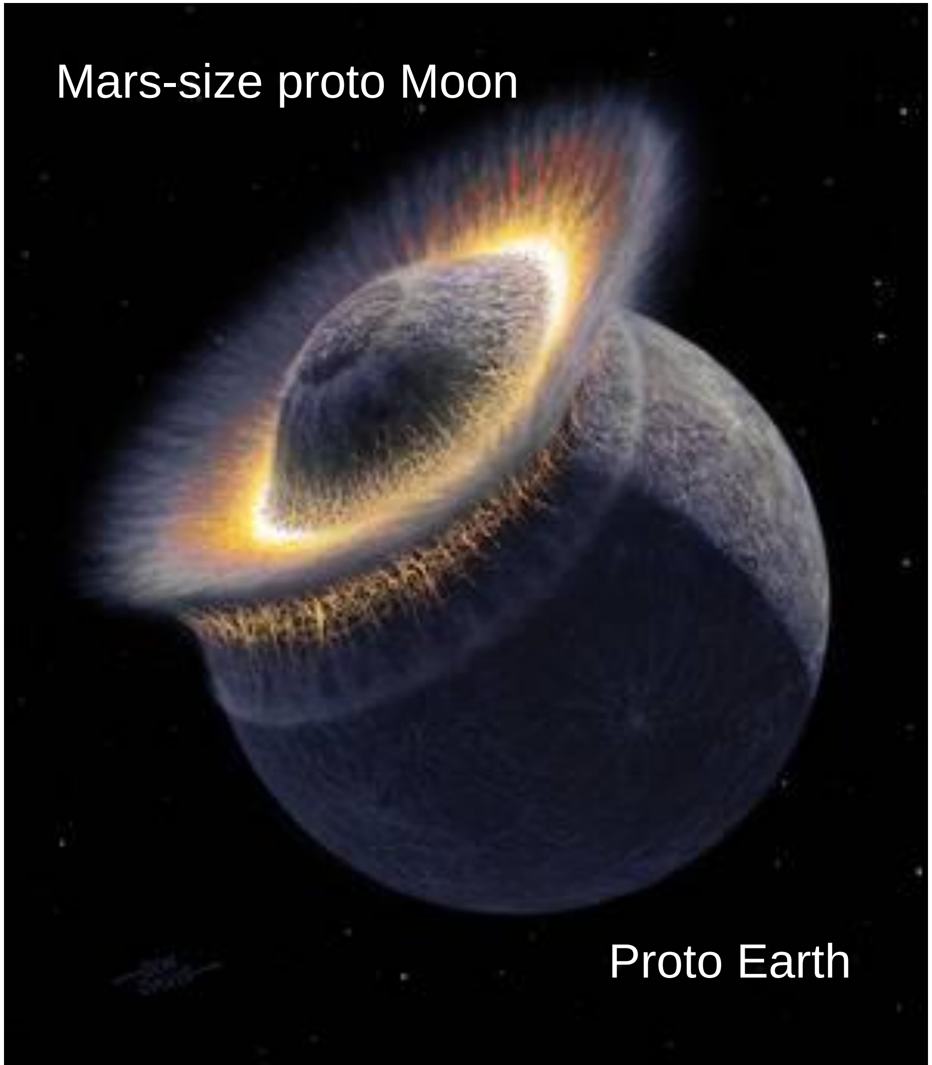
The Moon

- ¼ diameter of the Earth
- 1/100 mass of the Earth
- 3/5 density of the Earth

How did the Moon form?

Giant impact!

Hartmann and Davis 1975;Cameron and Ward 1976



Moon

Earth

Detailed questions on giant-impact theory

The nature of the impactor

- Where did the impactor come from?
- How big is the impactor?
- What is the composition of the impactor? Similar to Earth

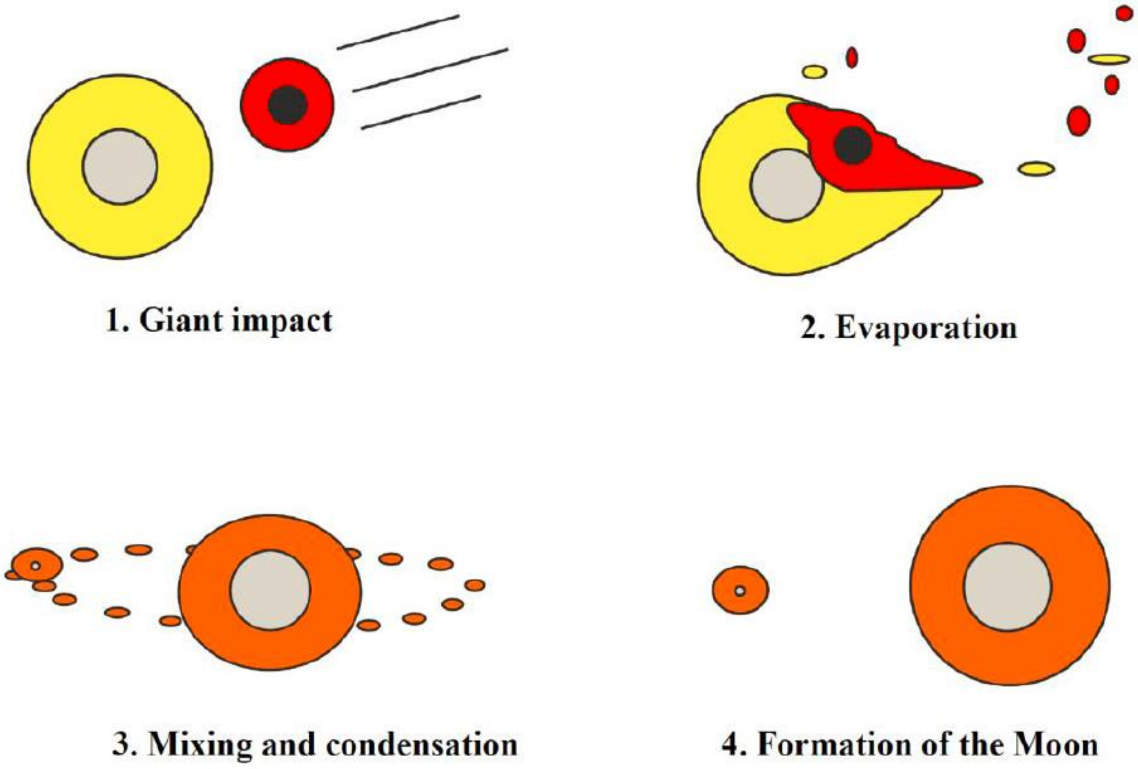
What happened during the impact

- When did it happen?
- Melting → magma ocean? Evaporation → gas? Or both?
- Well mixed between the impactor and proto-Earth?
- Open or close system i.e., anything lost to space?

After the impact: formation of the Moon and Earth

- Cool down → condensation→ collision growth→ Moon?
- Are all elements/isotopes condensated at the same time?
- The source materials for the Moon: impactor or Earth's mantle?

Giant-impact theory

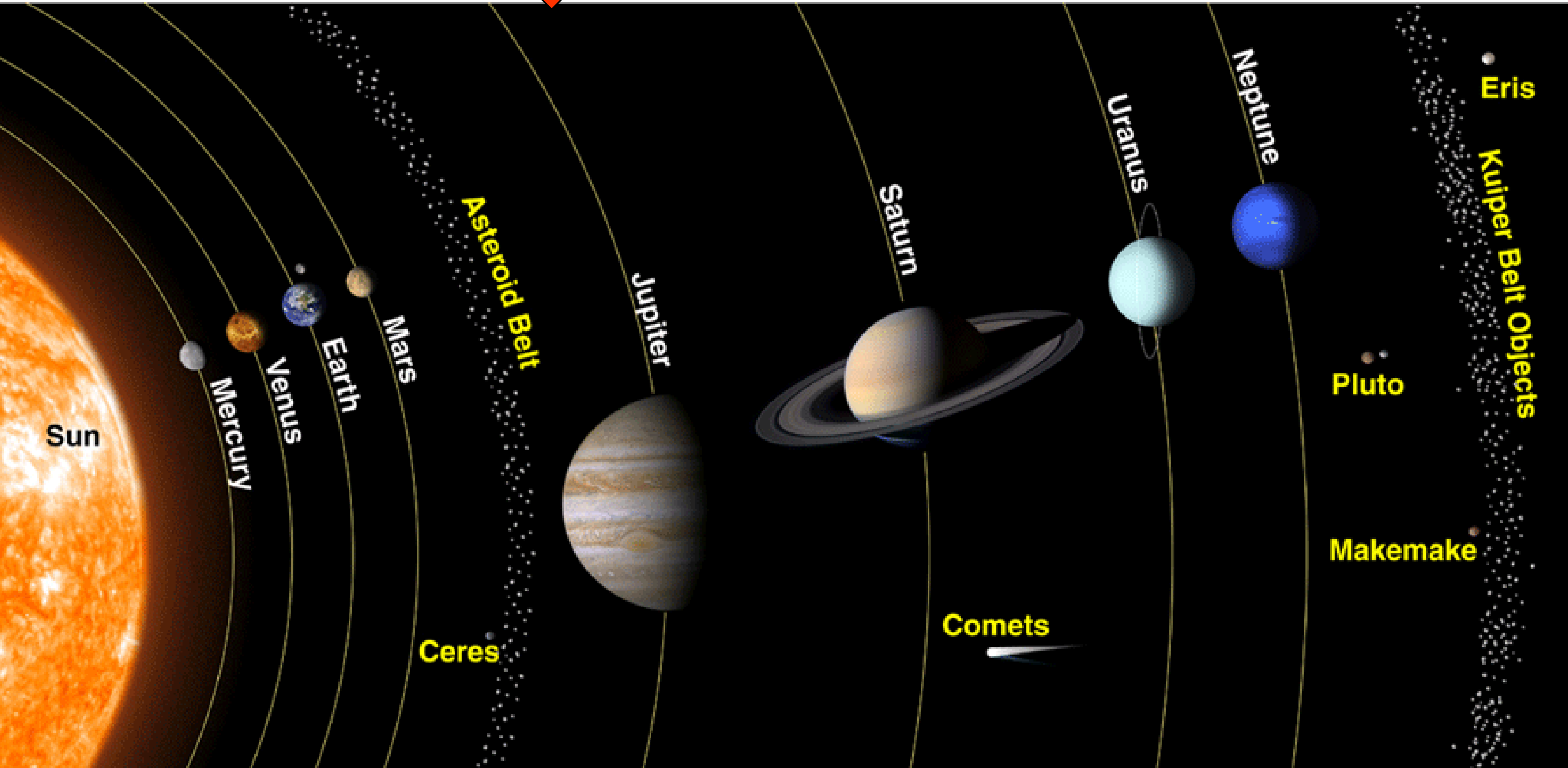


- *A mars-size impactor*
- >40% of the Moon-forming material from the impactor
- Impactor formed beyond the snow line

Snow line: where H-compounds (e.g., H_2O)→ solid

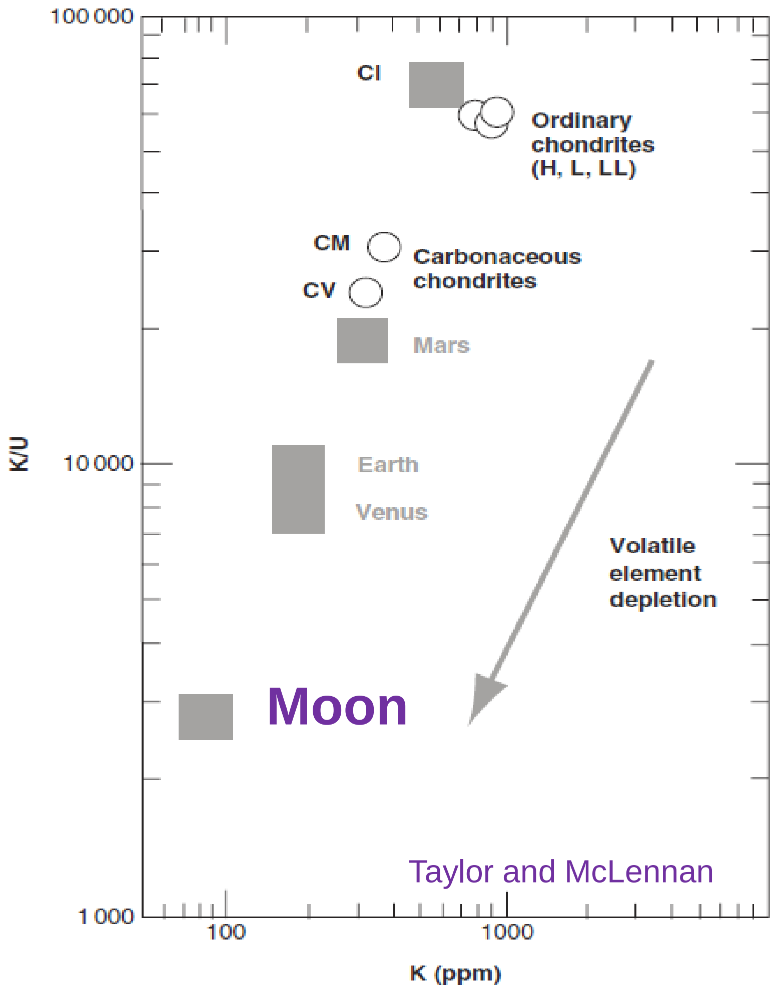
It separates terrestrial planets from gaseous planets

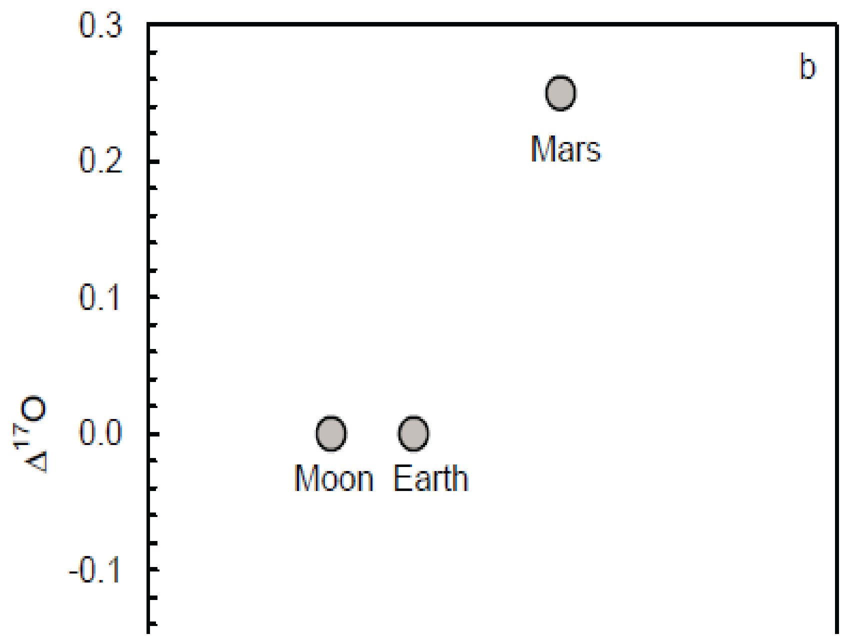
Snow line



The impactor should have different composition!

>40% of the Moon-forming material from the impactor
The Moon inherited the impactor→ has different compositions





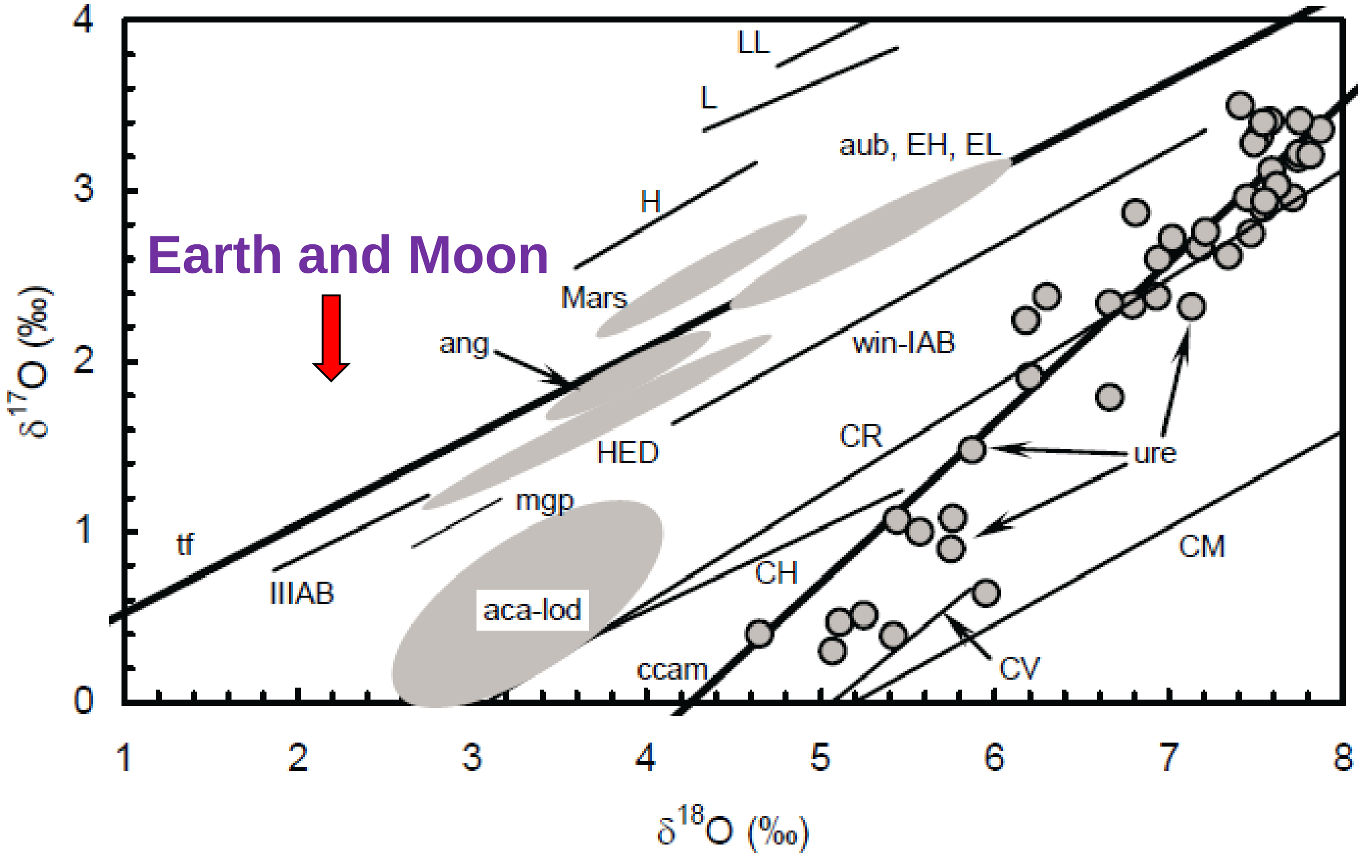
Moon vs. Earth

- **Different bulk chemical composition**
- **Similar to Earth mantle**
- **Identical O isotopic composition**

mantle FeO (wt%)

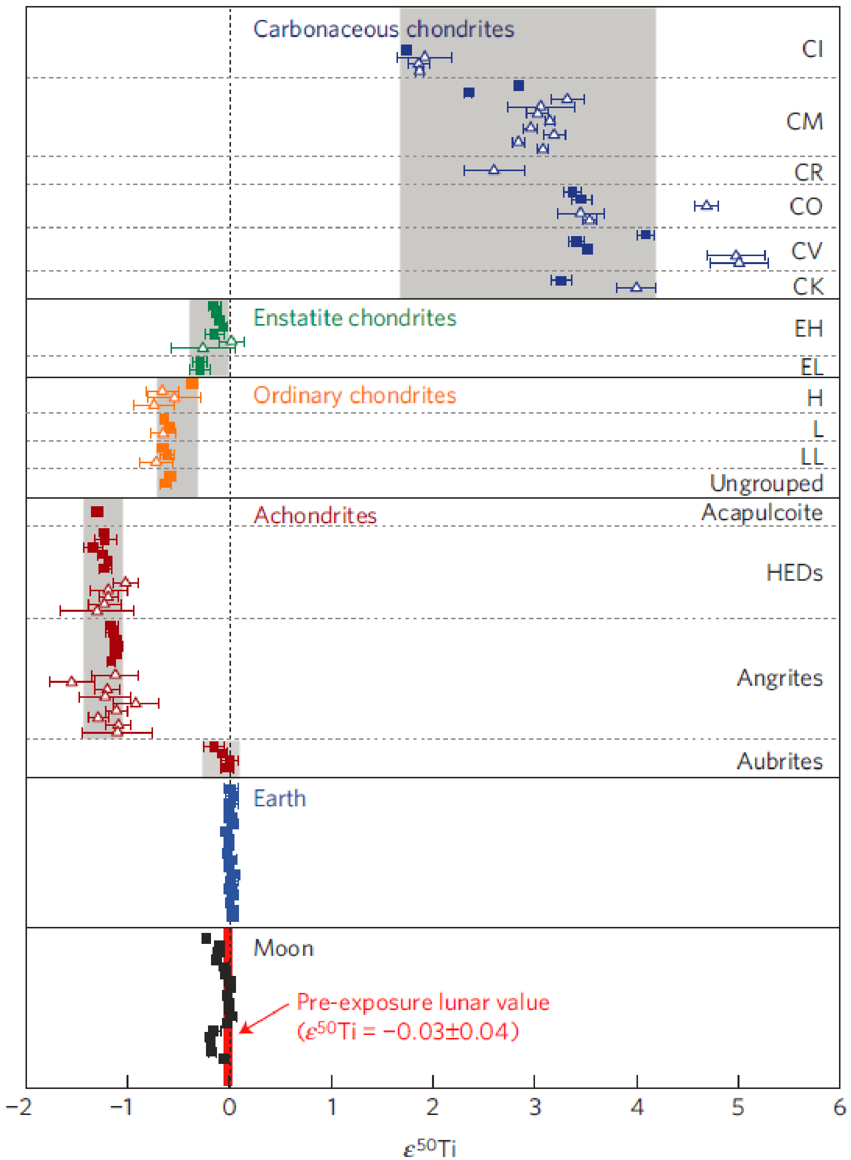
The Moon/Earth have identical $\Delta^{17}O$!

The Moon and Earth have identical O isotopic composition but different from most of other planetary bodies



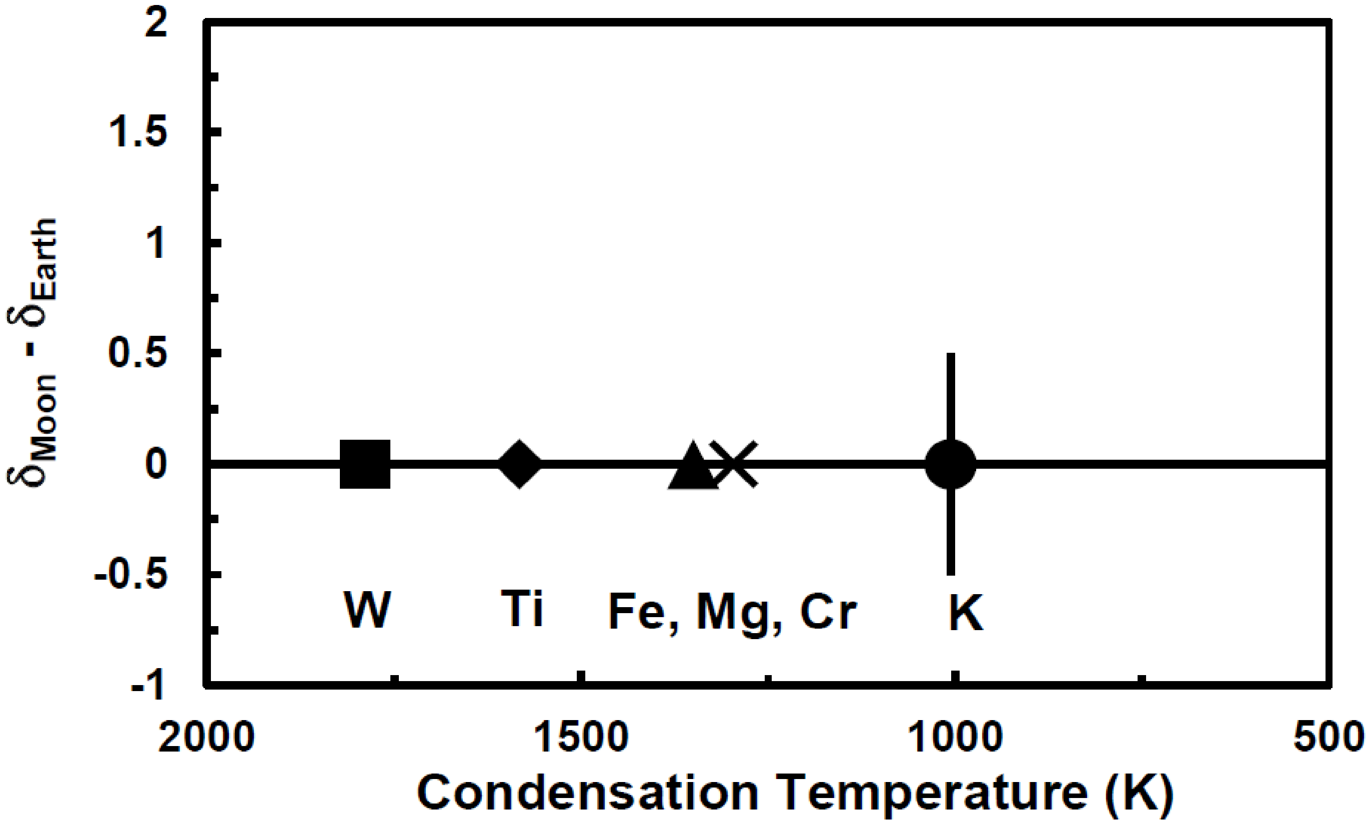
Mittlefehldet et al 2008

The Moon/Earth have identical Ti isotopic ratios!



Zhang et al. 2012

Identical isotopic ratios for other elements!



Cond. T. = at which elements condensate from solar nebula.

Refractory elements = high cond. T

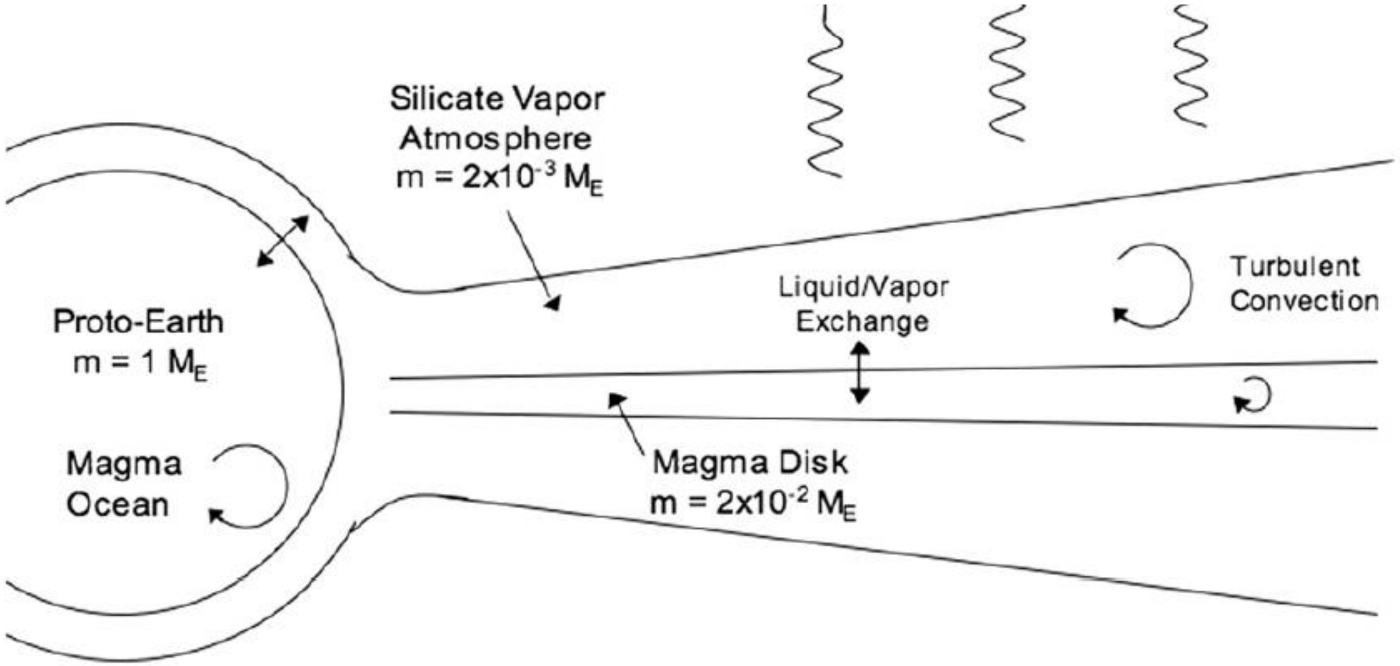
Volatile elements = low cond. T.

Well-mixed between impactor and Earth

Giant impact melt whole Earth mantle and impactor→

Form a magma disk and silicate vapor atmosphere →

Isotopes were well mixed before Moon formation



Pahlevan and Stevenson 2007 EPSL

Do not work well for refractory elements

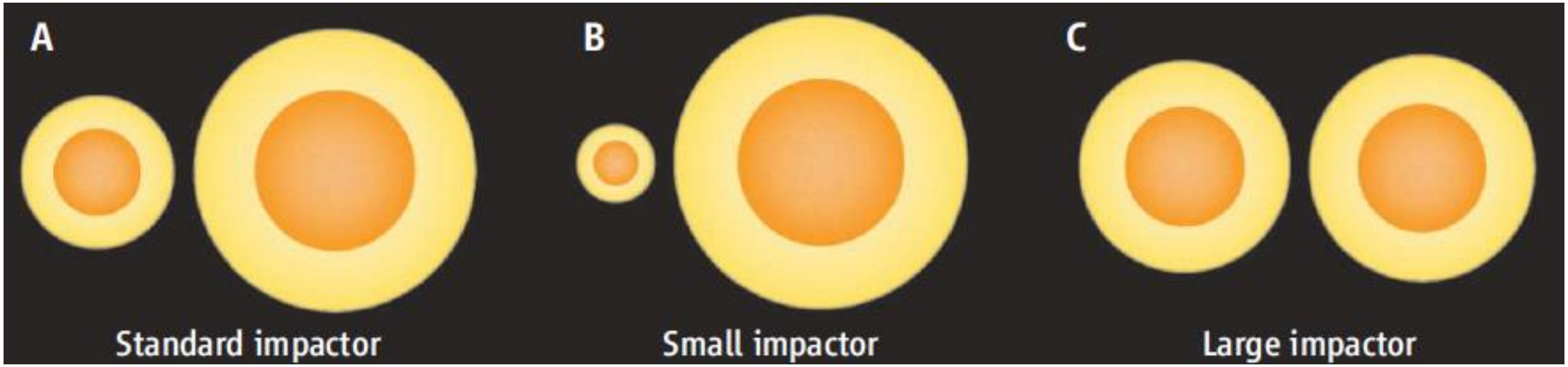
Refractory elements are the last to evaporate during impact and the first to condensate during moon formation

Moderately volatile elements (e.g., Cr, Mg and Fe) will be mixed within weeks.

Refractory elements (e.g., Ti, W) will be mixed within 30 years

The identical isotopic compositions of refractory elements require a long cooling time after the impact, which may not work

New Giant-impact models



Halliday 2012

Small impactor theory: Cuk and Stewart 2012 Science

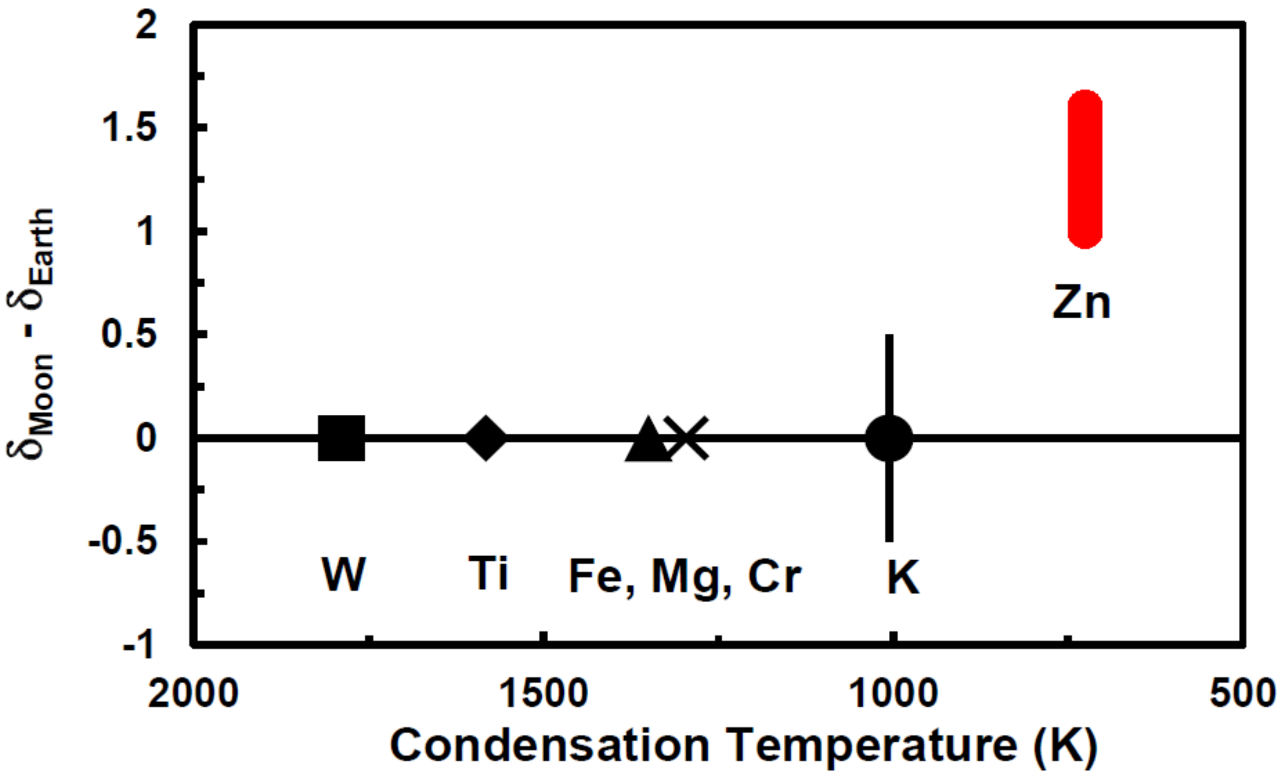
Moon formed from Earth's mantle with 8% from impactor

Large impactor theory: Canup 2012 Science

More vigorous impact mixed the impactor and Moon with about 1 to 1 mass ratio

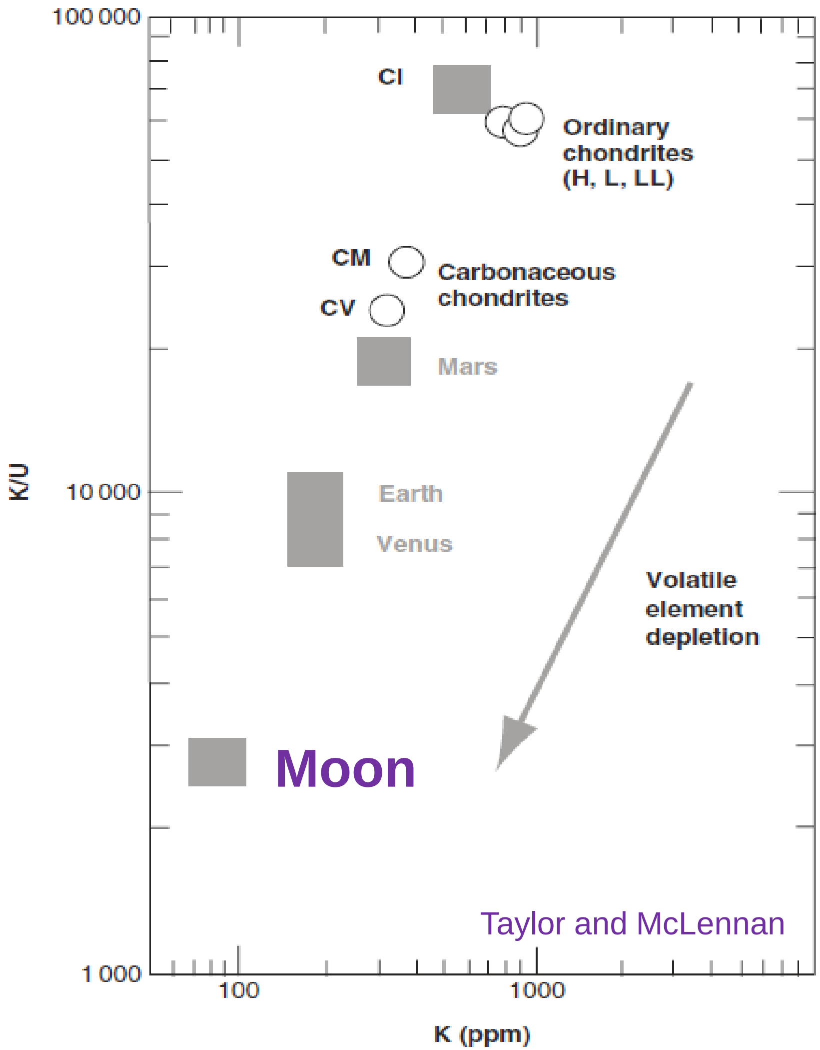
If the new theory works, then isotopes of all elements should be well-mixed

The Moon has a heavier Zn isotopic composition than Earth i.e., light Zn isotopes were lost during the Moon formation



Zinc data are from Paniello et al 2012 Nature

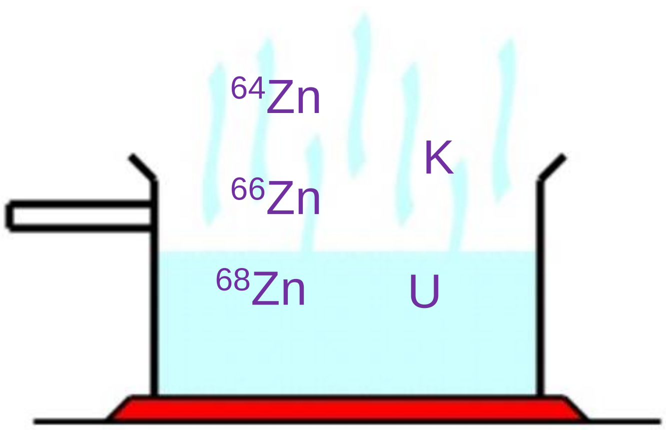
The Moon is also depleted in volatile elements!



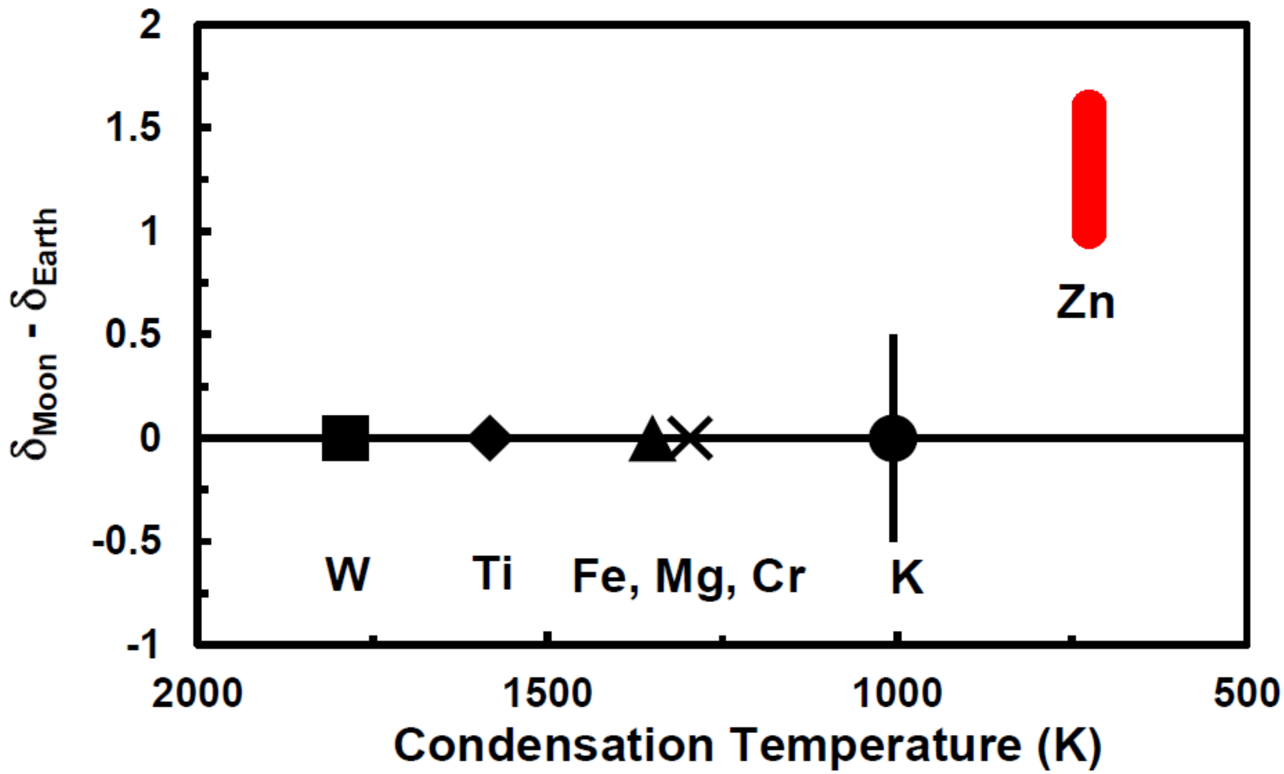
Volatile elements are easier to lose during evaporation.

Same is true for light isotopes

Volatile elements were lost before Moon formation



K is also volatile, why no isotope fractionation?



Zinc data are from Paniello et al 2012 Nature

K is also volatile, why no isotope fractionation?

LETTER

doi:10.1038/nature19341

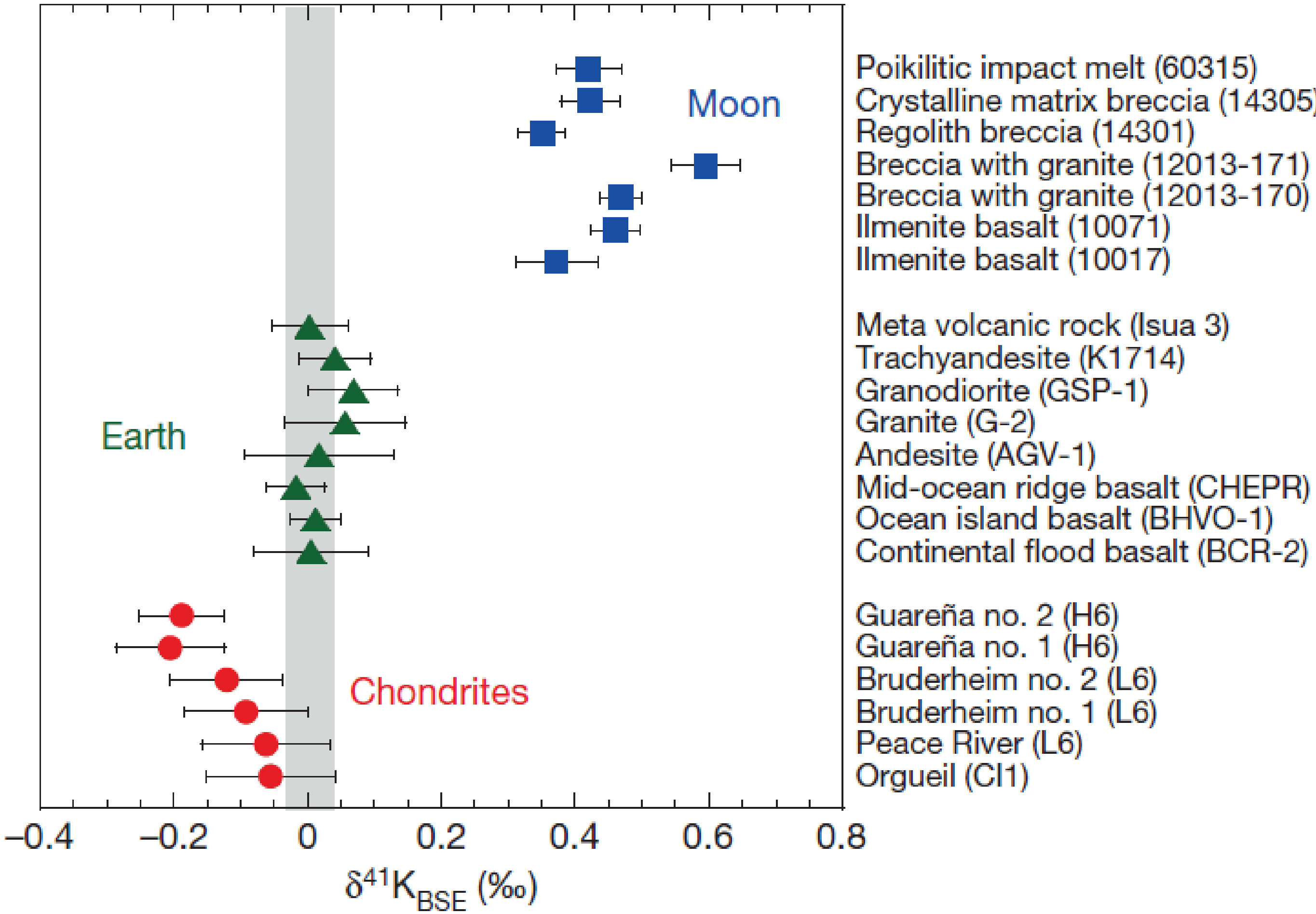
Potassium isotopic evidence for a high-energy giant impact origin of the Moon

Kun Wang[1,2] & Stein B. Jacobsen[1]

Wang and Jacobsen 2016 Nature

K is also volatile, why no isotope fractionation?

The Moon is indeed enriched in heavy K isotopes!



Wang and Jacobsen 2016 Nature

More evidence…

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Geochimica et Cosmochimica Acta 280 (2020) 263–280

Geochimica e
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Acta

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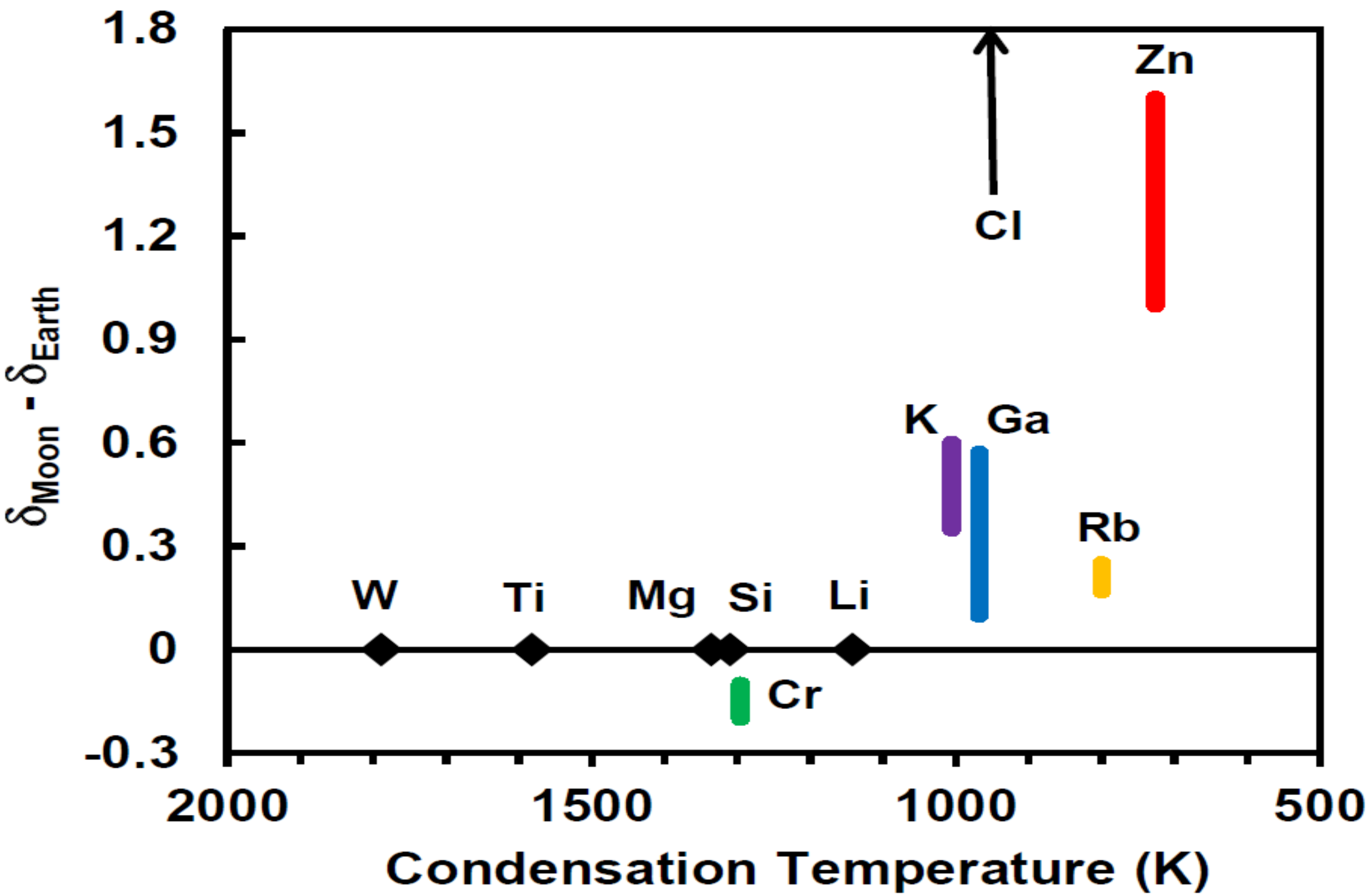
Potassium isotopic composition of the Moon

Zhen Tian [a,*], Bradley L. Jolliff [a], Randy L. Korotev [a], Bruce Fegley Jr [a]
Katharina Lodders [a], James M.D. Day [b], Heng Chen [a,c], Kun Wang (王昆) [a,*]

Then isotopes of elements more volatile than K are expected to be fractionated



Indeed, volatile elements are isotopically fractionated between the Earth and Moon

Summary

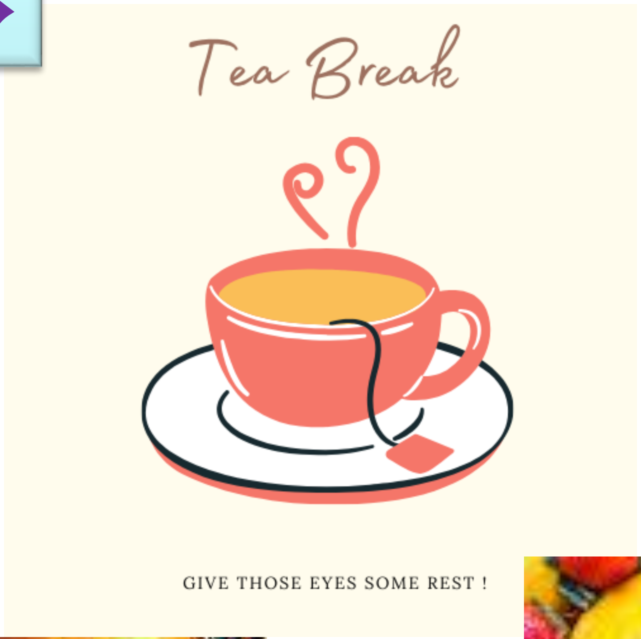
- Studies of non-traditional isotopes of refractory elements (W, Ti, Fe, Mg) show identical compositions, suggesting the Moon formed from an Earth-like composition

- Isotope fractionation of volatile elements (K, Ga, Zn, Rb) between the Earth and Moon suggests loss of volatile elements during giant impact

- Giant-impact theories have to explain these isotopic signatures. Both recent models suggest a more significant proportion of Earth's mantle into the lunar formation

- More detailed isotopic studies and modeling are needed to better understand the origins of the Moon

茶歇

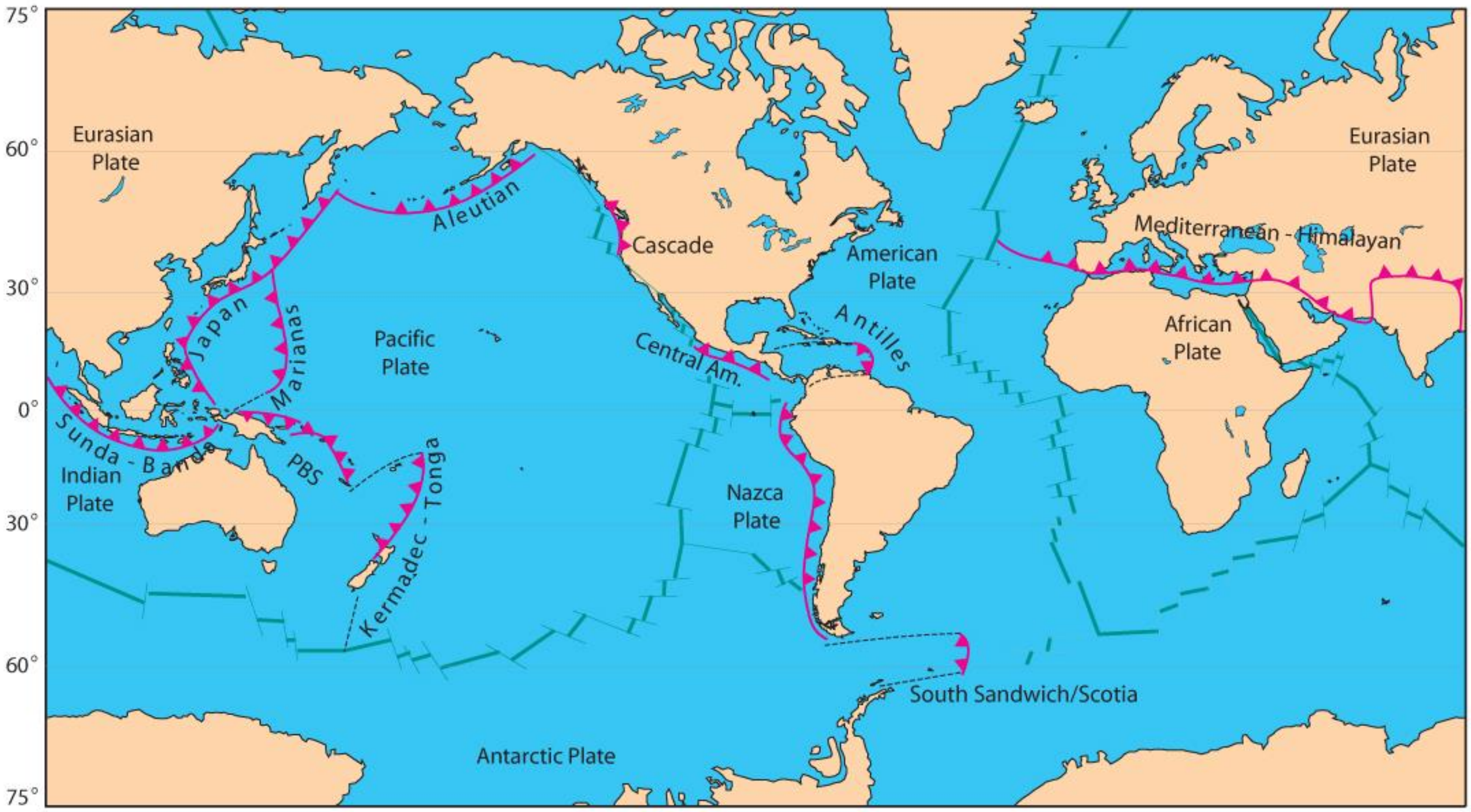


Outline

- K Isotope Analysis
- Moon-Forming Giant Impact
- Crust-Mantle Interactions
- Continental Weathering
- Biological/Medical/Others

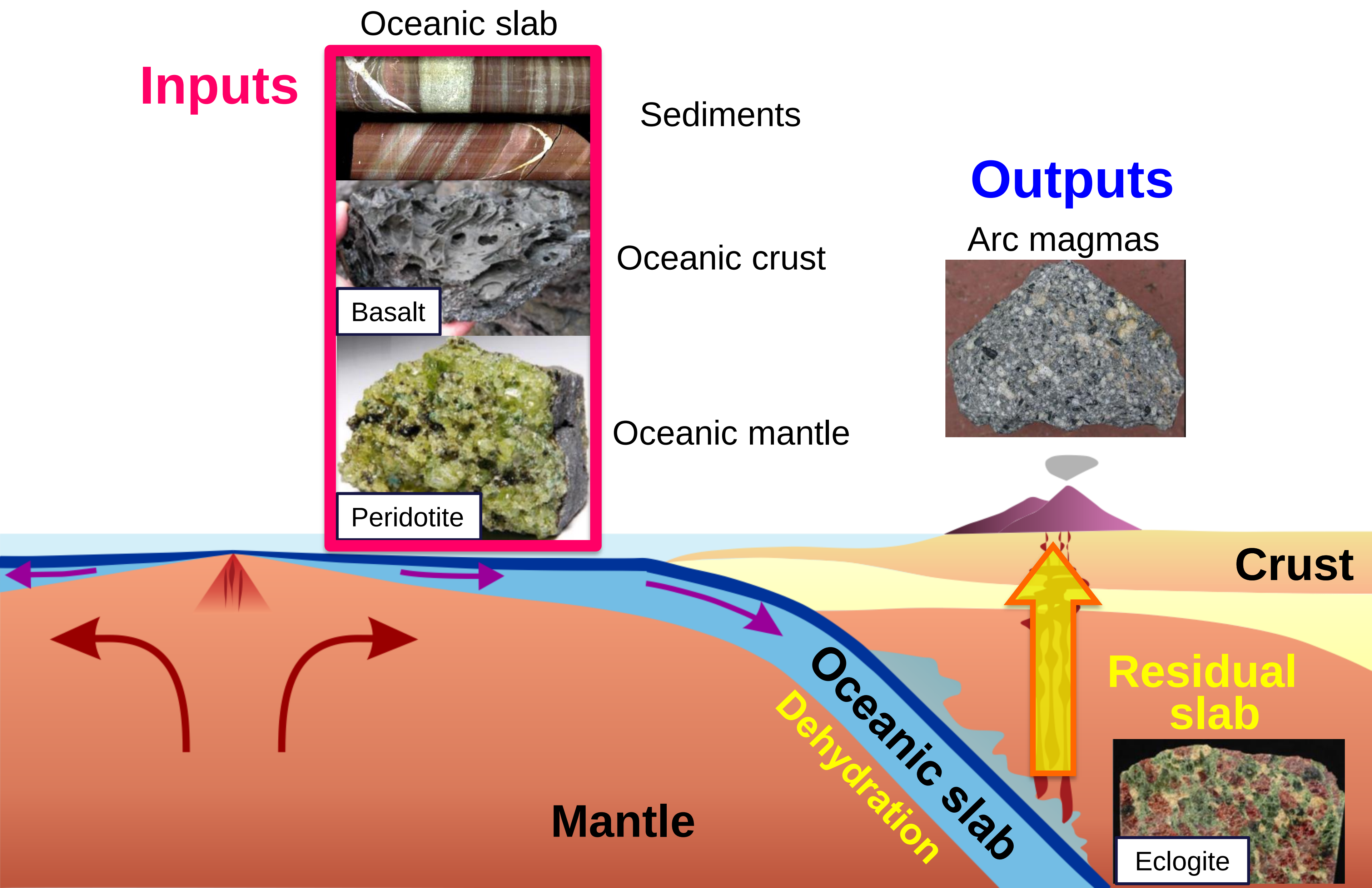
Mantle heterogeneity produced by subduction

Subduction zones are where oceanic plates dive into the mantle and form juvenile continental crust



Winter, J. Introduction to Igneous & Metamorphic Petrology

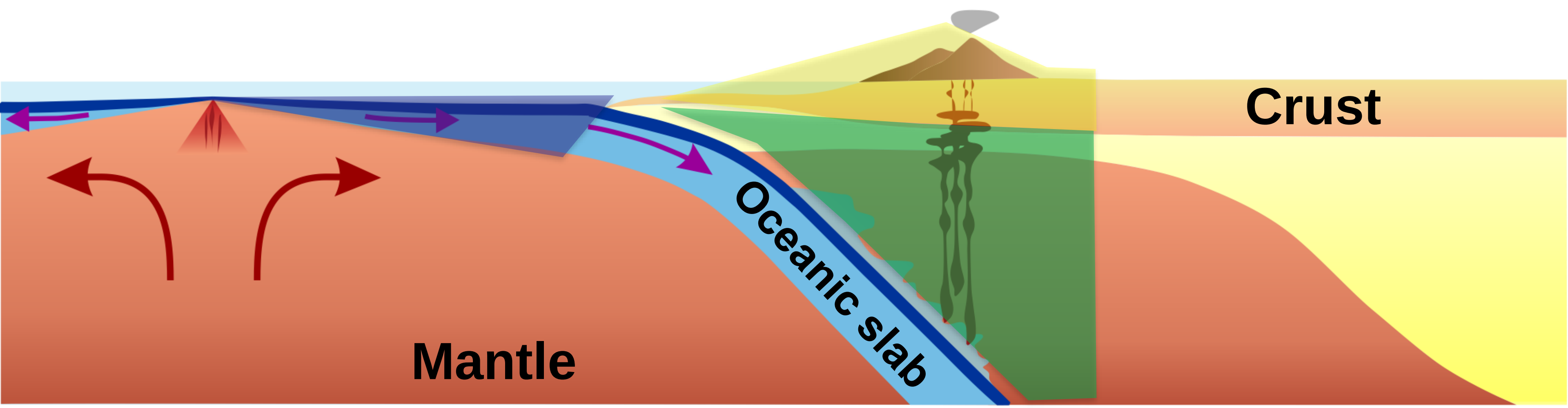
Subduction zone processes



Main objectives

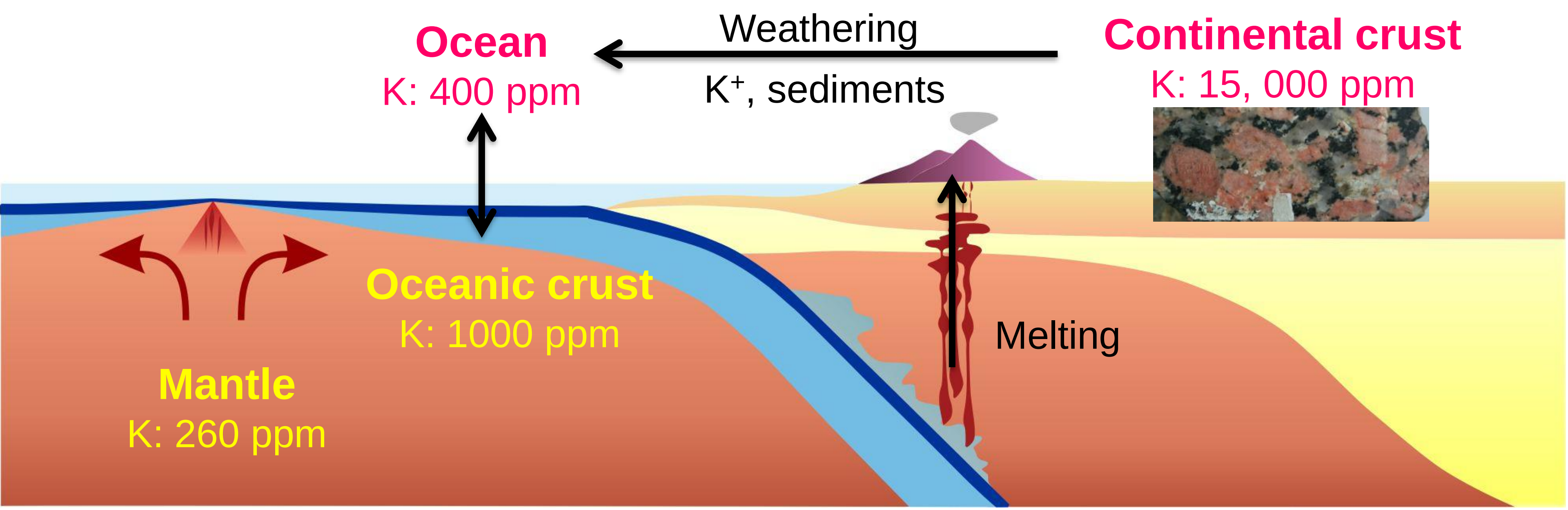
1. What processes control the compositional variation in subducting slab?

2. How does slab signature transfer to:
   - ❑ Arc lavas
   - ❑ Mantle-derived magmas



Global potassium cycle

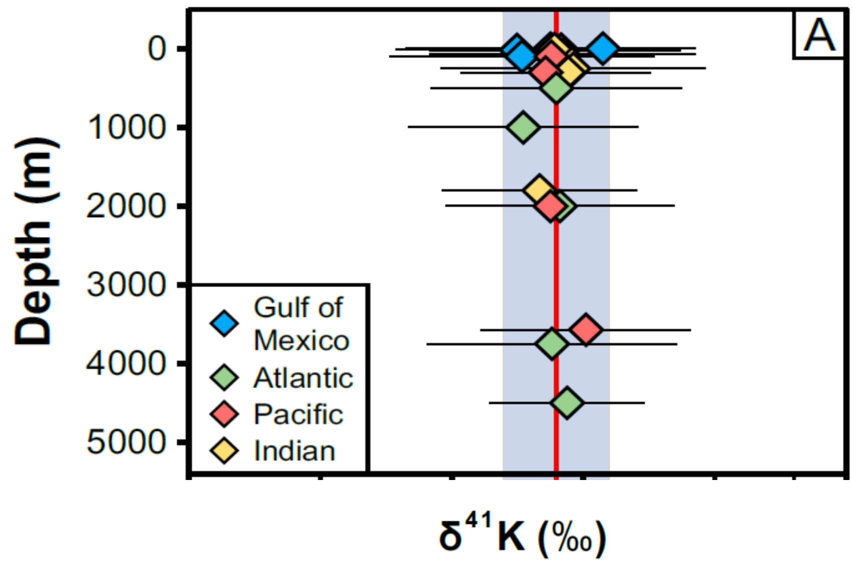
- Global K cycle is important for understanding Earth's dynamics because K is abundant in oceans, crust, mantle and maybe core.
- K activity is closely linked to global carbon and water cycling via continental weathering, oceanic subduction, and arc magmatism.



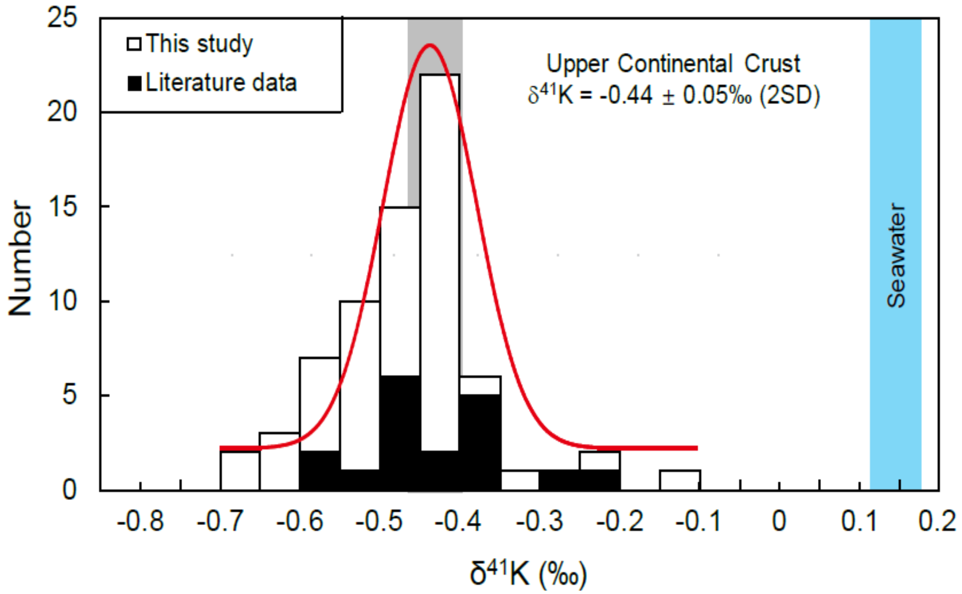
A major heat source, helping to power mantle dynamics

Broecker & Peng, 1982; Su, 2002; Palme and O'Neil, 2014; Rudnick & Gao, 2014

Potassium isotope geochemistry



Hille et al., 2019 SB; Wang et al., 2020 ACS



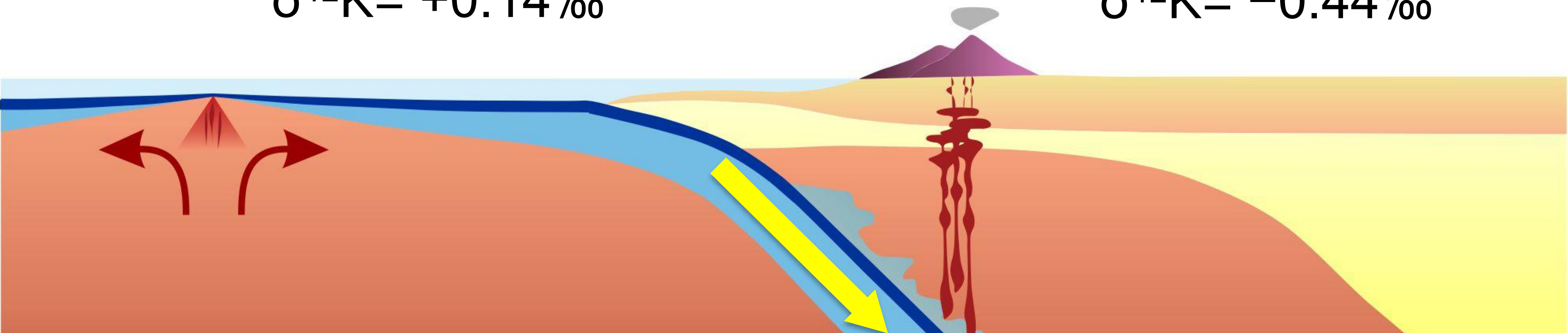
Huang et al. 2020 GCA

Ocean

$\delta^{41}K = +0.14‰$

Continental crust

$\delta^{41}K = -0.44‰$



Potassium isotope geochemistry

Oceanic crust should have highly variable $\delta^{41}K$

Sediments

Altered oceanic crust

Continental weathering?

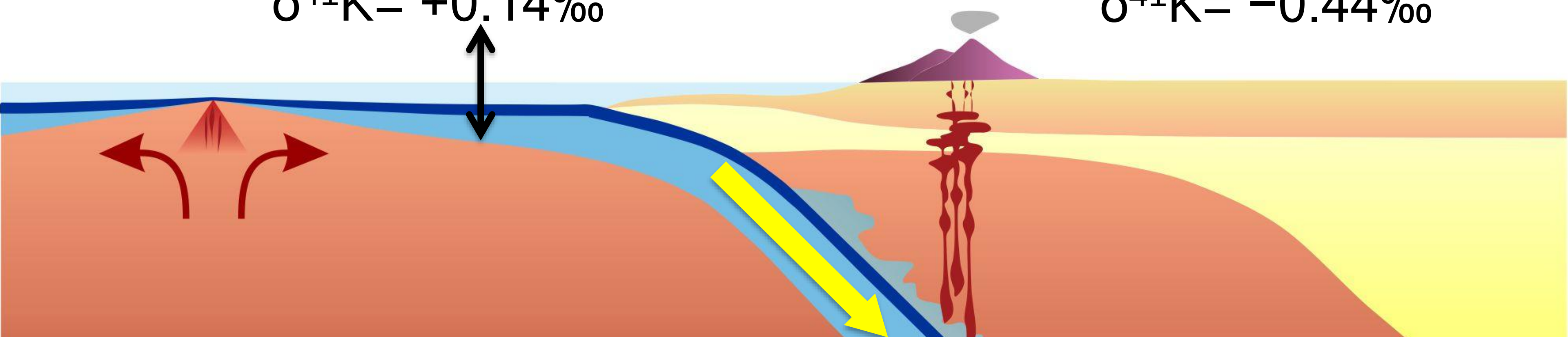
Interaction with oceanic crust?

Ocean

$\delta^{41}K = +0.14‰$

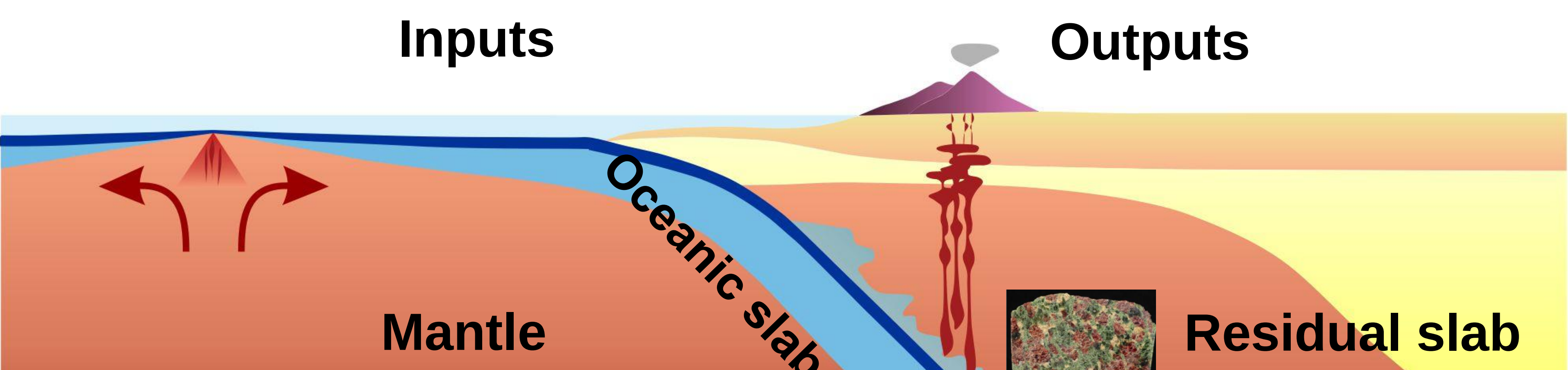
Continental crust

$\delta^{41}K = -0.44‰$



Outline

1. K isotopic compositions of subducting slabs
2. Arc magmas
3. Mantle-derived magmas



Samples

- **Altered Oceanic Crust** in front of Mariana trench

Reference site, the oldest (~170 Ma) AOC drilled, extensive alteration

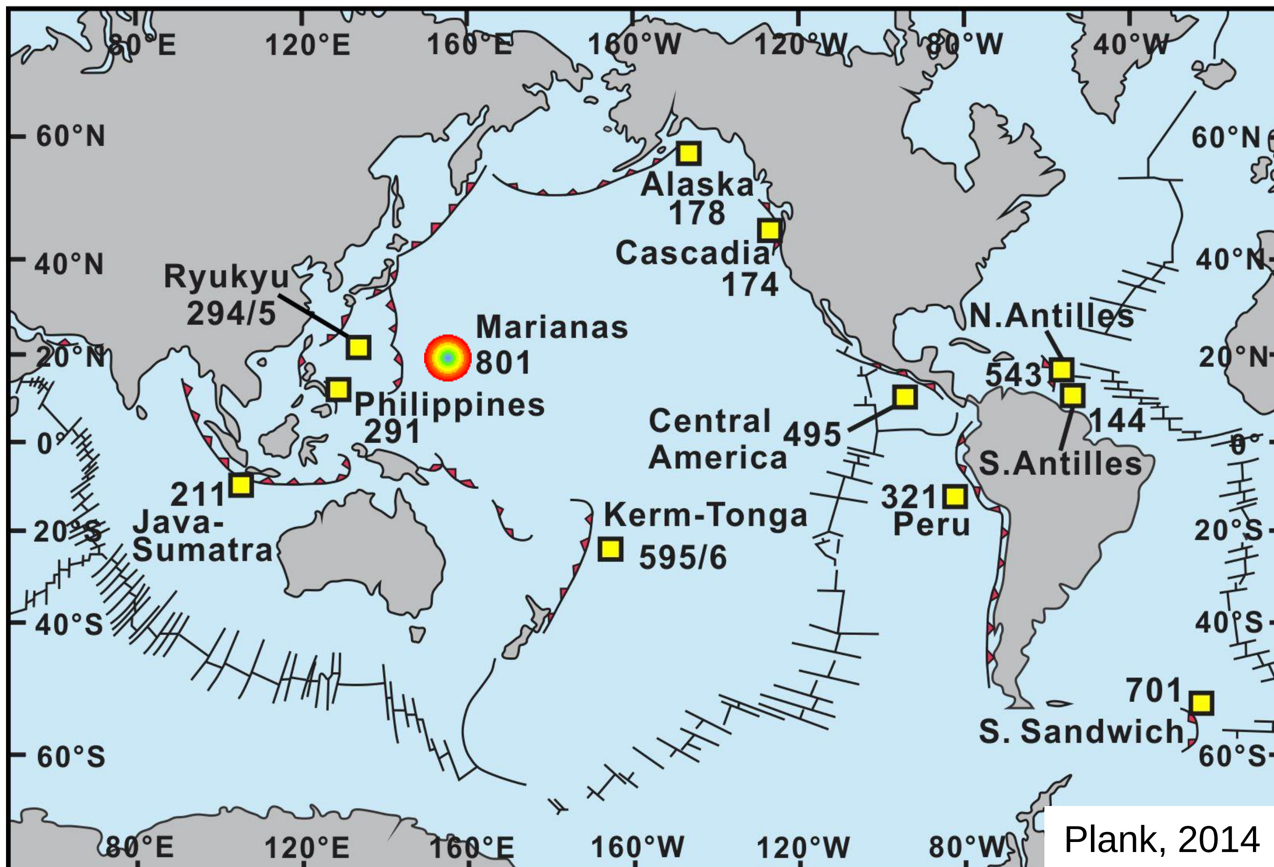
- **Bulk sediments** from 11 trenches

Compositions of GLOSS (major, trace element, Nd-Hf-Li-Mg isotopes, etc.)

GLObal Subducting Sediments (Plank, 2014)

Sediments

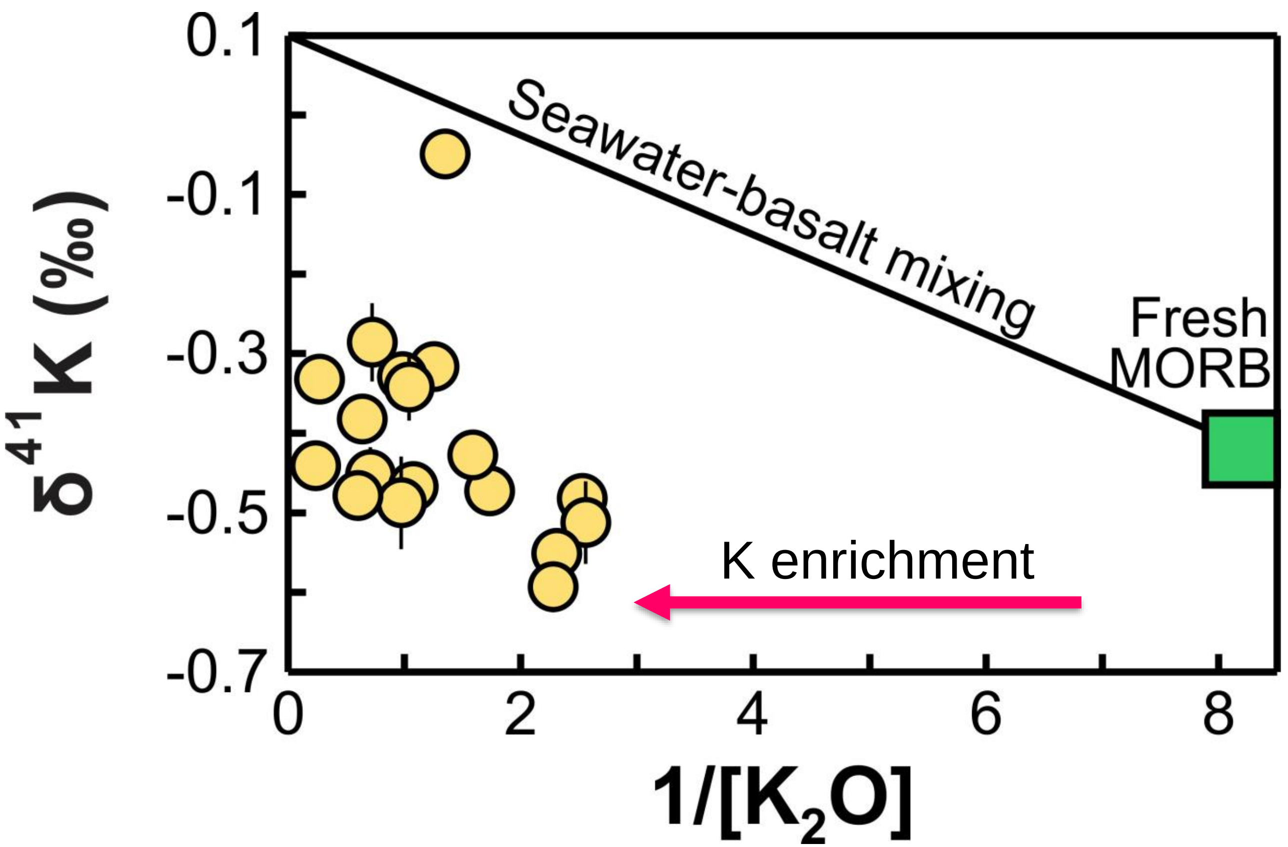
AOC



Plank, 2014

Results: altered oceanic crust

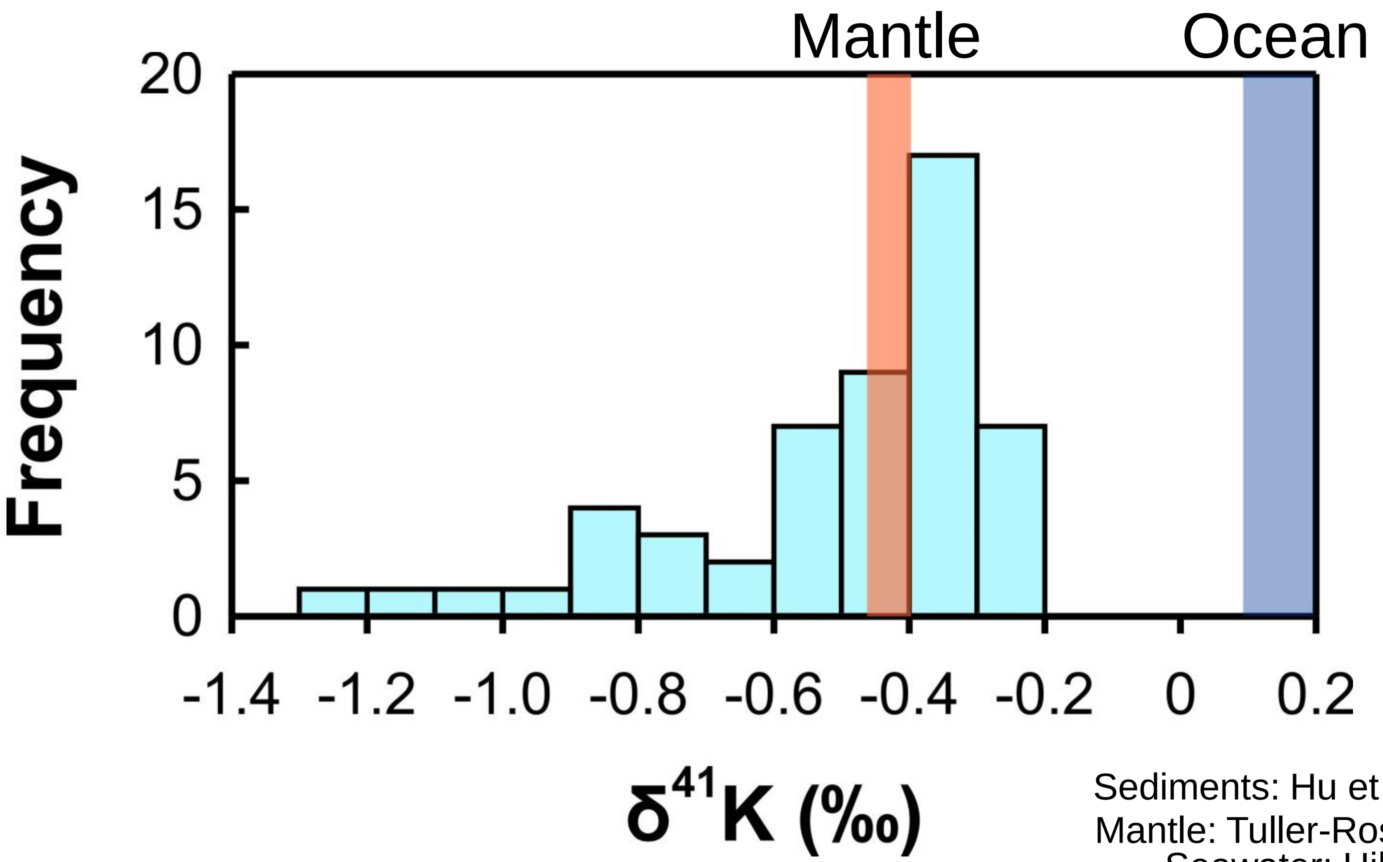
- AOC samples are enriched in K and highly heterogeneous
- AOC samples preferentially take up light K from seawater



Hu et al., submitted

Results: marine sediments

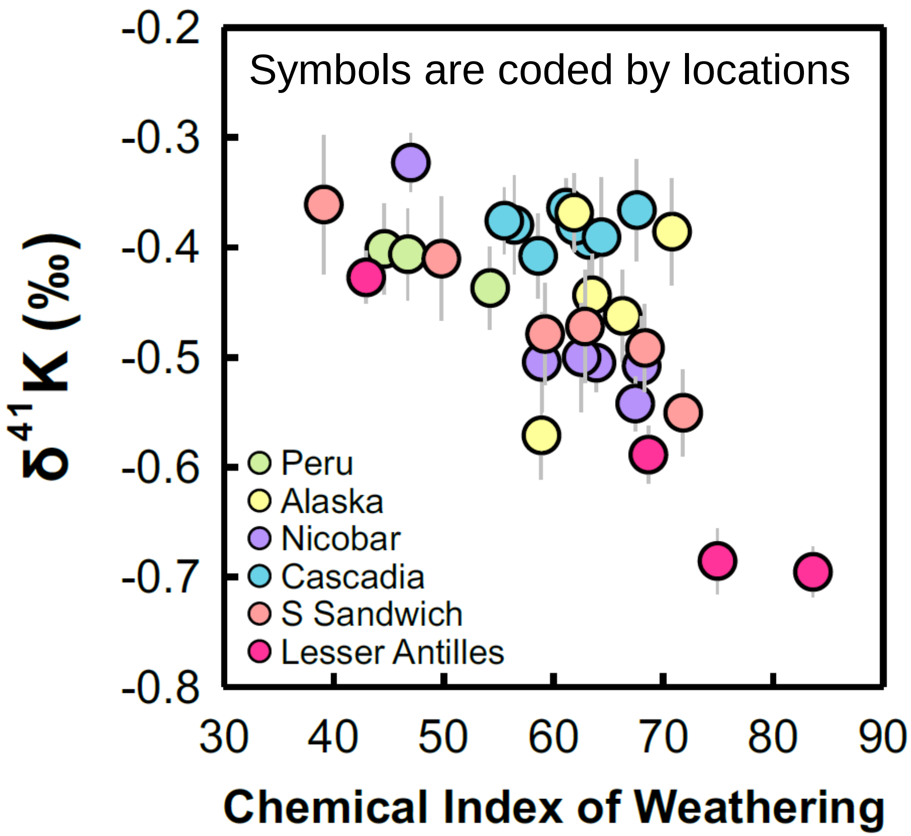
- Sediments are highly heterogeneous
- Both lighter and heavier than the **mantle**
- All isotopically lighter than **seawater**



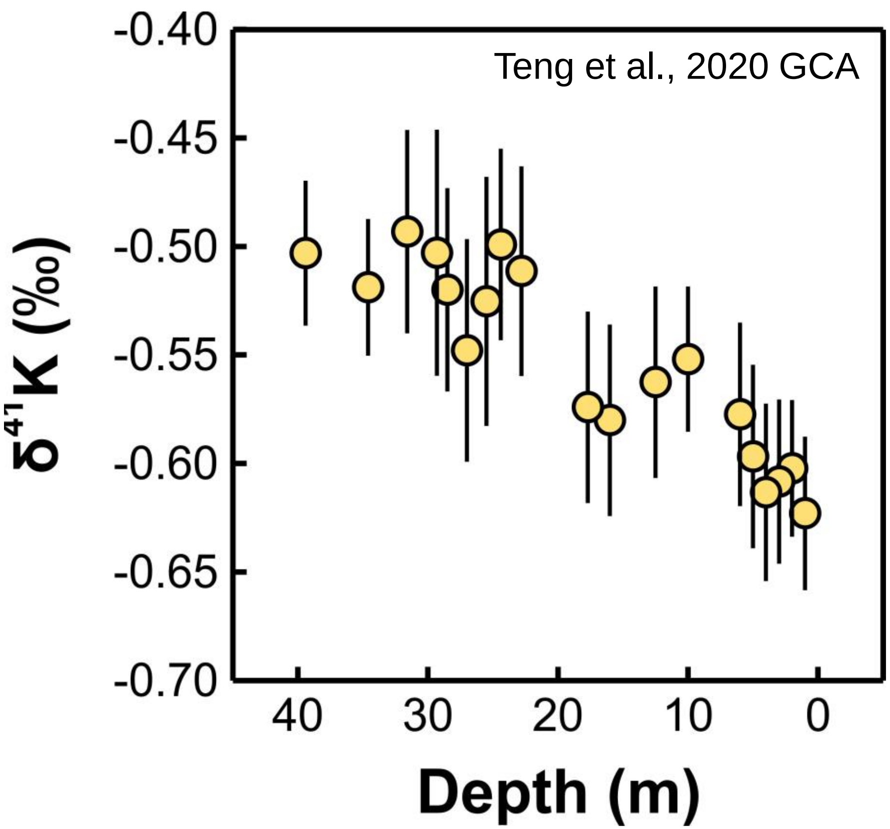
Sediments: Hu et al., submitted
Mantle: Tuller-Ross et al., 2019
Seawater: Hille et al., 2019
Wang et al. 2020

Controls on sediment δ^{41}K

- Chemical weathering forms sediments with low δ^{41}K
- Consistent with observations from weathering profile



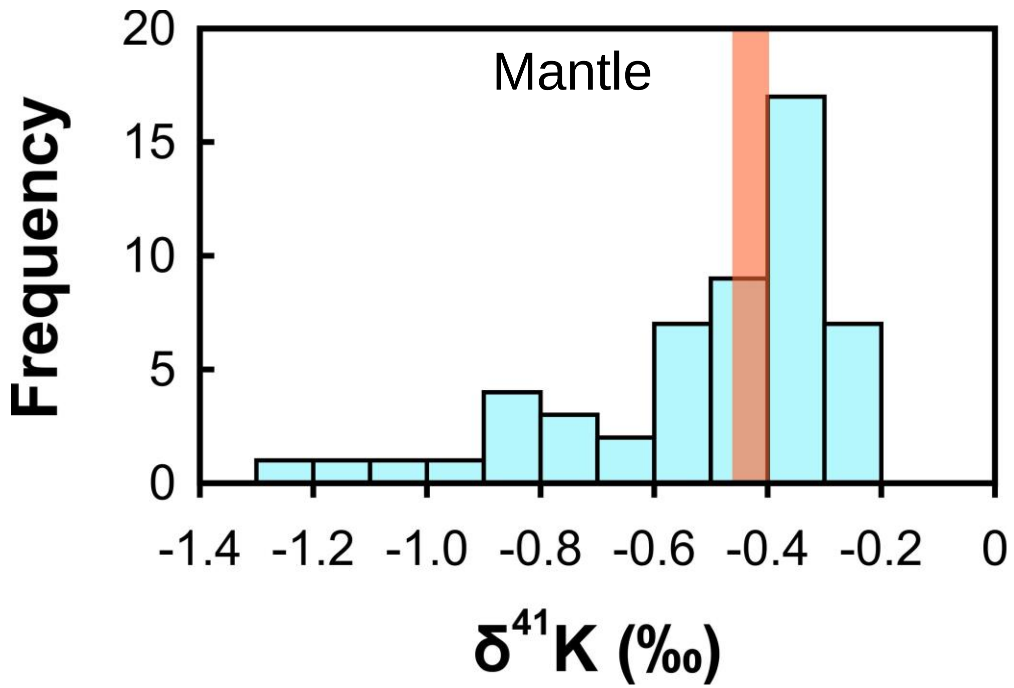
= clay/feldspar ratio



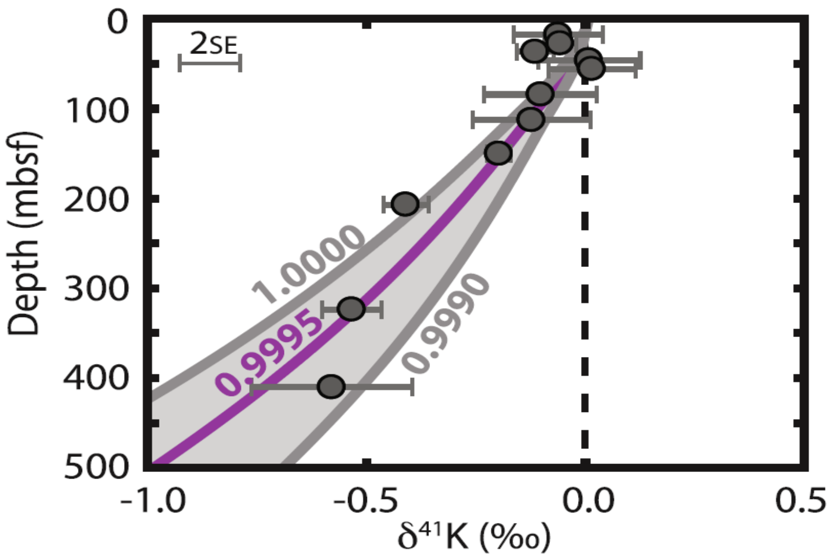
Hu et al., submitted

Controls on sediment δ⁴¹K

Low-δ⁴¹K sediments: clay authigenesis is also important



Pore-fluid profile

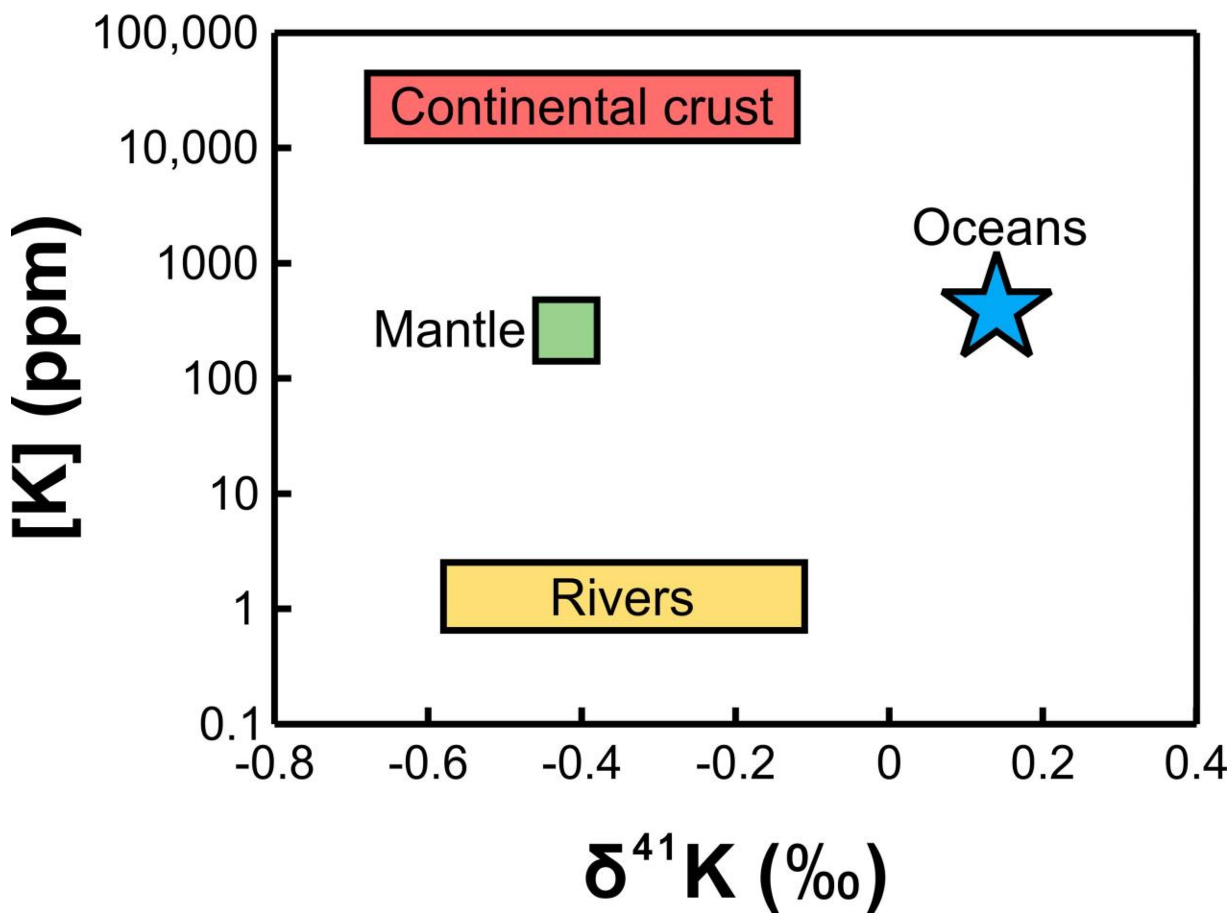


Predicted authigenic clay δ⁴¹K:
–0.53 to –2.72‰

(Santiago Ramos et al., 2018)

Implication for oceanic K cycle

Why are the oceans isotopically heavier than rivers?



Oceans: Hille et al., 2019
Wang et al., 2020
Rivers: Lee et al., 2018
Li et al., 2019
Teng et al., 2020
Crust: Huang et al., 2019

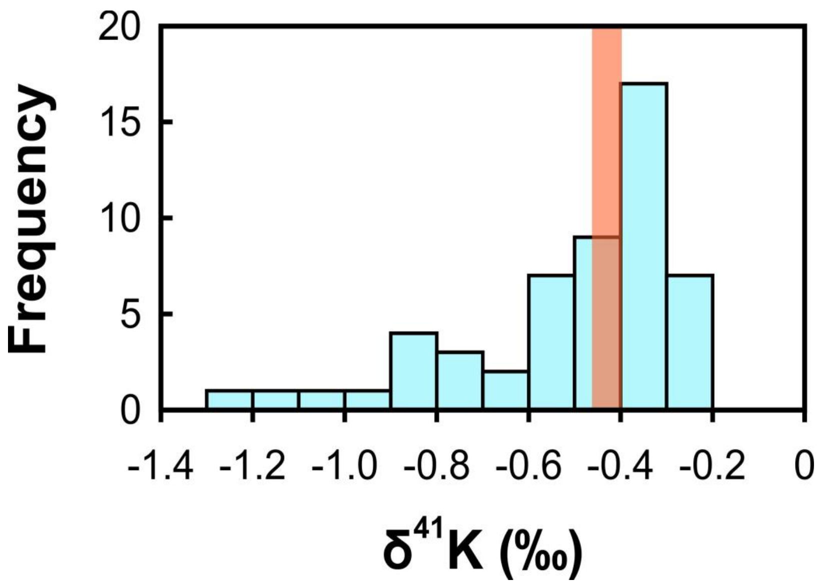
Implication for oceanic K cycle

Seawater $\delta^{41}K$ reflects the balance between K input and output

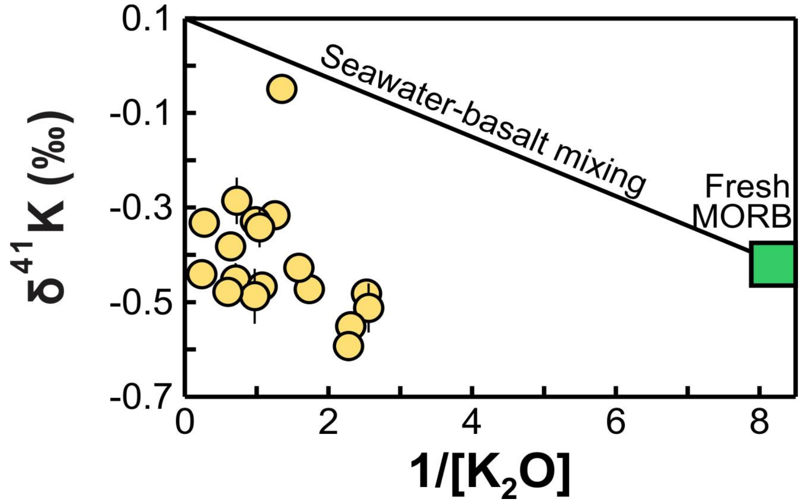
Seawater is heavier than riverine inputs

Isotopically light outputs are required

Authigenic clays



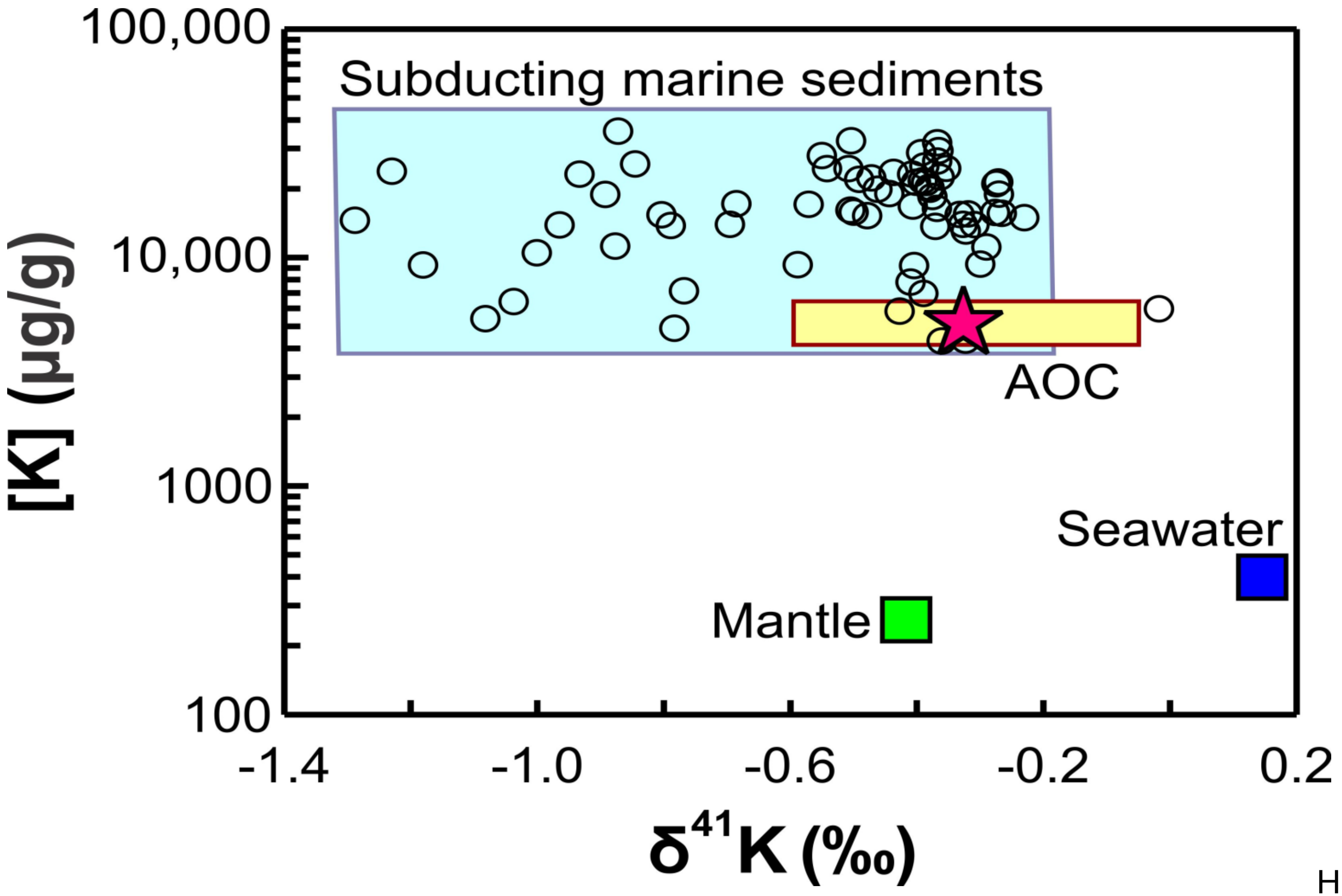
Altered oceanic crust



Hu et al., submitted

A brief summary

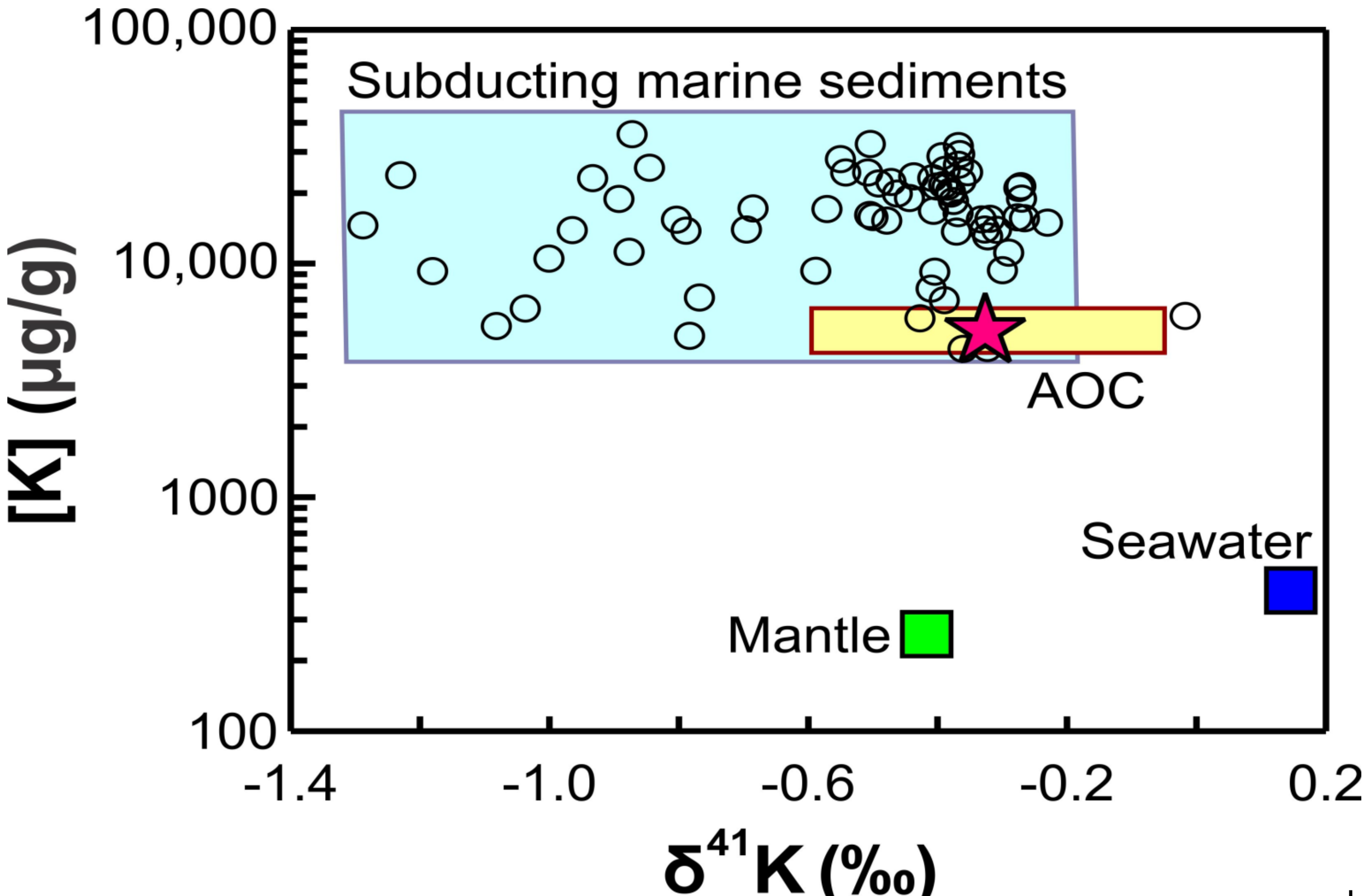
Altered oceanic crust has heterogeneous and overall slightly heavy K isotopic composition than the mantle



Hu et al., submitted

A brief summary

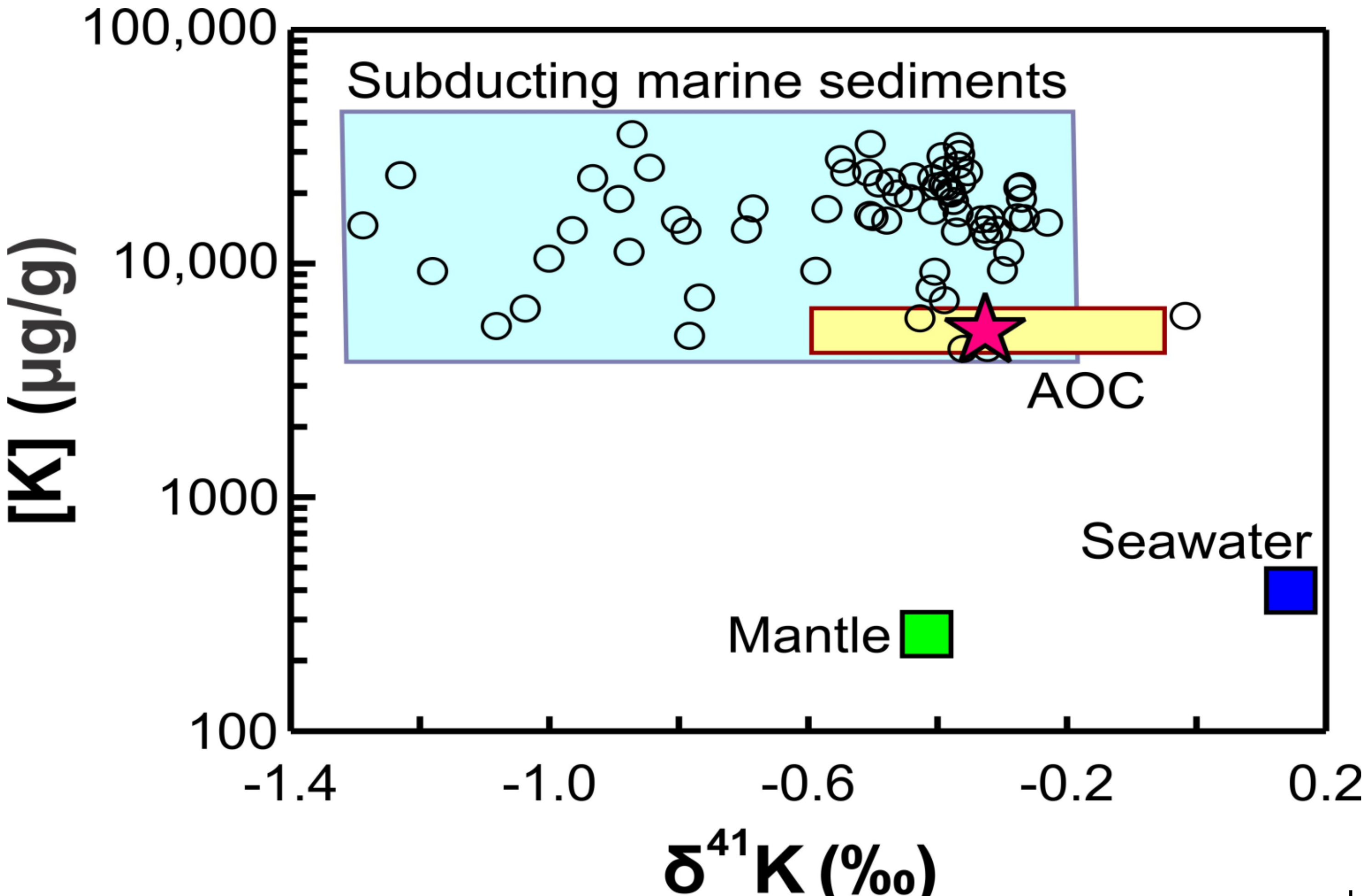
Marine sediment has heterogeneous and overall slightly lighter K isotopic composition than the mantle



Hu et al., submitted

A brief summary

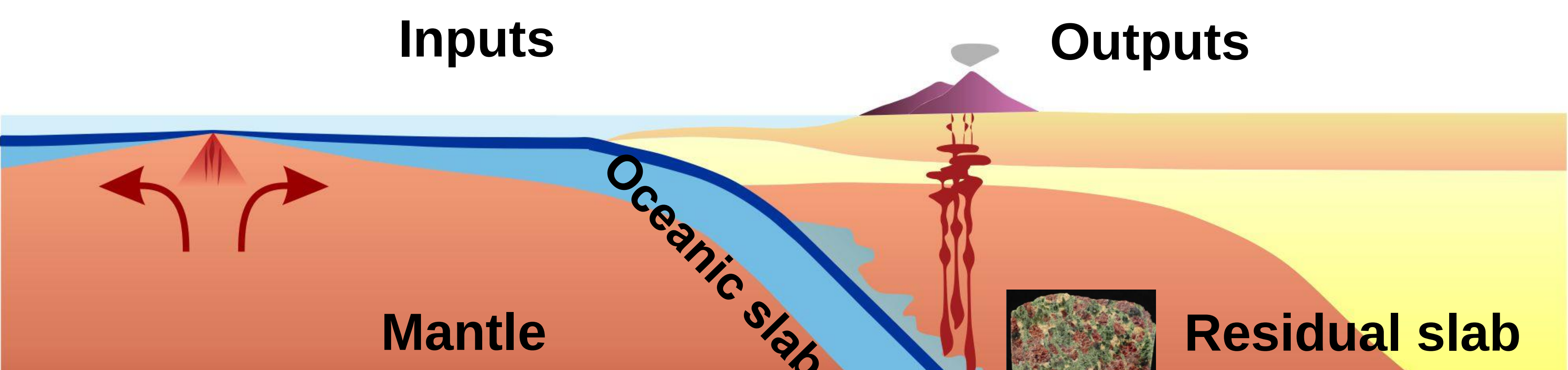
Both altered basalt and marine sediment are highly enriched in K when compared to the mantle



Hu et al., submitted

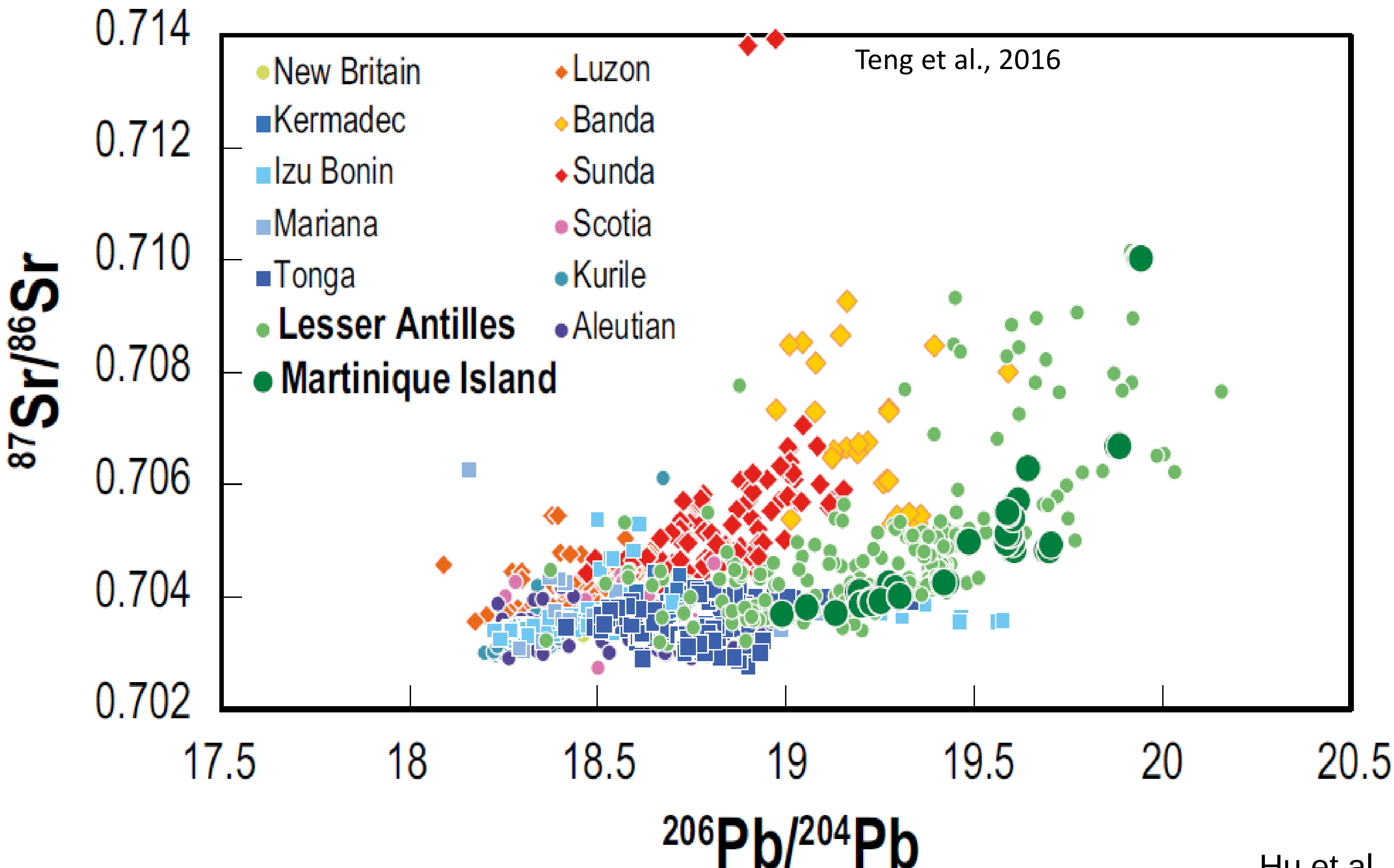
Outline

1. K isotopic compositions of subducting slabs
2. Arc magmas
3. Mantle-derived magmas



Samples: Lesser Antilles arc

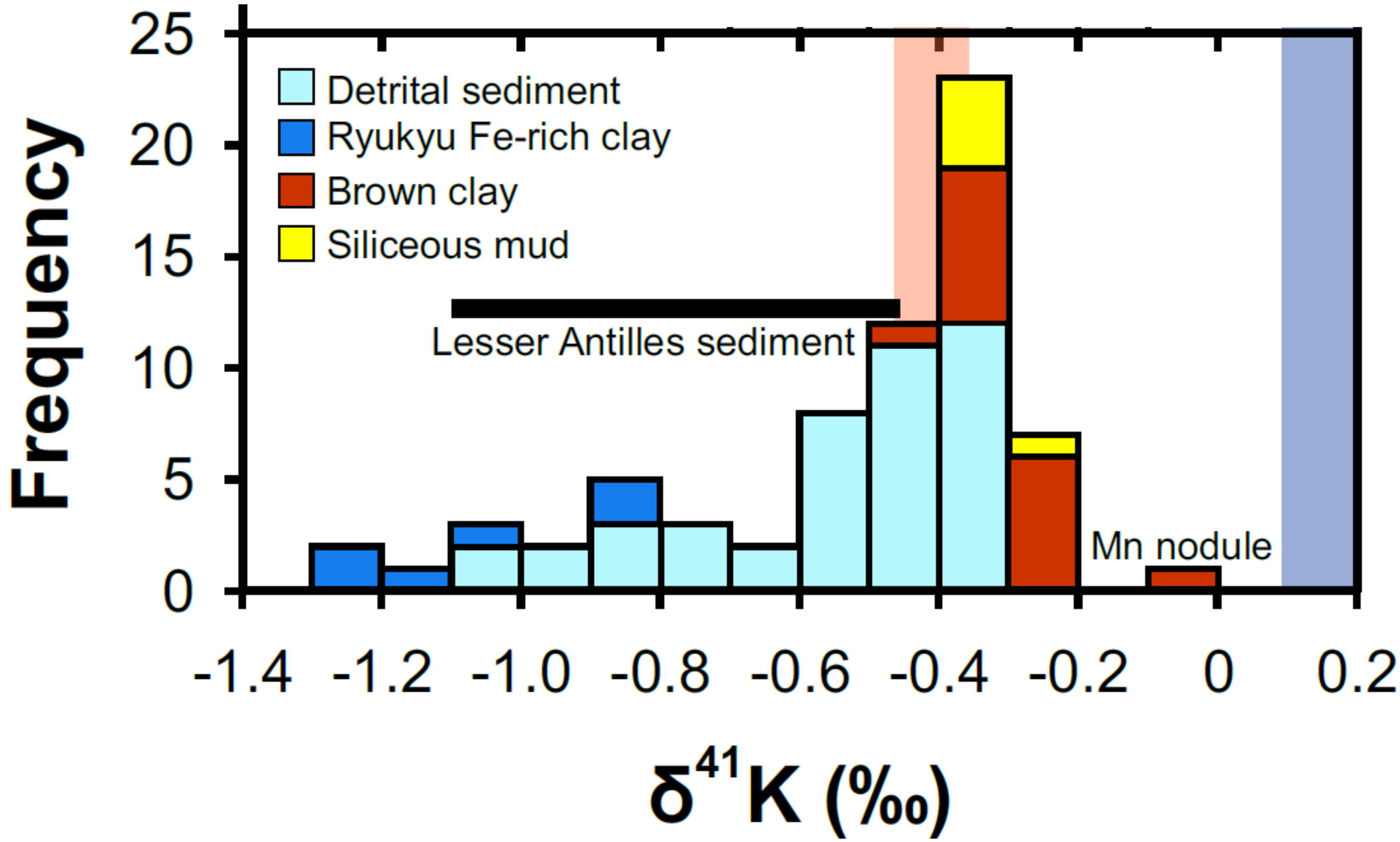
A compositional end-member of global island arcs



Hu et al., submitted

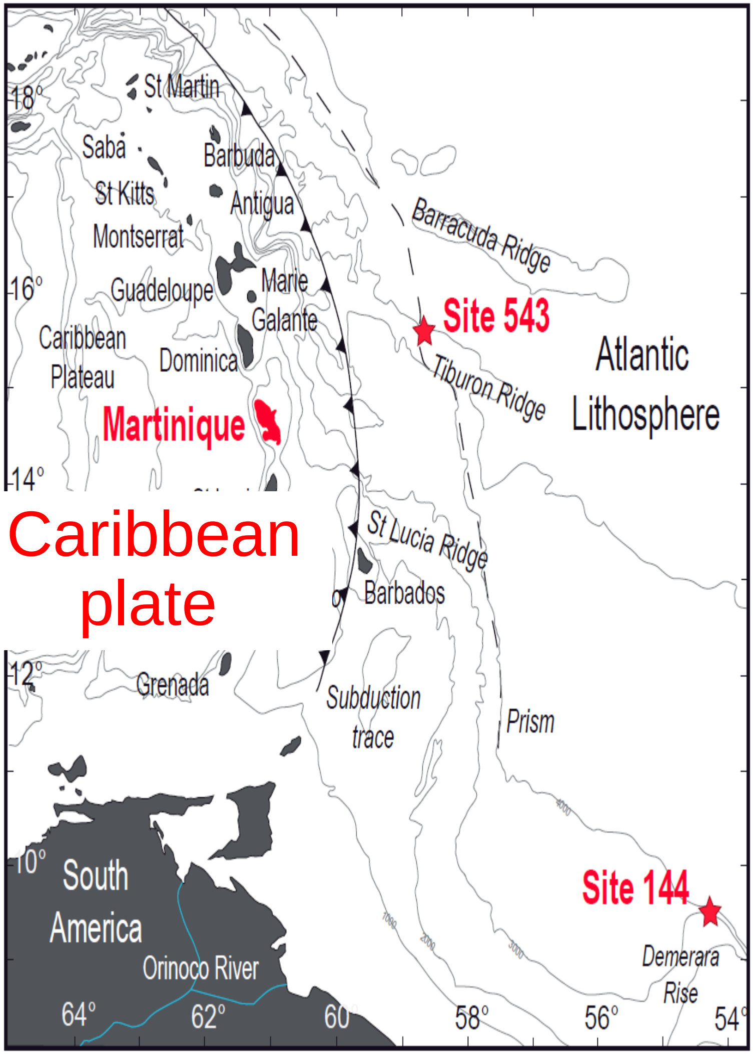
Samples: Lesser Antilles arc

Extremely light K isotopic composition of subducting sediments



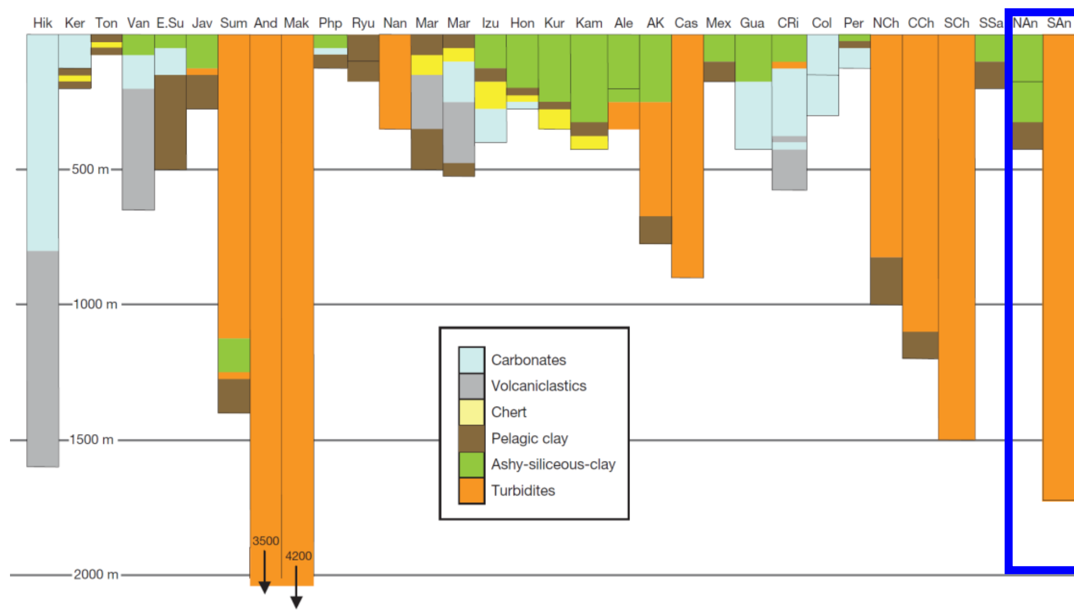
Hu et al., submitted

Geological settings



Modified from Labanieh et al., 2010

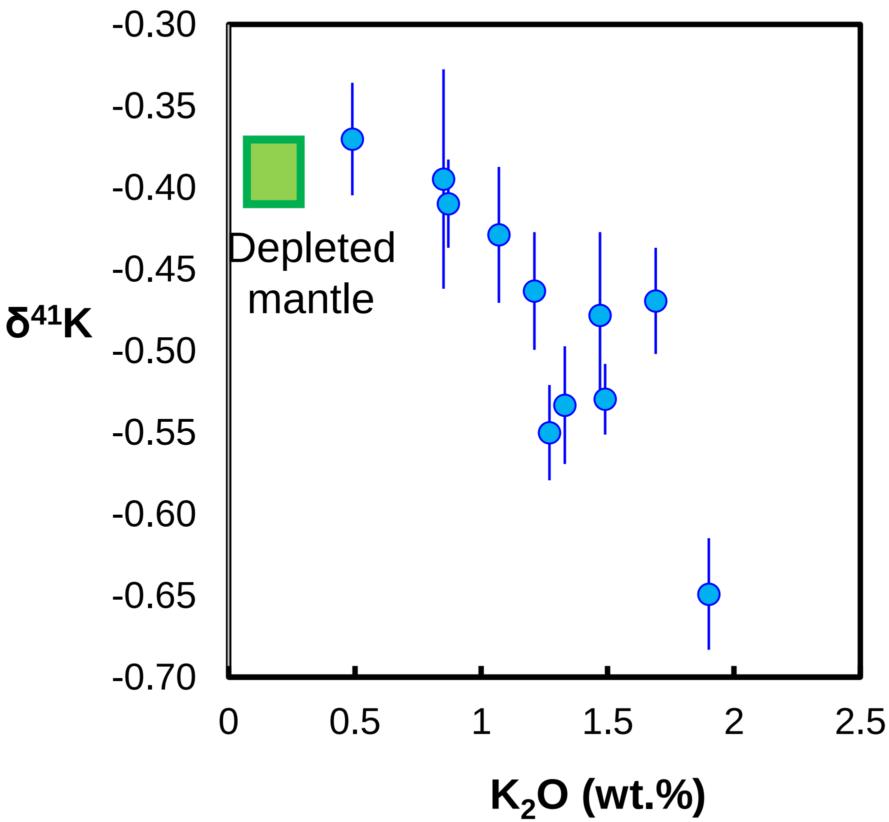
- Subduction of Atlantic lithosphere beneath the Caribbean plate
- Orinoco river delivers highly weathered sediments to the Atlantic ocean

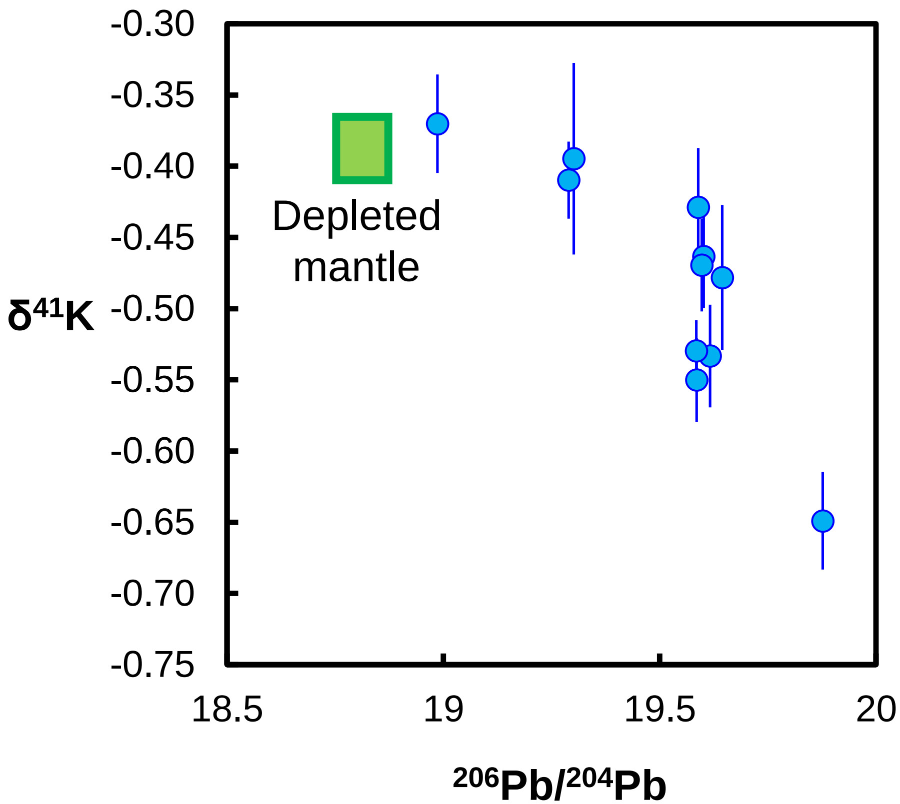


Plank, 2014

Results

- Arc lavas are isotopically lighter than the depleted mantle
- $\delta^{41}K$ correlates with K_2O and radiogenic isotopes

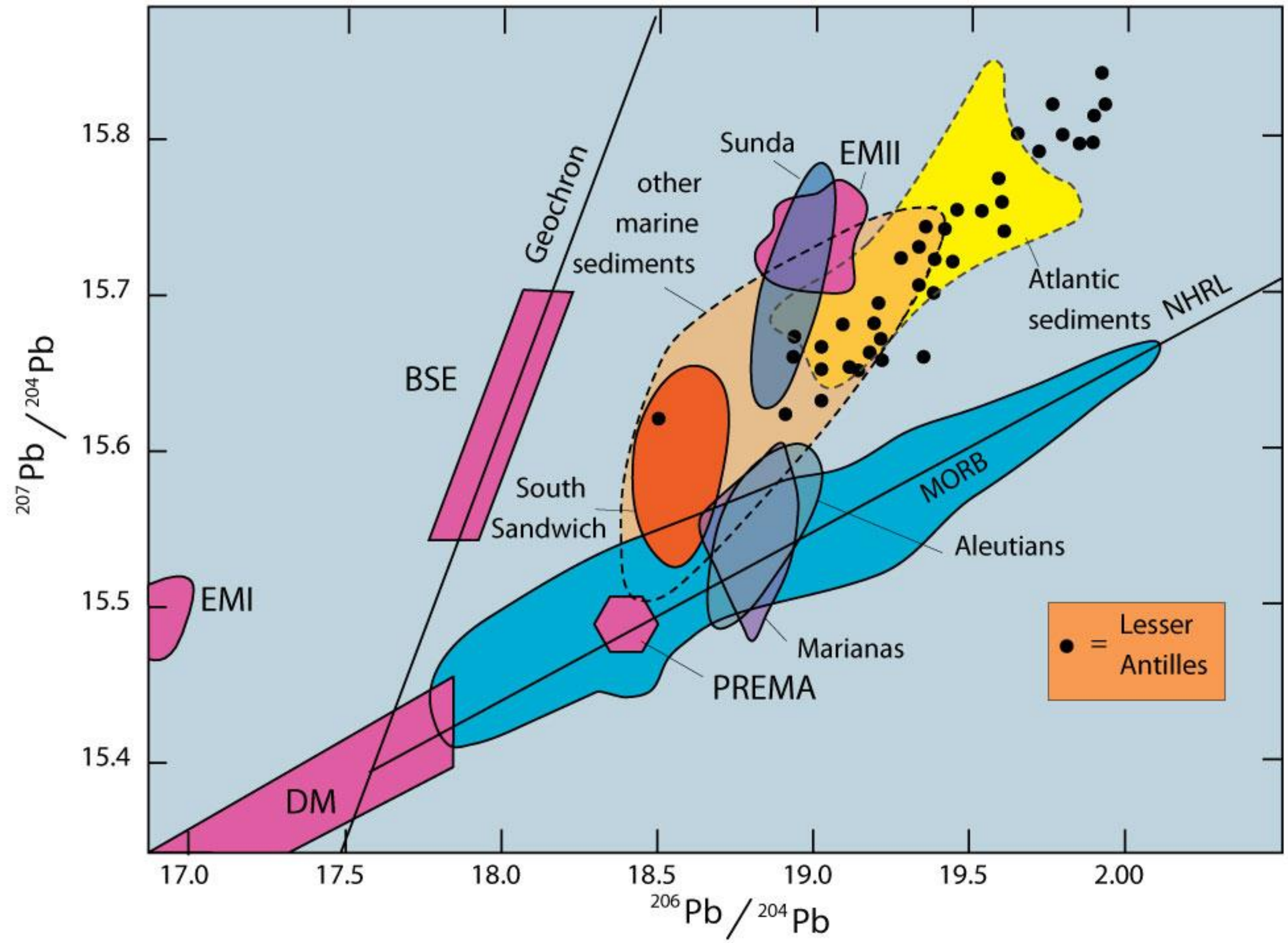




Hu et al., submitted

Origins of Lesser Antilles arc lavas

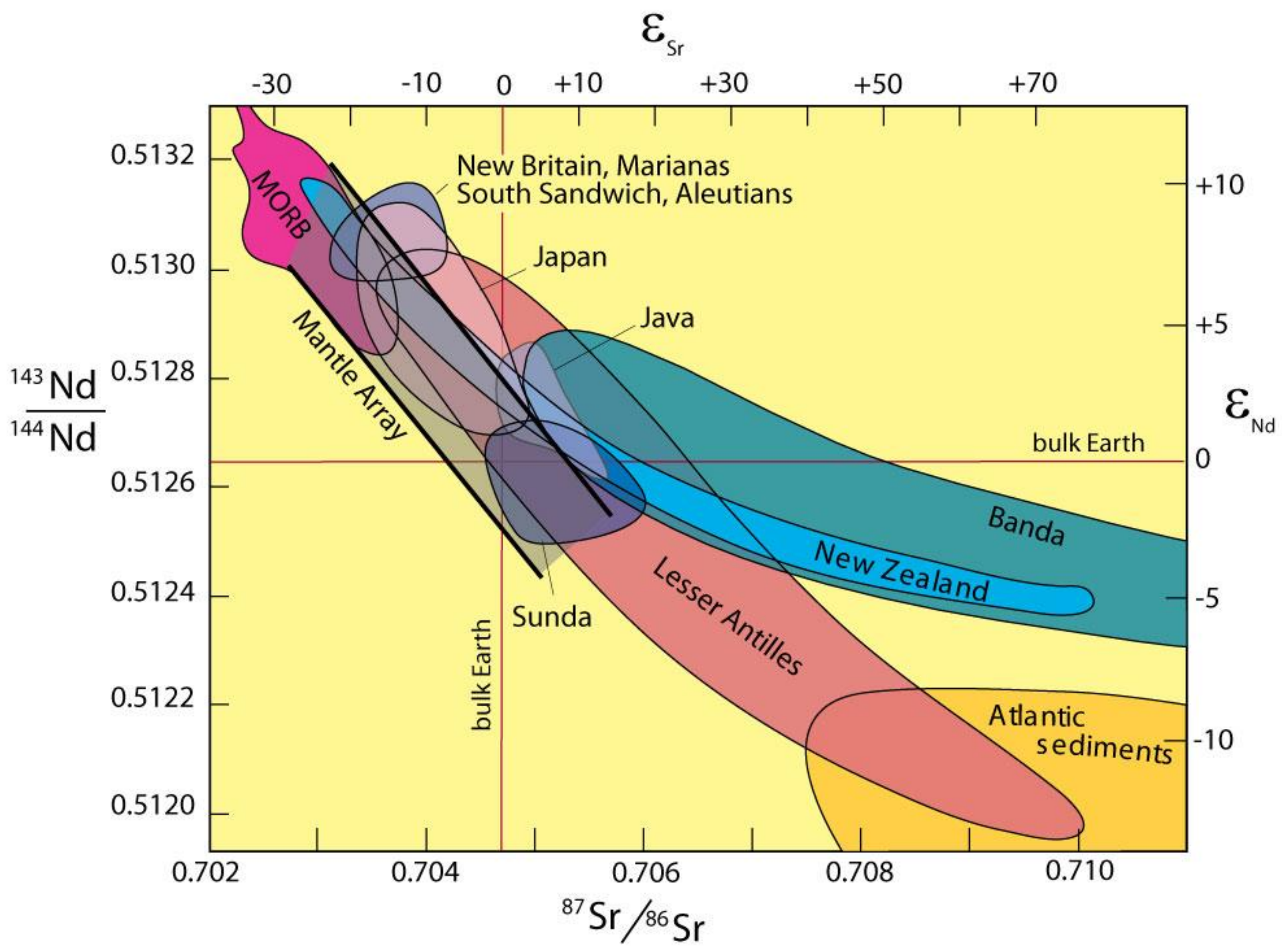
Significant sedimentary inputs: Pb isotopes



Winter, J. Introduction to Igneous & Metamorphic Petrology

Origins of Lesser Antilles arc lavas

Significant sedimentary inputs: Sr-Nd isotopes



Winter, J. Introduction to Igneous & Metamorphic Petrology

Debates on origins of Lesser Antilles arc lavas

Where and how the sediment was incorporated into the lavas?

- Mantle wedge: through fluids derived from the subducted slab in the mantle wedge

  No, fluids should be heavy and can't produce such low $\delta^{41}K$

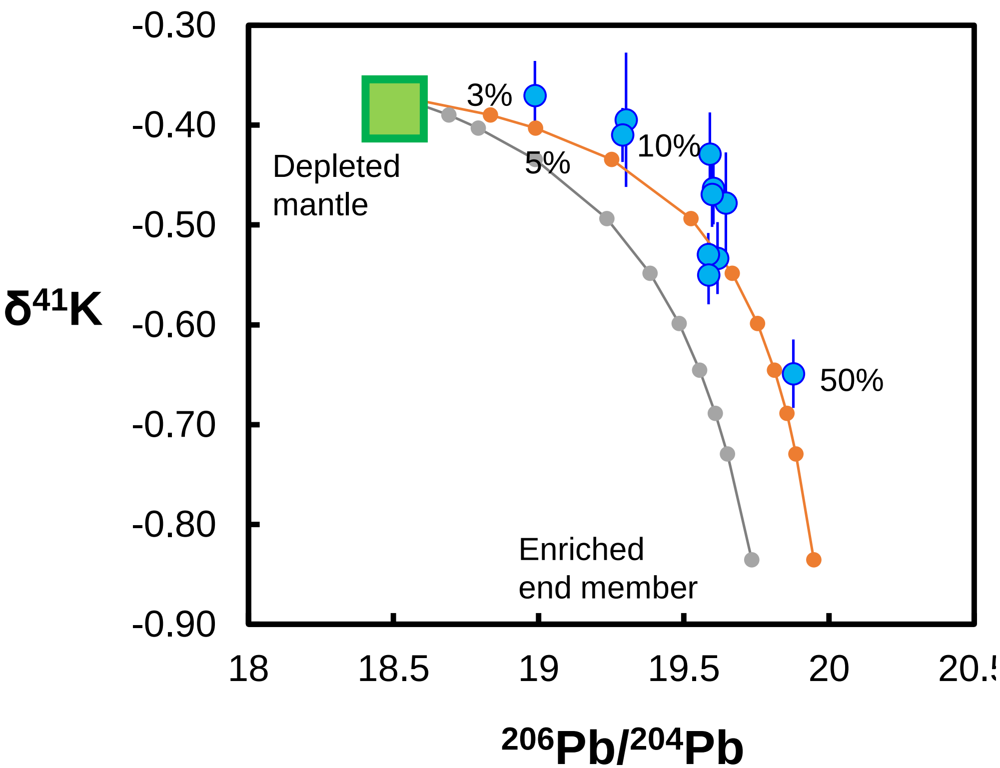
- Arc crust: sediment was added in the arc crust through mixing or AFC processes

- Mantle wedge: sediment or its melt added in the mantle wedge

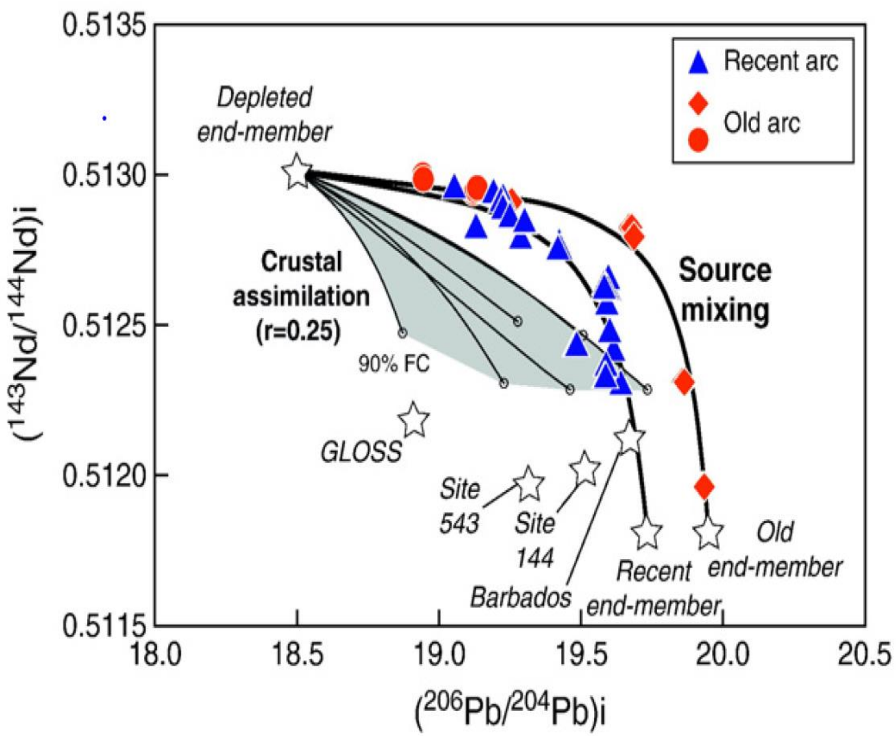
- Potassium isotopic data can help to solve the debate

Mixing in the arc crust

- Unrealistically high proportions of sediments (50%)
- Cannot reproduce radiogenic isotopic variations



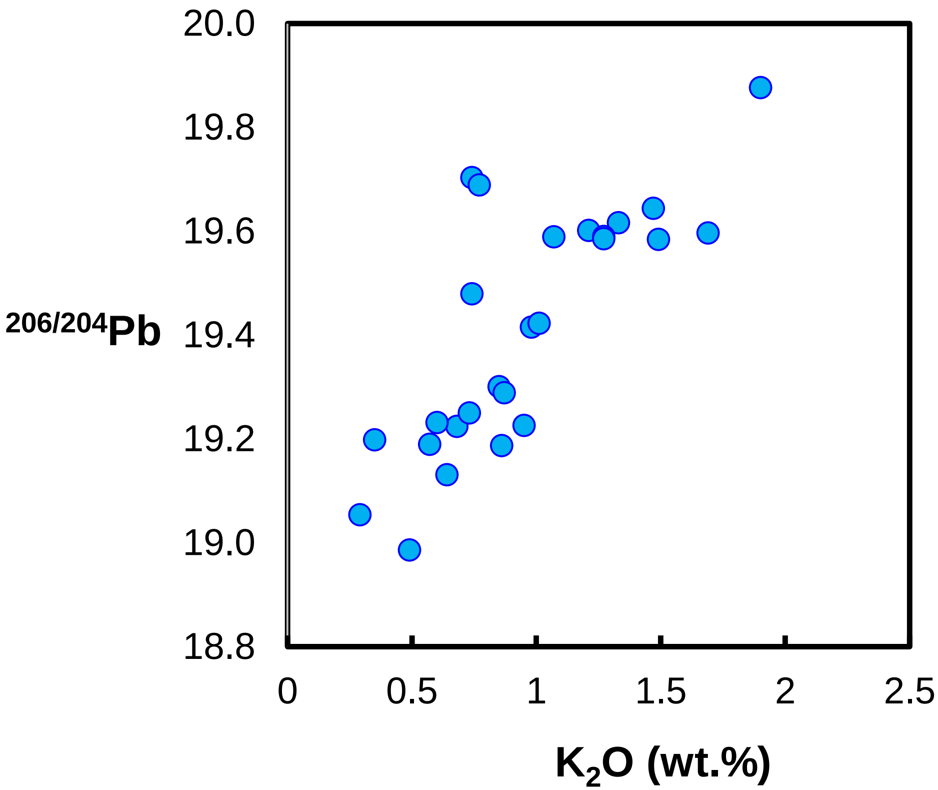
Hu et al., submitted

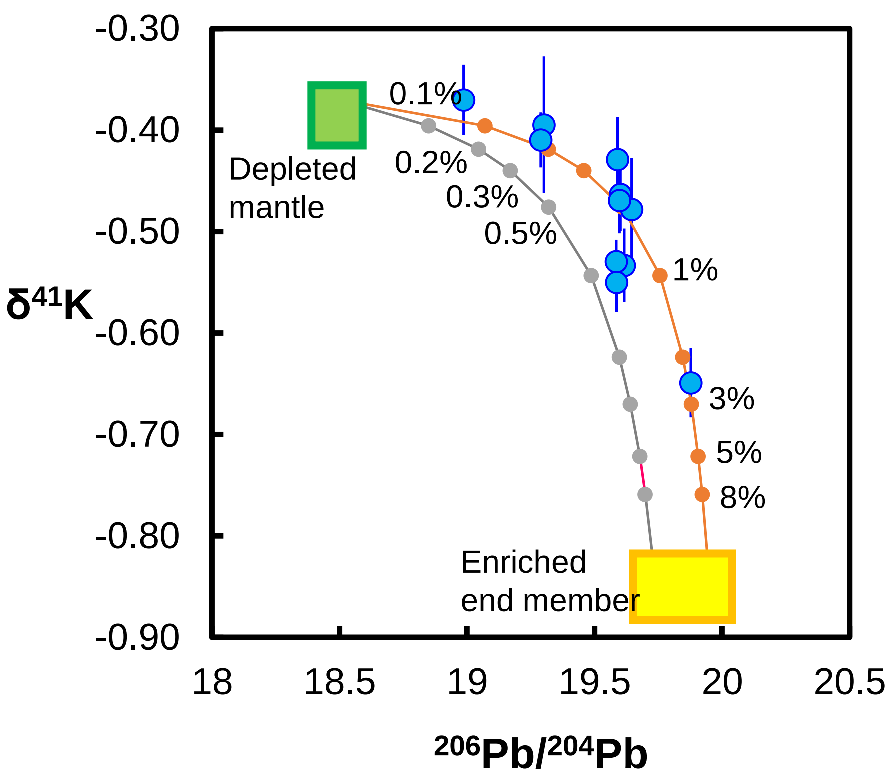


Labanieh et al., 2010

Mixing in the mantle wedge

- < 3% sediment addition explains the isotopic variation
- Consistent with previous estimates (0.1 to 5%)





Hu et al., submitted

Outline

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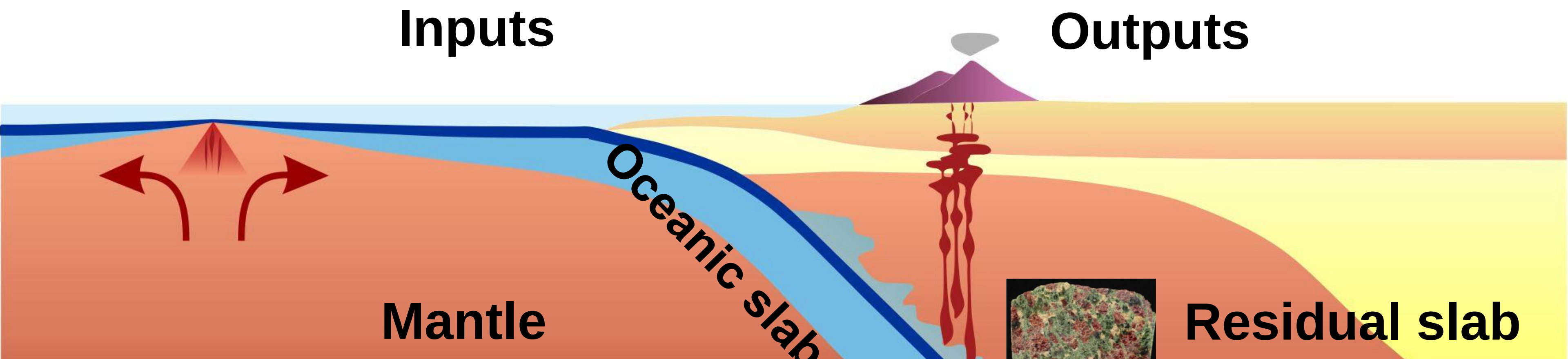
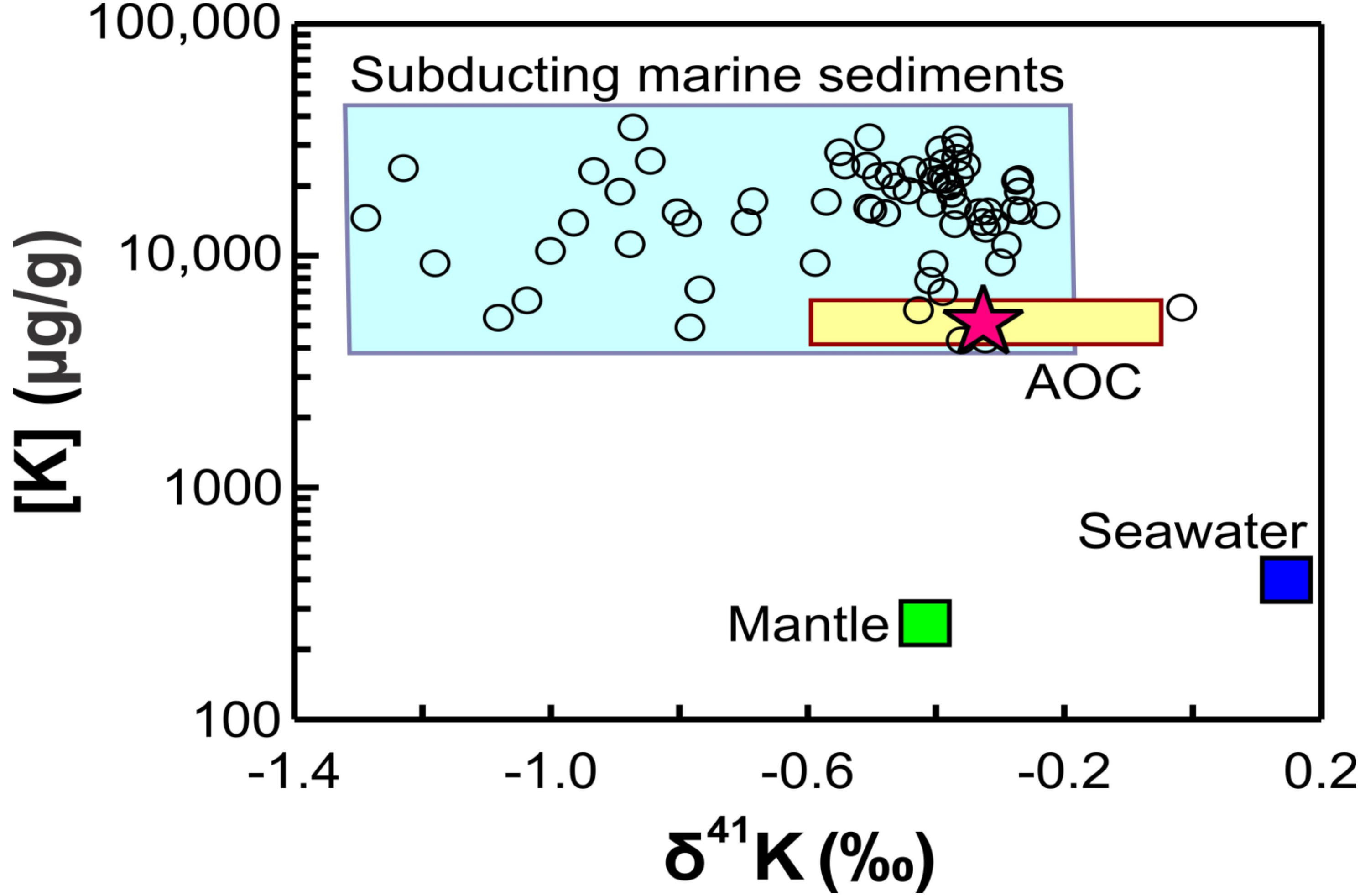


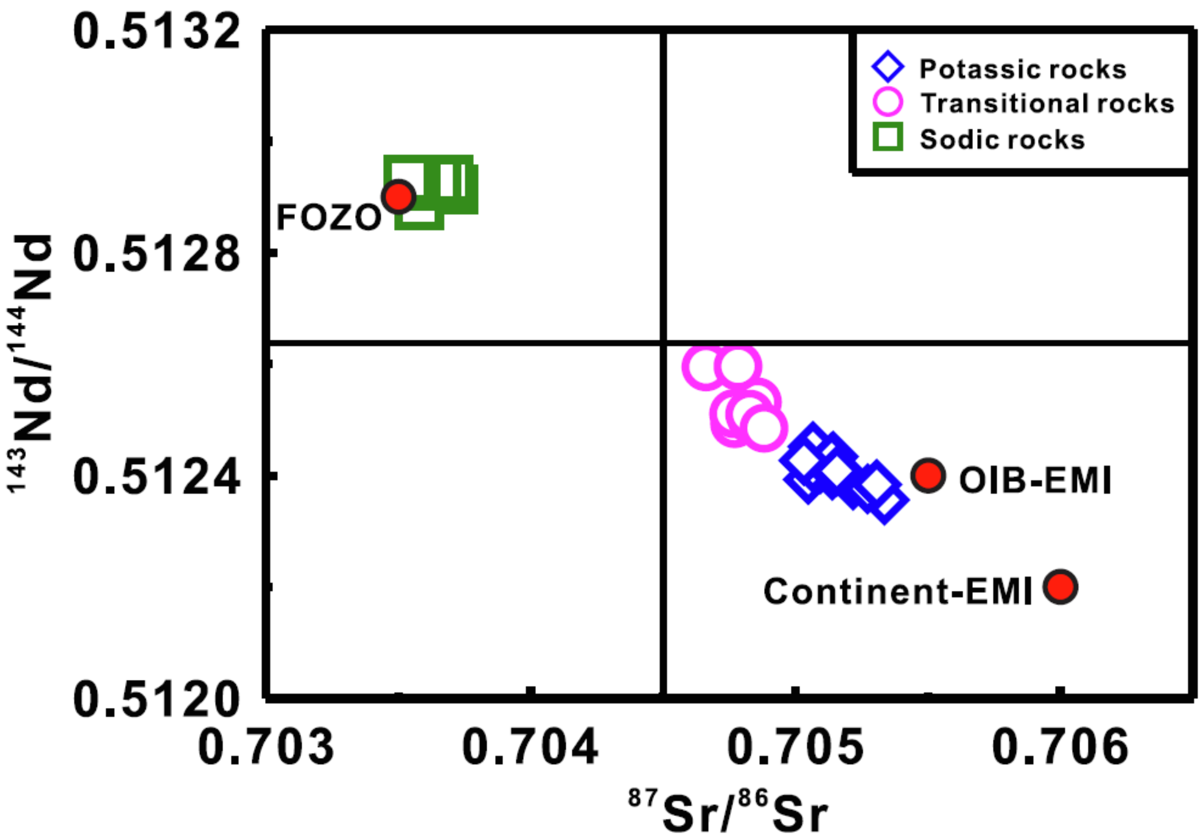
Great tracer for subducted AOC vs. sediments



Hu et al., submitted

Great tracer for subducted AOC vs. sediments

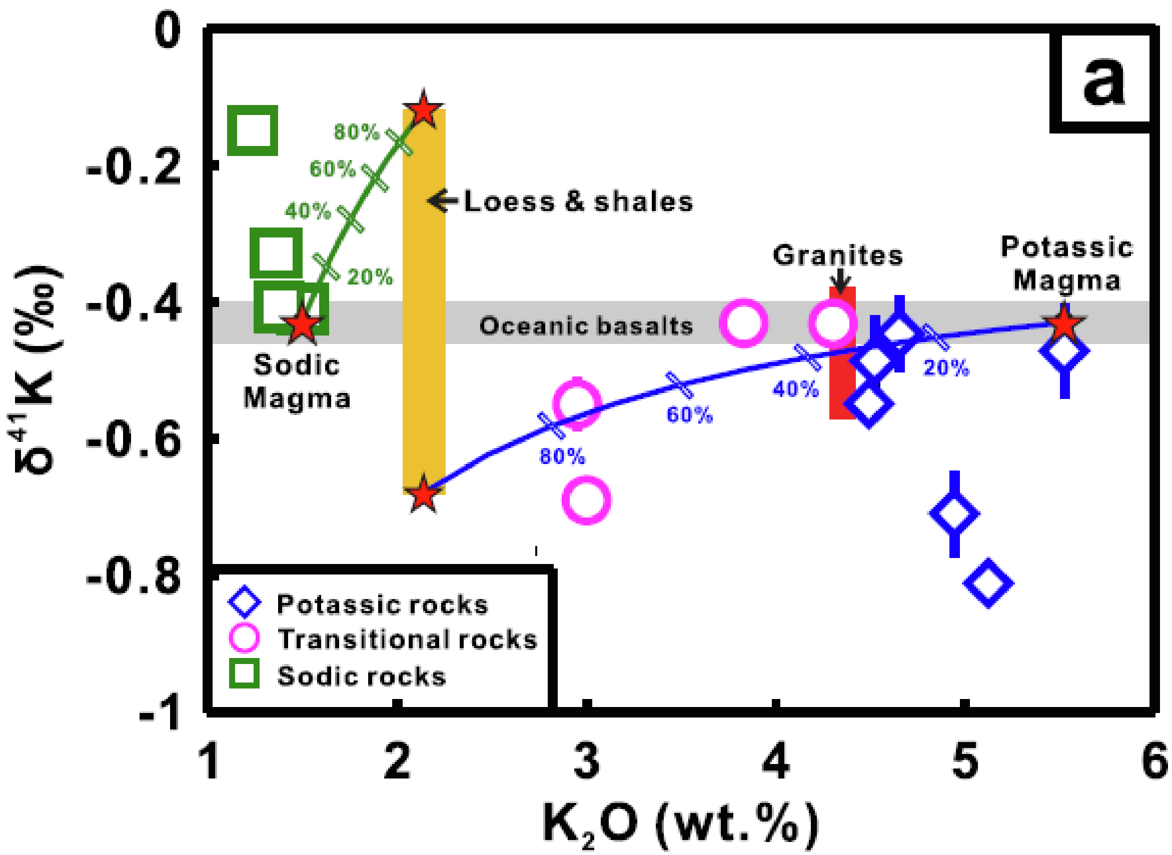
- Continental basalts from Northeast China
- Radiogenic isotopes → recycled crusts in the source



Sun et al., 2020 GCA

Great tracer for subducted AOC vs. sediments

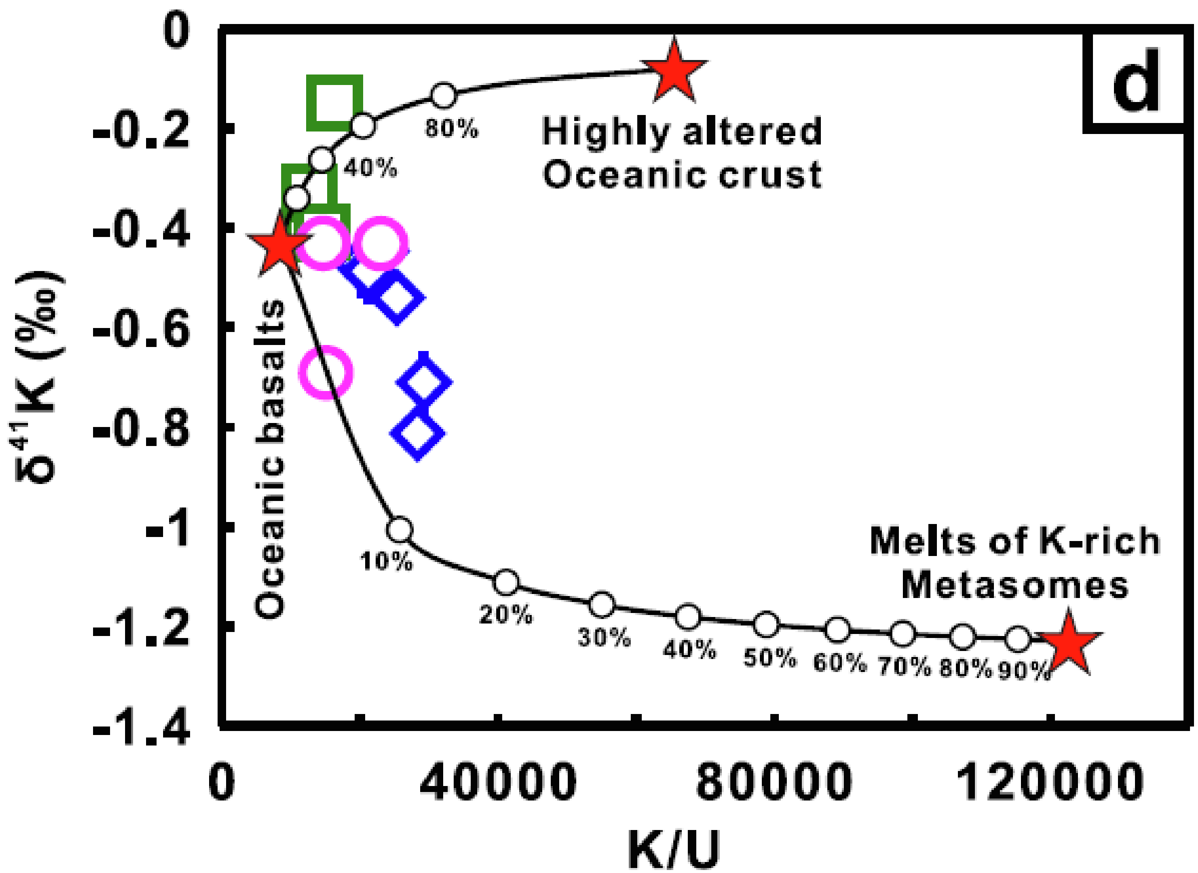
Crustal assimilation can't explain the data due to unrealistic high crustal contribution



Sun et al., 2020 GCA

Great tracer for subducted AOC vs. sediments

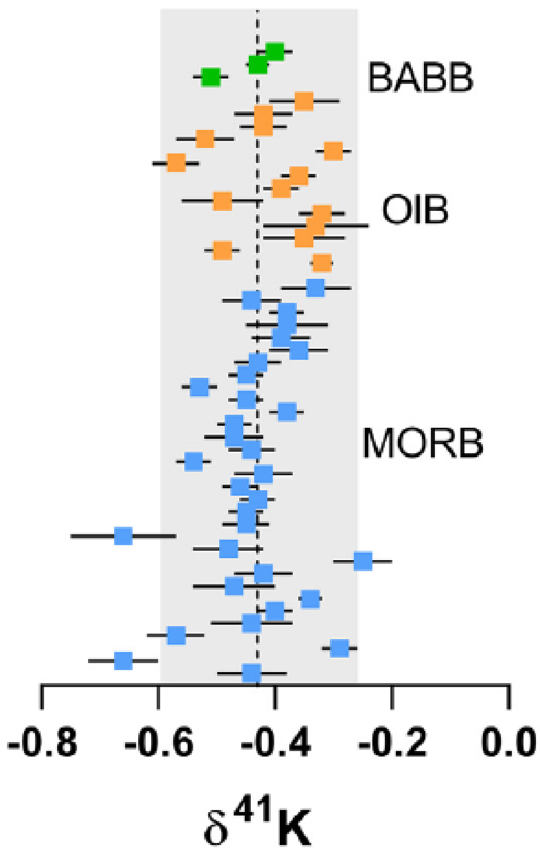
- Altered crust: high $\delta^{41}K$ samples
- Sediments: low $\delta^{41}K$ samples

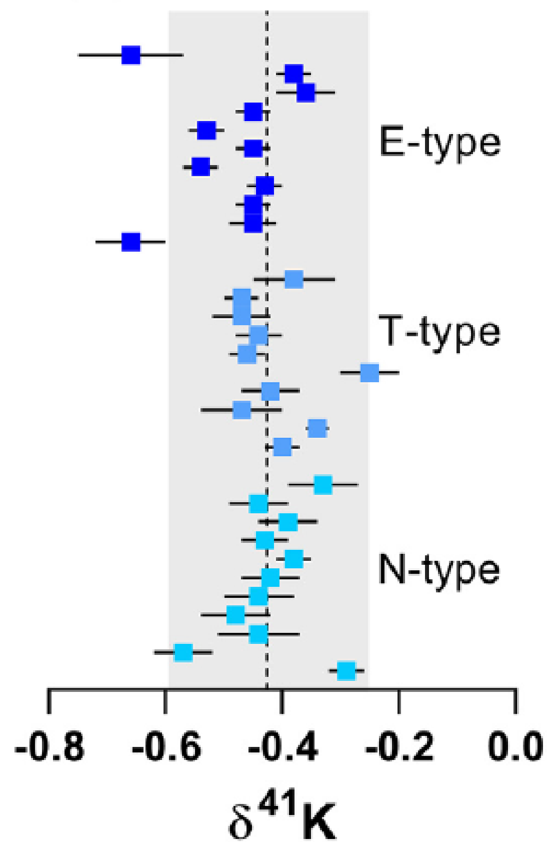


Sun et al., 2020 GCA

How about MORBs and OIBs?

- Global MORBs and OIBs are homogenous
- Dehydration→ K loss during subduction?

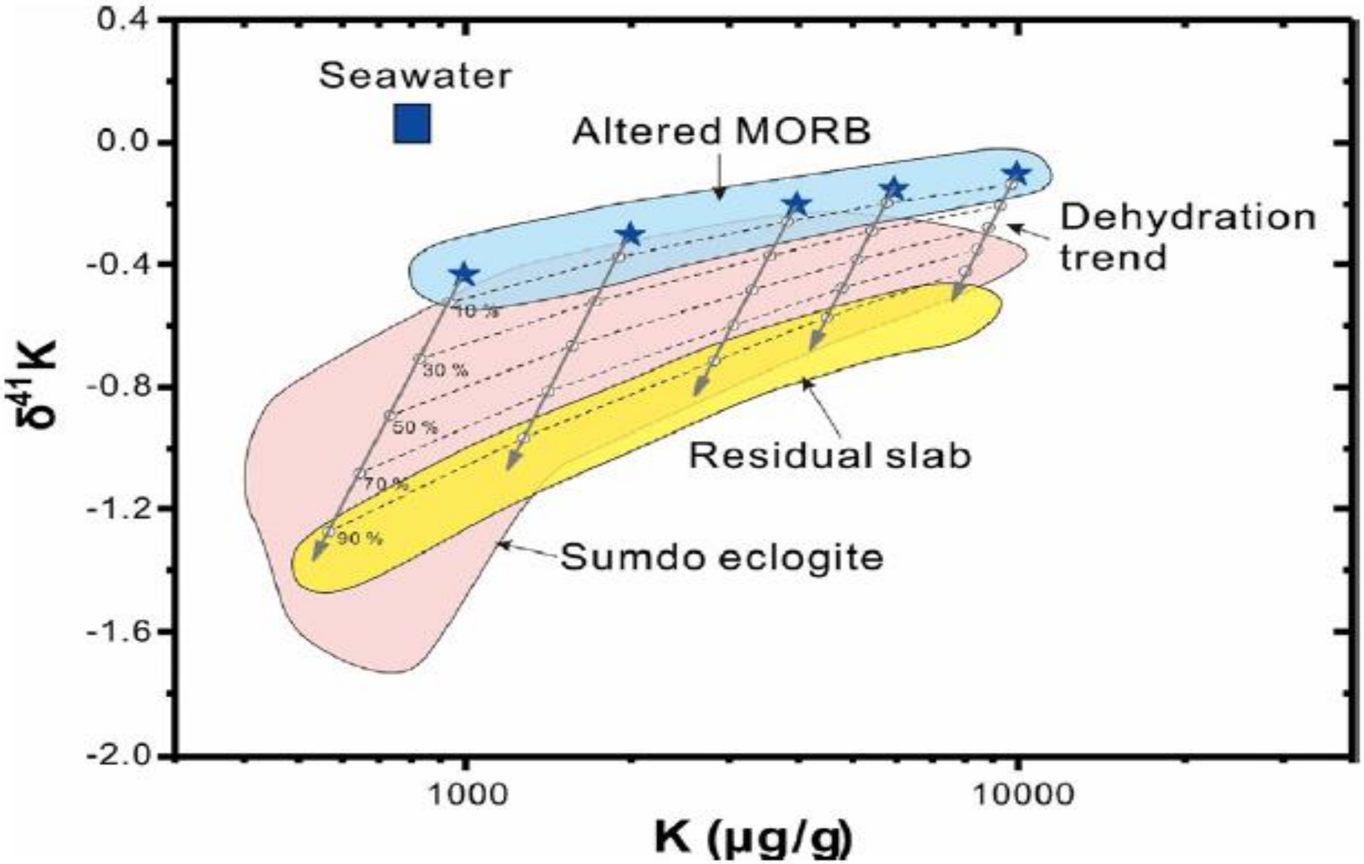




Tuller-Ross et al., 2019 GCA

Dehydration removes K from altered MORB

- Heavy K isotopes into fluids
- Light residue? → eclogites



Liu et al., 2020 GCA

Summary

- Altered oceanic crust has heterogeneous and overall slightly heavy K isotopic composition than the mantle

- Marine sediment has heterogeneous and overall slightly light K isotopic composition than the mantle

- K isotopic data indicate a sedimentary input in the mantle wedge is responsible for the Lesser Antilles arc lava

- Continental basalts from Northeast China reflect inputs from both subducted AOC and sediments

Outline

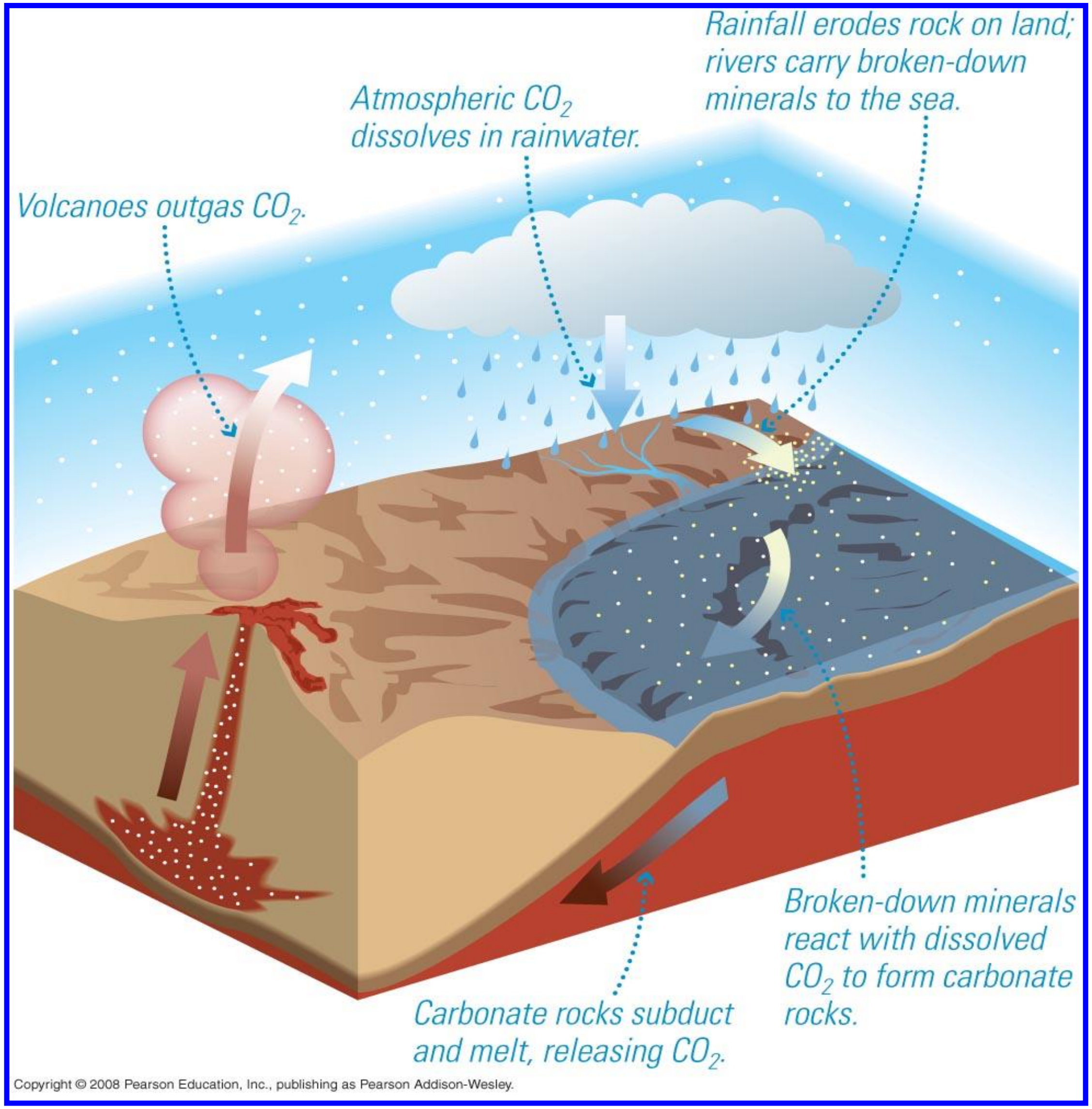
- K Isotope Analysis
- Moon-Forming Giant Impact
- Crust-Mantle Interactions
- Continental Weathering
- Biological/Medical/Others

The importance of continental weathering

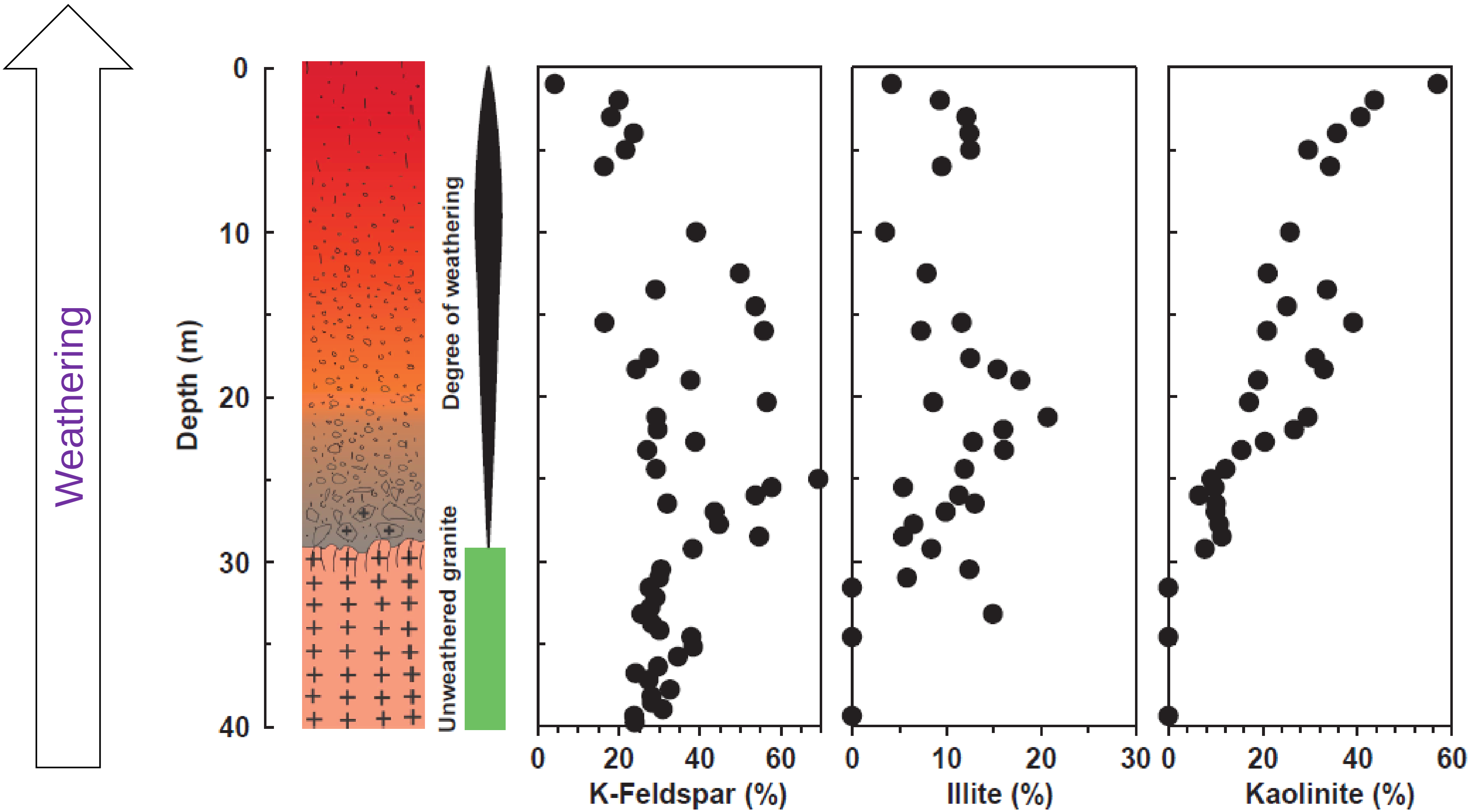
Regulates the global CO_2 cycle

Controls composition of rivers and oceans

Modifies compositions of the continental crust



K isotope fractionation during granite weathering

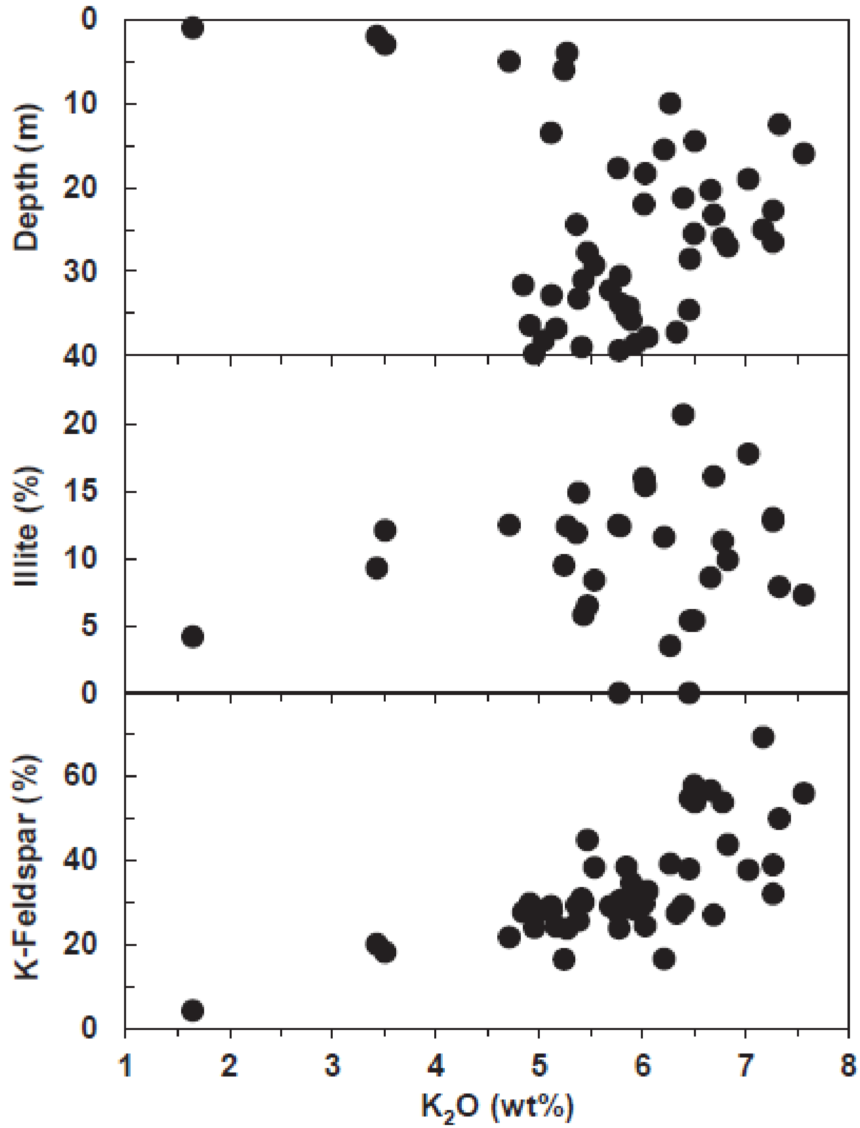


Kaolinite is a great index of degree of weathering

Teng et al. 2020 GCA

K isotope fractionation during granite weathering

K_2O content is controlled by K-feldspar in weathered residue



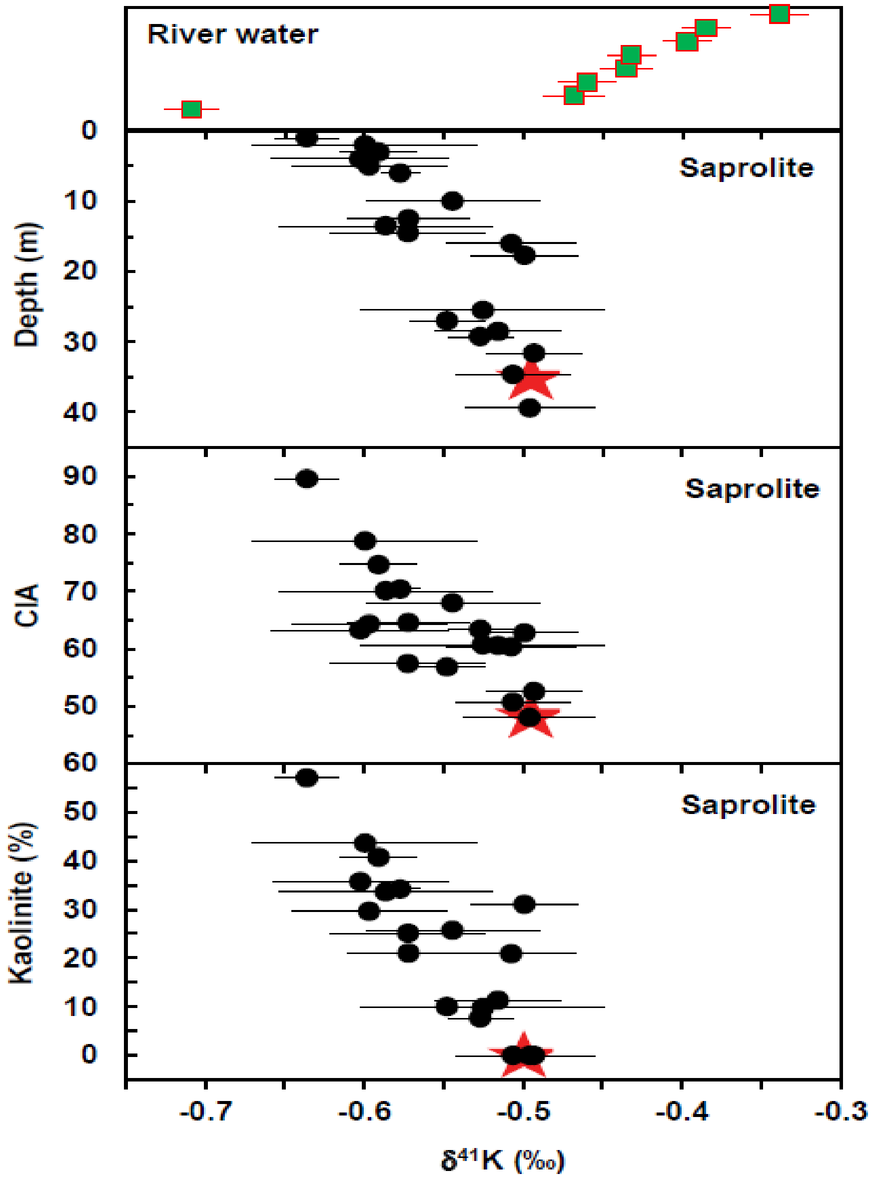
Teng et al. 2020 GCA

K isotope fractionation during granite weathering

K_2O content is controlled by K-feldspar in weathered residue

$\delta^{41}K$ is controlled by the degree of chemical weathering

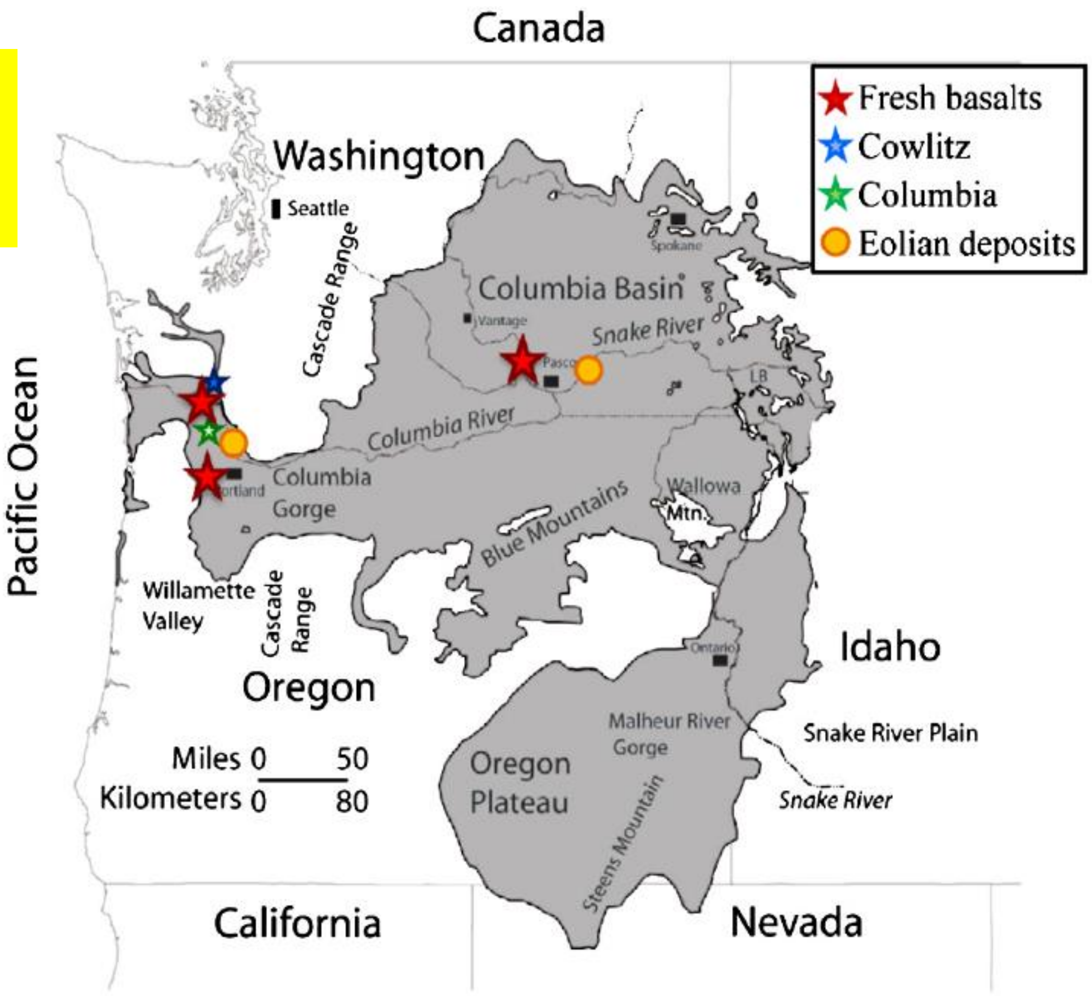
Heavy K isotopes prefer rivers to saprolites during weathering



Teng et al. 2020 GCA

K isotope fractionation during basalt weathering

- Columbia River basalts
- Two drilling cores

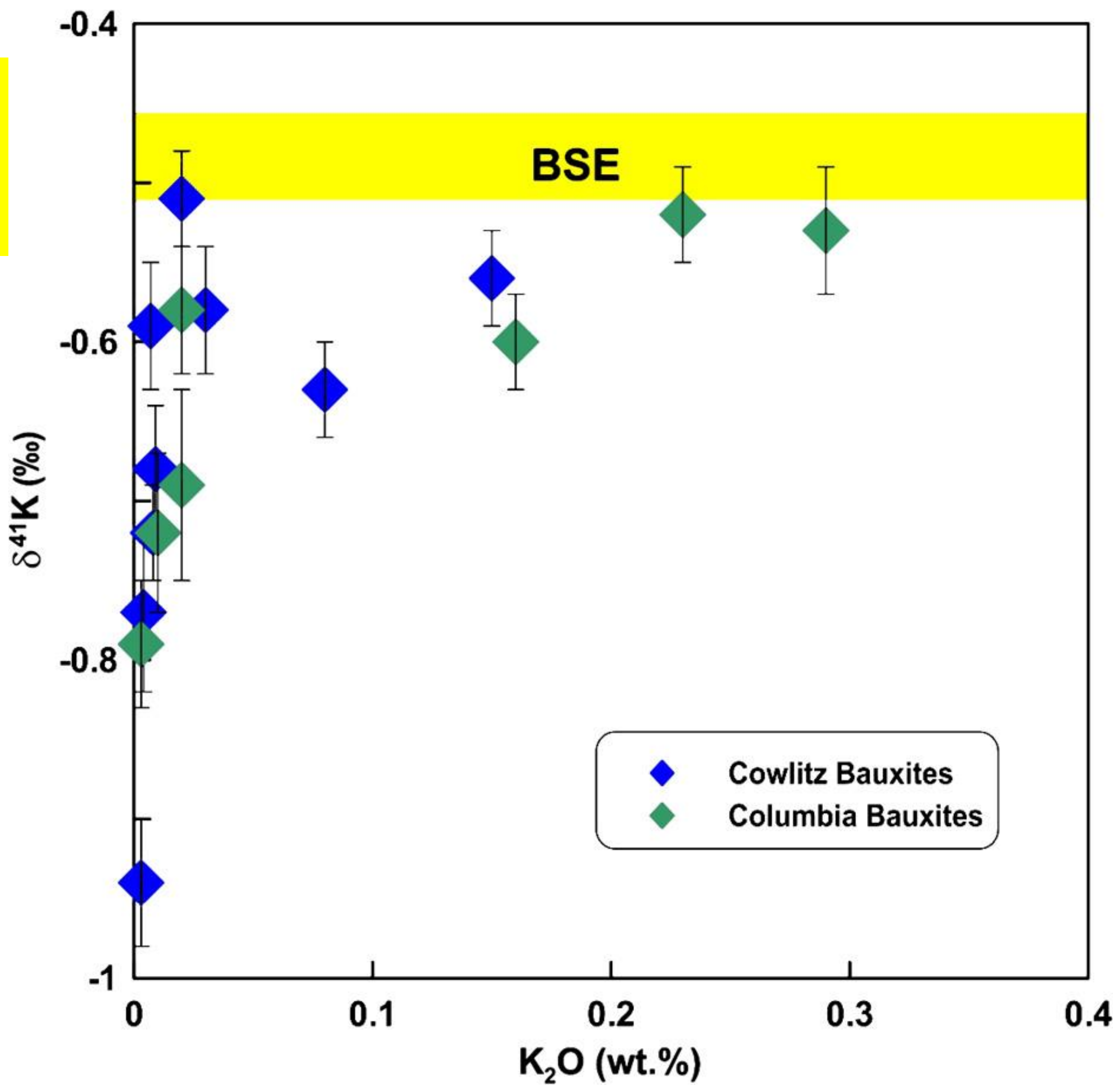


Liu et al., 2013 GCA
Chen et al. 2020 EPSL

K isotope fractionation during basalt weathering

- Columbia River basalts
- Two drilling cores

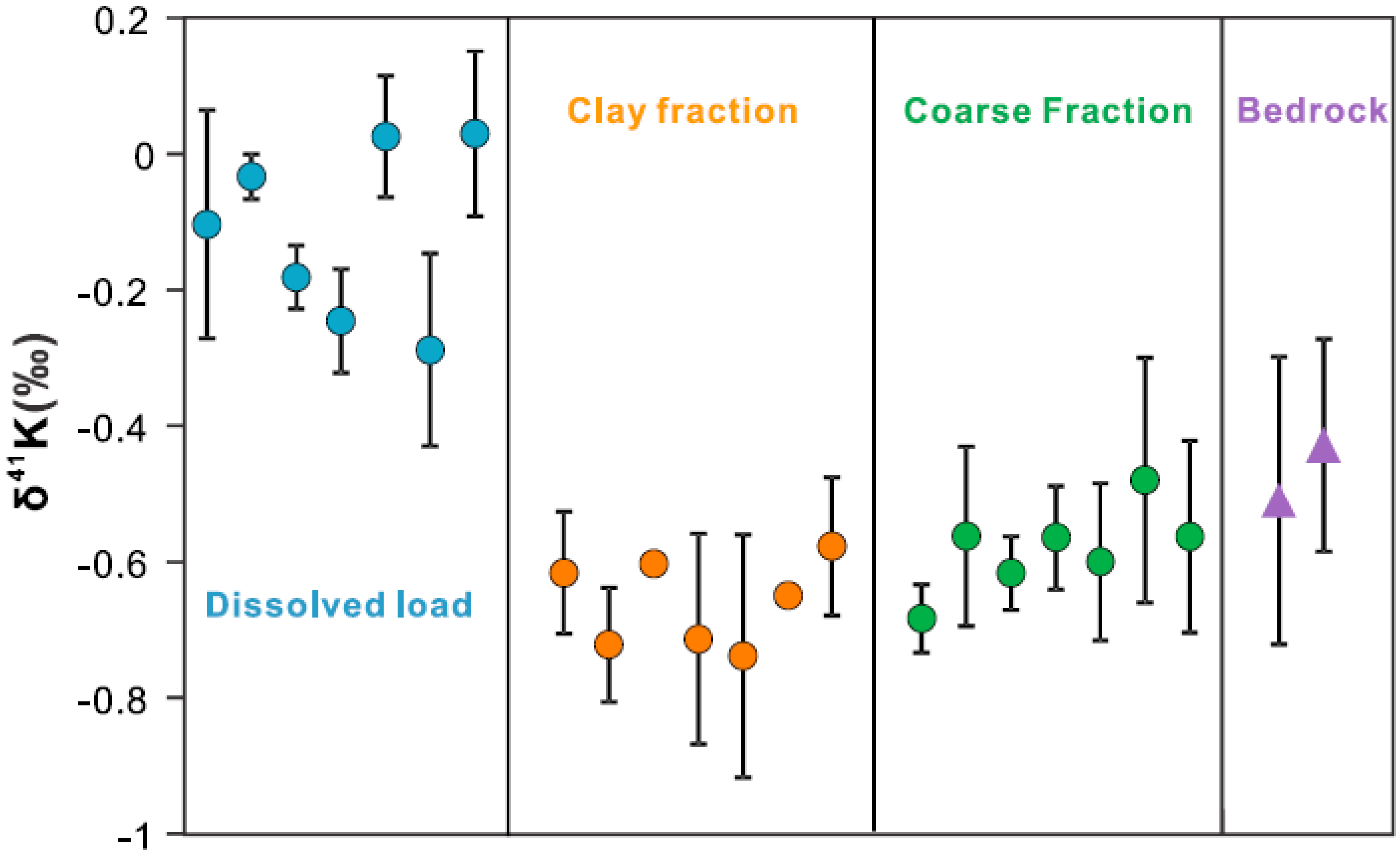
- K_2O is lost during weathering
- Heavy isotopes lost to the hydrosphere



Liu et al., 2013 GCA
Chen et al. 2020 EPSL

K isotope fractionation in riverine system

Dissolved load is heavier than rocks



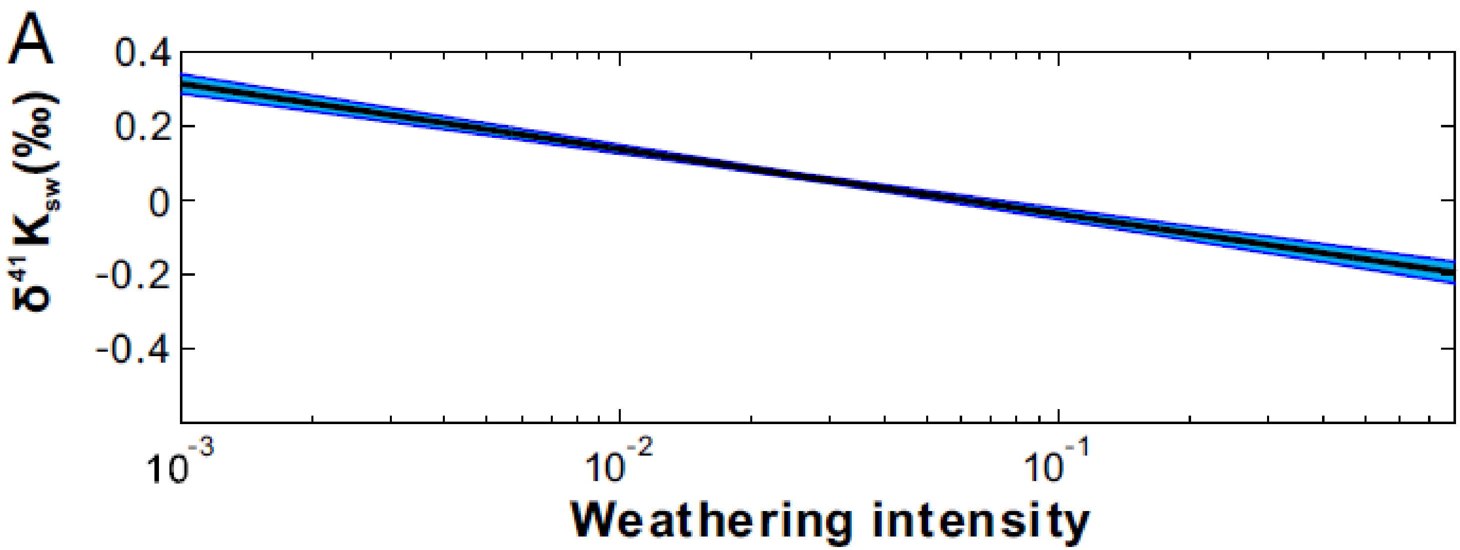
Li et al. 2019 PNAS

K isotopes: Index of chemical weathering?

K isotopic composition of river water → weathering intensity

K isotopic composition of river water → seawater

K isotopic composition of seawater → weathering intensity

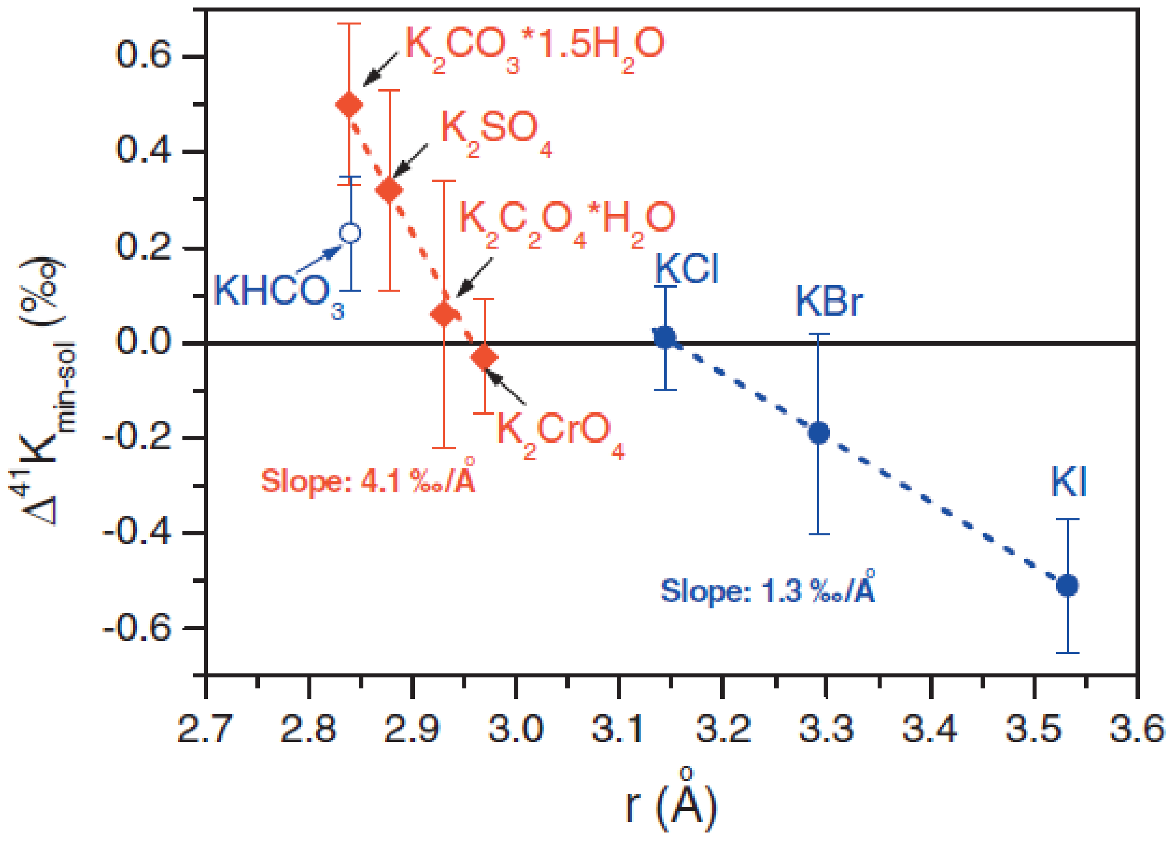


Li et al. 2019 PNAS

K isotopes: Index of chemical weathering?

Evaporates → seawater in the deep time?

KCl = seawater since no fractionation at room temperature



Li et al. 2017 GCA

Outline

- K Isotope Analysis
- Moon-Forming Giant Impact
- Crust-Mantle Interactions
- Continental Weathering
- Biological/Medical/Others

Biological/Medical/Others

Goldschmidt2020 Abstract

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Goldschmidt2020 Abstract

Potassium st
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[2]Applied & Analytic
Johannes Gutenb
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Goldschmidt2020 Abstract

Tracing diage
transition us

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Elliott[3], Clark M. John

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Goldschmidt2020 Abstract

Stable K isotope characteristics at mid-ocean ridge hydrothermal vents and their implications for the modern and ancient K cycle

XIN-YANG CHEN[1], BRIAN BEARD[2], MASON NEUMAN[2], MARIA FAHNESTOCK[3], JULIA BRYCE[3], CLARK JOHNSON[2], XIN-YUAN ZHENG[1]

[1]Department of Earth and Environmental Sciences, University of Minnesota–Twin Cities, Minneapolis MN 55455, USA (xinychen@uw.edu, zhengxy@umn.edu)

[2]Department of Geoscience, University of Wisconsin–Madison, Madison WI 53706, USA

Future Directions

Fractionation factors:
- Theoretical calculation
- Natural samples
- Lab experiments

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First-principles investigation of the concentration effect on equilibrium fractionation of K isotopes in feldspars

Yonghui Li[a], Wenzhong Wang[a], Shichun Huang[b], Kun Wang[c], Zhongqing Wu[a,*]

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Geochimica et Cosmochimica Acta
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First-principles investigation of equilibrium K isotope fractionation among K-bearing minerals

Yonghui Li[a,1], Wenzhong Wang[a,1], Zhongqing Wu[a,b,*], Shichun Huang[c]

SPACE CHEMISTRY
Cite This: *ACS Earth Space Chem.* XXXX, XXX, XXX–XXX
http://pubs.acs.org/journal/aesccq

Ab Initio Calculation of Equilibrium Isotopic Fractionations of Potassium and Rubidium in Minerals and Water

Hao Zeng,[†,‡] Viktor F. Rozsa,[‡] Nicole Xike Nie,[†] Zhe Zhang,[†] Tuan Anh Pham,[§] Giulia Galli,[‡,∥,⊥] and Nicolas Dauphas[*,†]

Future Directions

- Reservoirs/Processes

- Technique: LA-Collision Cell-MC-ICPMS

- Applications:
    - geochemical
    - cosmochemical
    - biological
    - medical

Acknowledgements

欢迎大家来华大访问交流！