第三届“非传统稳定同位素” 暑期学校
2020年8月13日，西北大学

镁同位素地球化学

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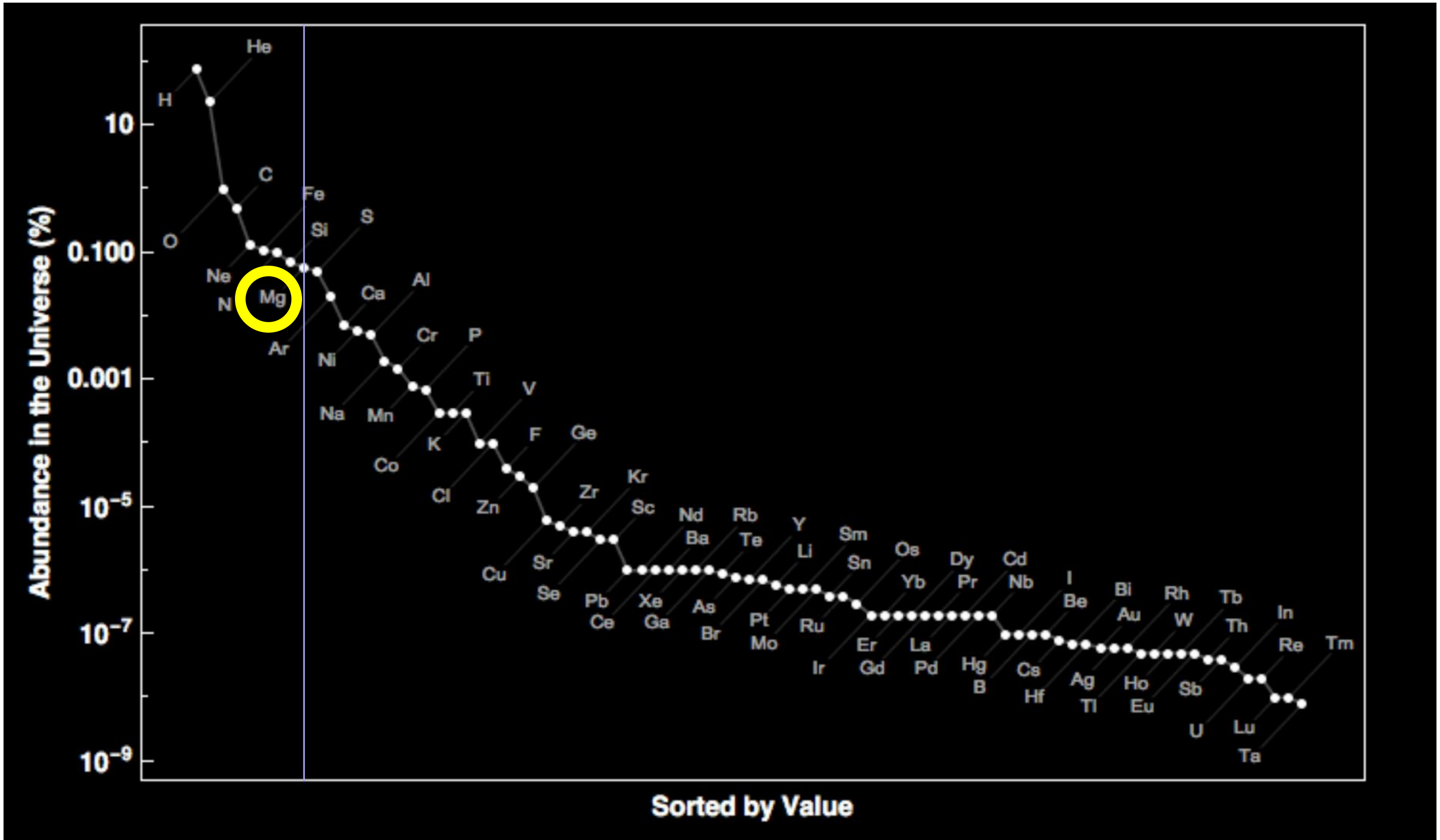
地球与空间科学系

Outline

1. Introduction to Mg and Mg isotopes
2. Analytical methods for Mg isotopes
3. Mechanisms of Mg isotope fractionation
4. Mg isotopic compositions of major reservoirs
5. Mg isotope studies in chemical weathering
6. Mg isotope studies in subduction recycling

Abundance of Mg in the Universe

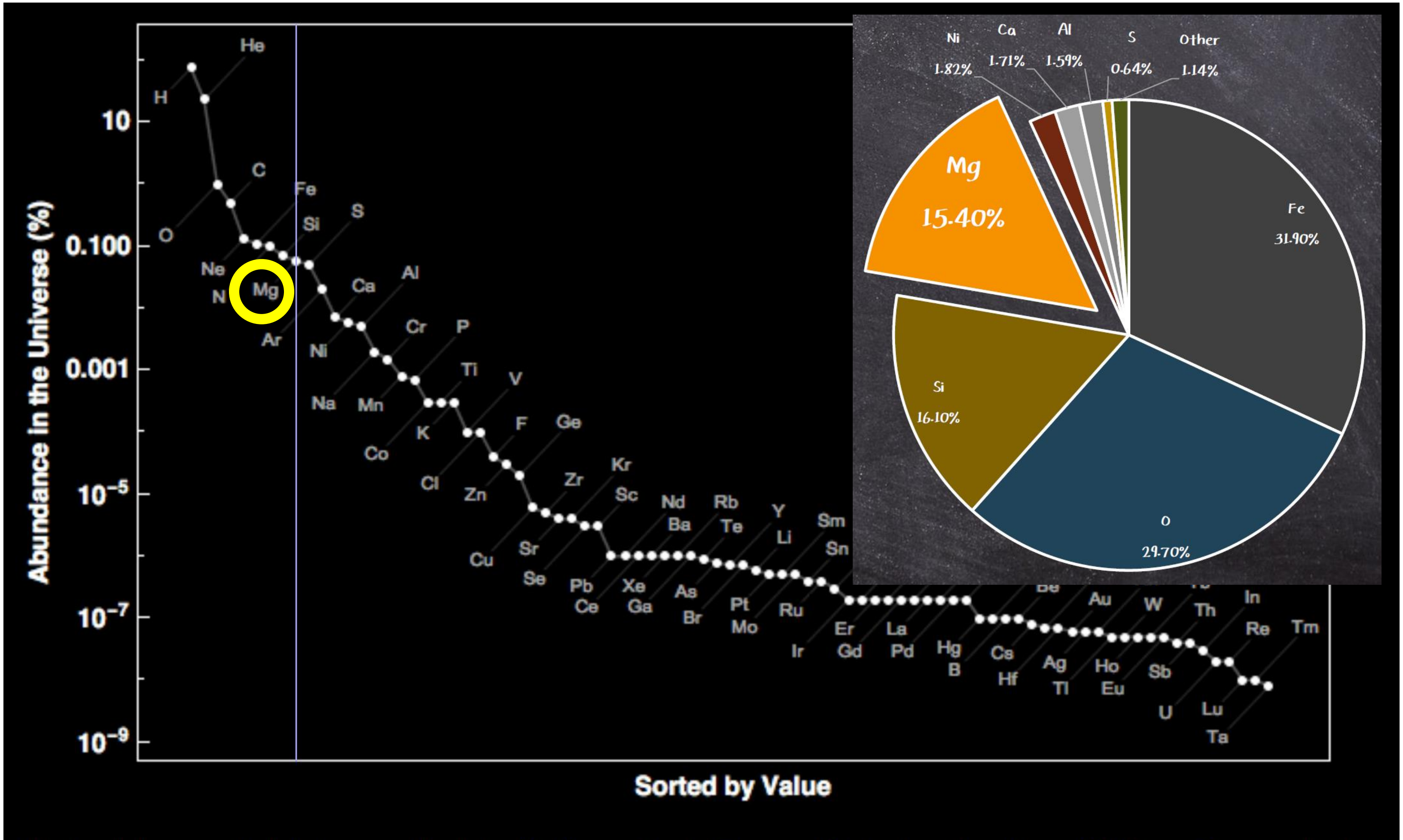
- The 9th most abundant in the universe; 4th in CI chondrites



Up to date, curated data provided by *Mathematica*'s ElementData function from Wolfram Research, Inc.

Abundance of Mg on the Earth

- The 9th most abundant in the universe; 4th in CI chondrites
- The 4th most abundant in on the Earth

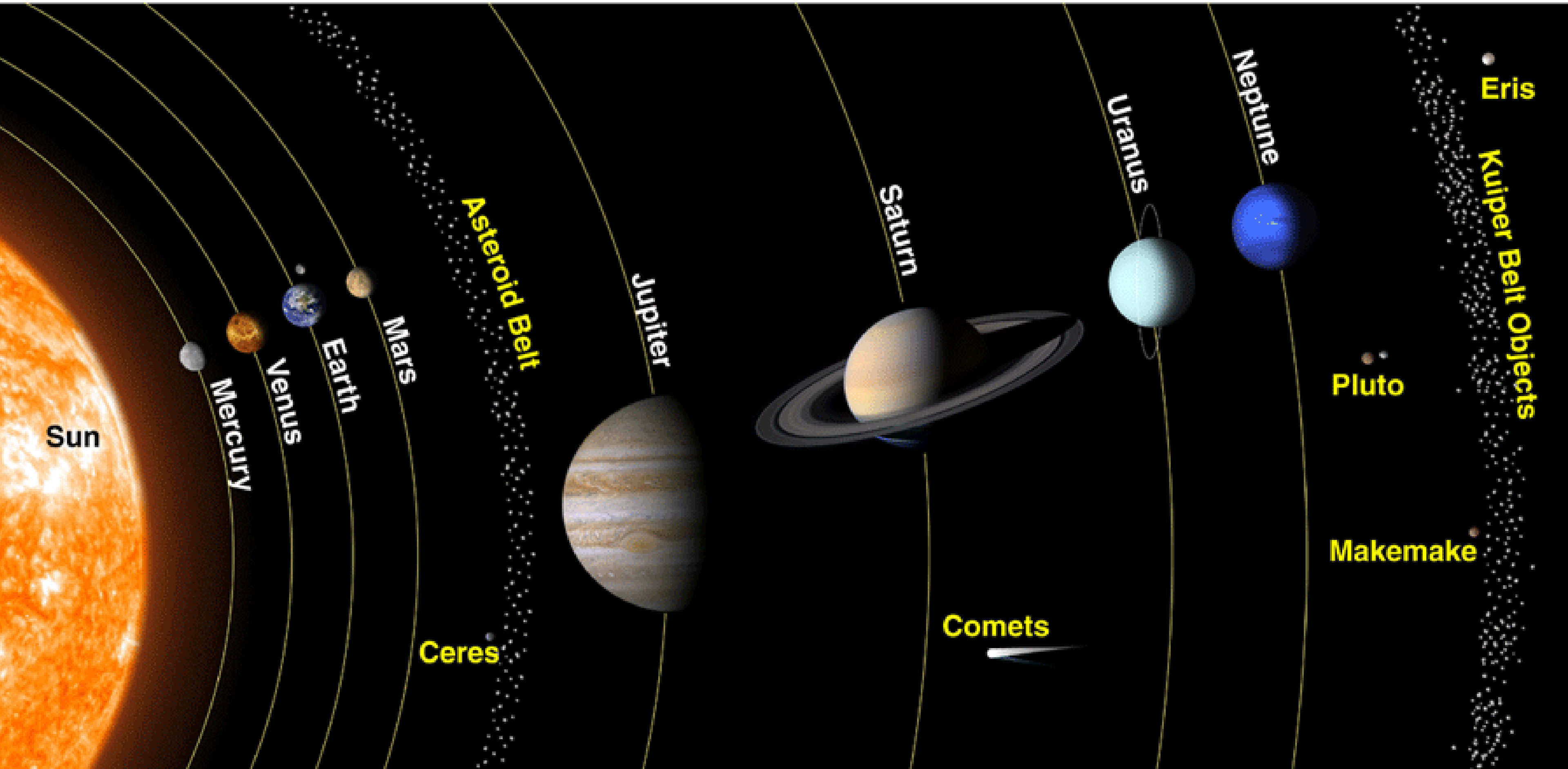


Up to date, curated data provided by *Mathematica*'s ElementData function from Wolfram Research, Inc.

Topics addressed by Mg

How planets accreted and differentiated in early time?

The Present Solar System: 4.567 Ga

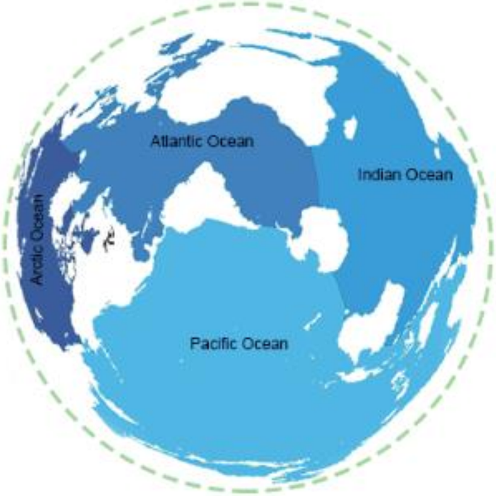


Terrestrial distribution of Mg

Silicates

Carbonates

Oceans & Rivers



Plants & Soils

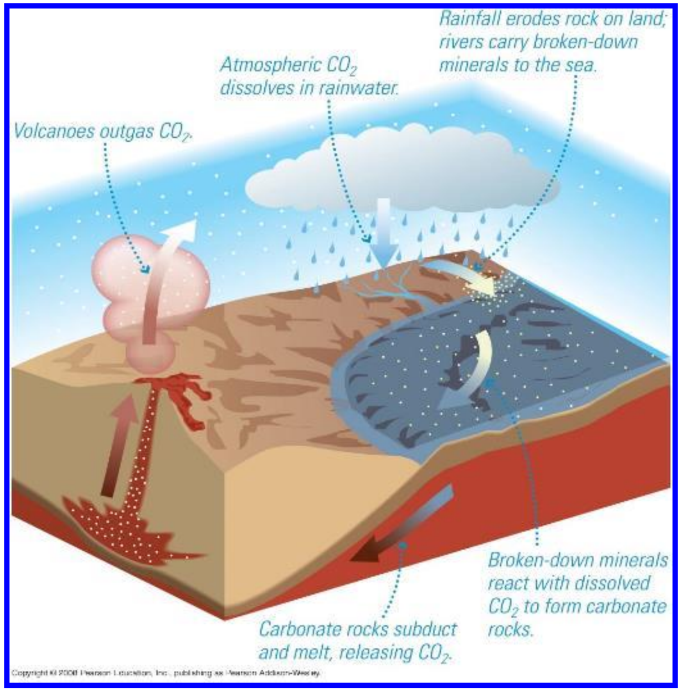
Topics addressed by Mg

Mg is a major element involved in chemical weathering

Silicate weathering is important in carbon sequestration and long-term climate dynamics

Silicate weathering: $MgSiO_3 + 2CO_2 + 3H_2O \rightarrow Mg^{2+} + H_4SiO_4 + 2HCO_3^-$

Carbonate precipitation: $(Ca,Mg)^{2+} + 2HCO_3^- \rightarrow (Mg,Ca)CO_3 + CO_2 + H_2O$

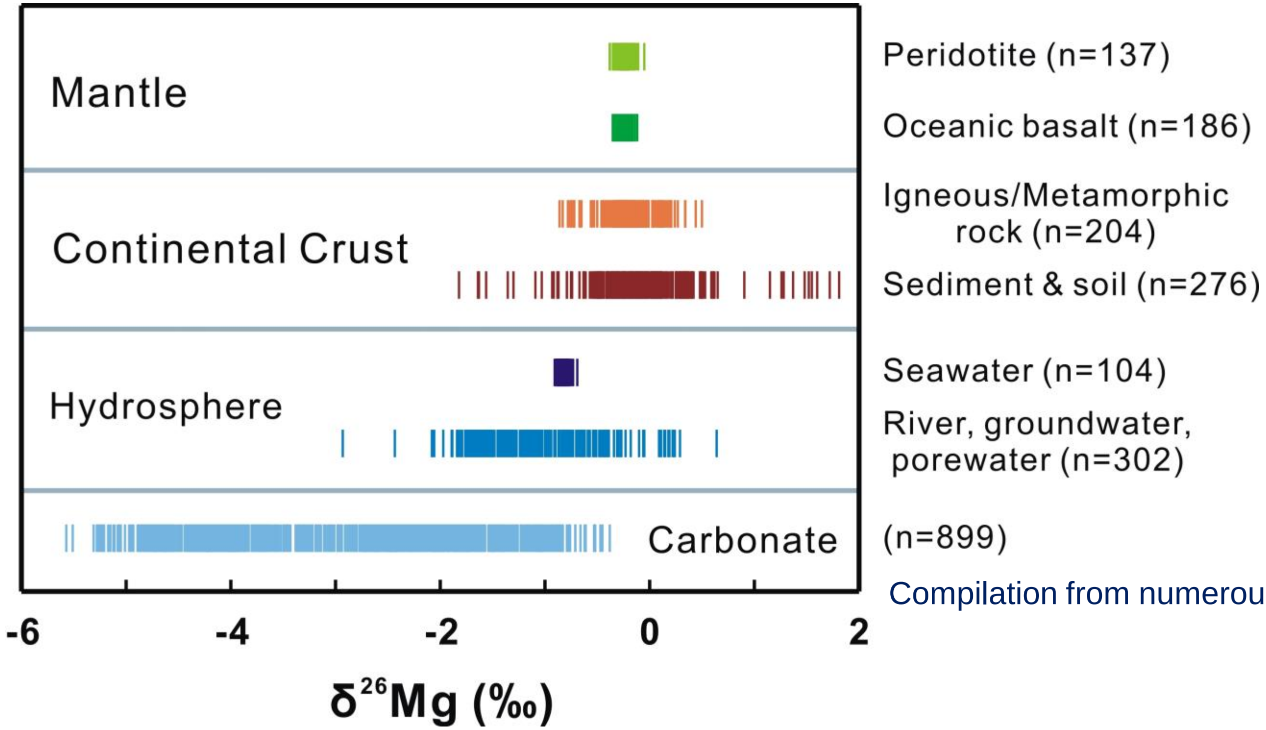


Topics addressed by Mg

Mg can help understand mass exchange in Earth reservoirs

Potential tracers of deep carbon recycling

(e.g., Li and Liu Engr 2015)



Compilation from numerous sources

- Low-T processes fractionate Mg isotopes significantly
- Carbonates have a distinctive low-δ^{26}Mg signature

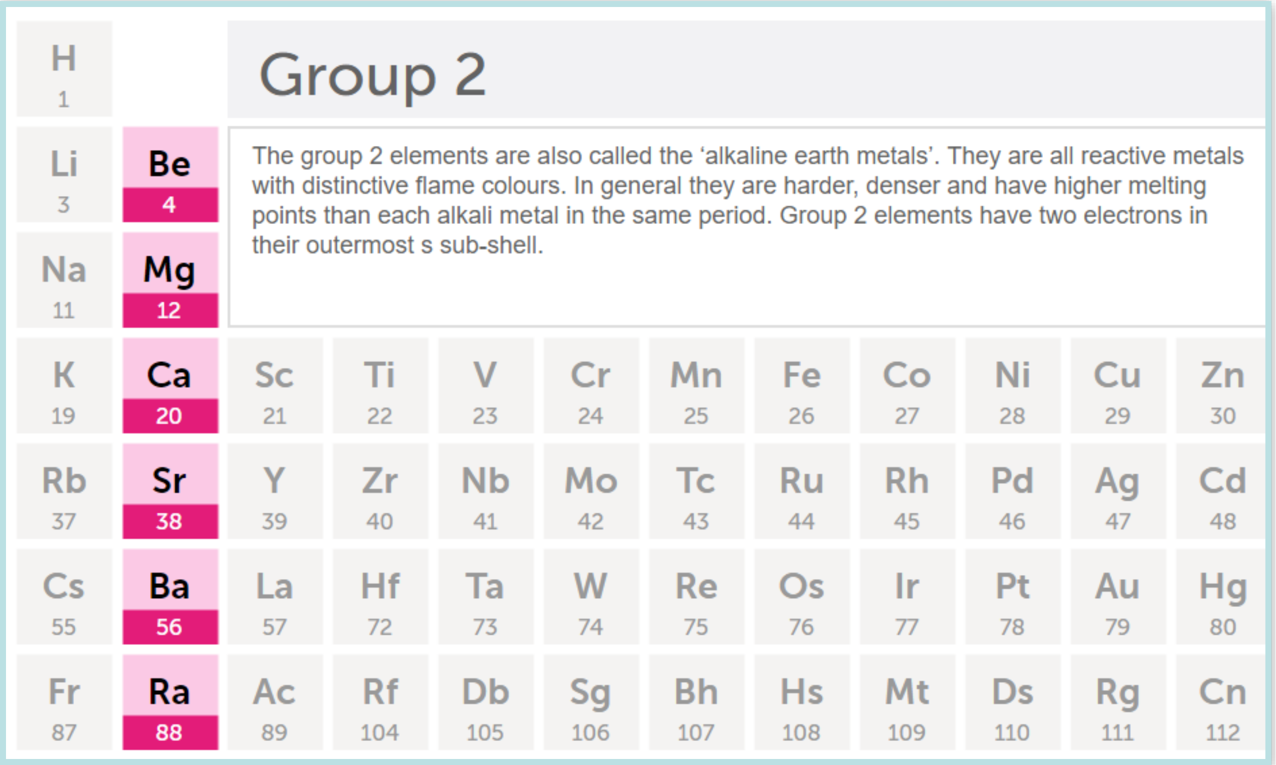
Geochemical behavior of Mg

Alkaline Earth metals

Forming alkaline solution (pH>7)

Oxides have high melting points

MgO: 2852 °C
Na_2O:1132 °C



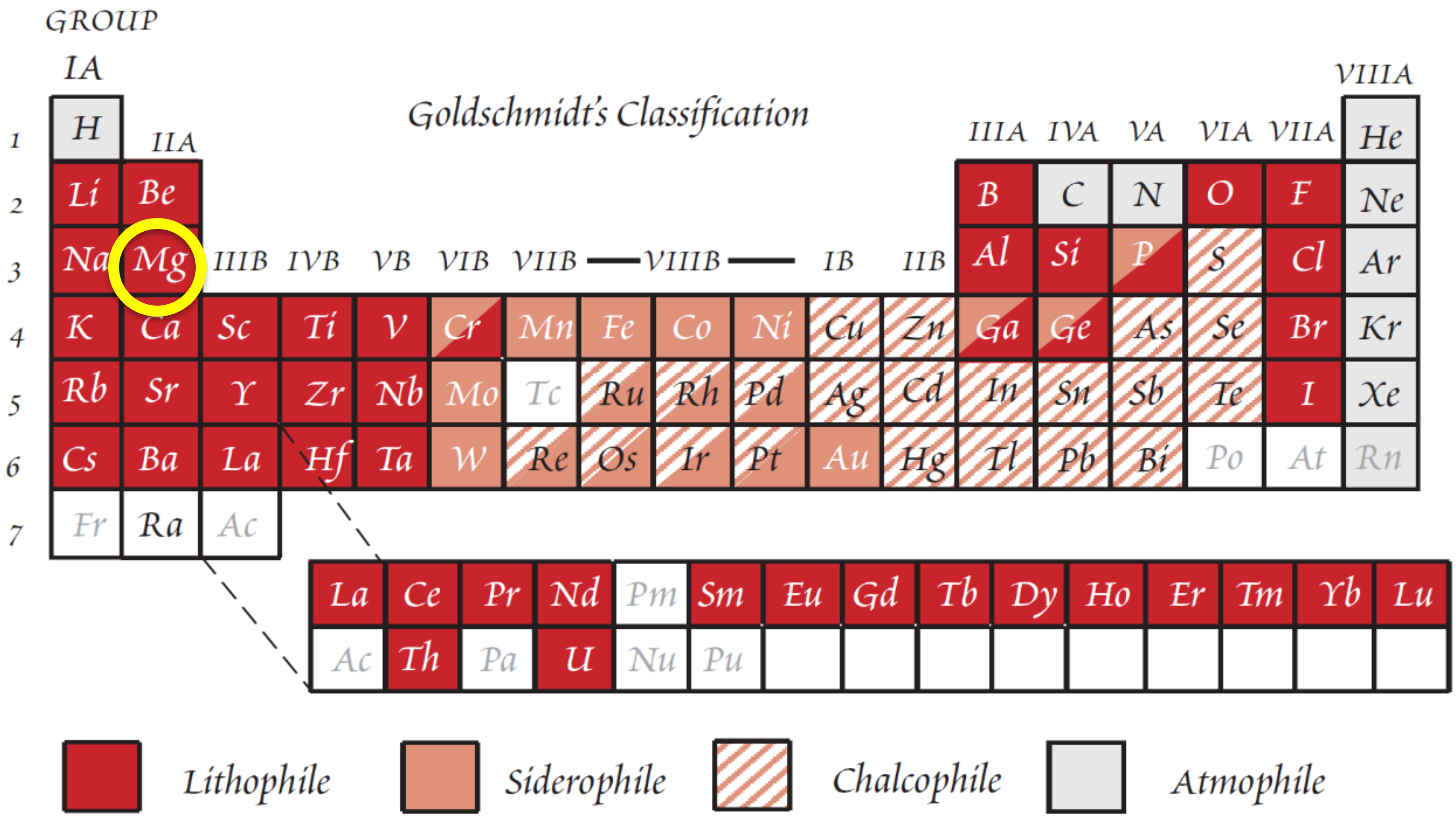
Group 2

The group 2 elements are also called the ‘alkaline earth metals’. They are all reactive metals with distinctive flame colours. In general they are harder, denser and have higher melting points than each alkali metal in the same period. Group 2 elements have two electrons in their outermost s sub-shell.

H 1											
Li 3	Be 4										
Na 11	Mg 12										
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112

Geochemical behavior of Mg

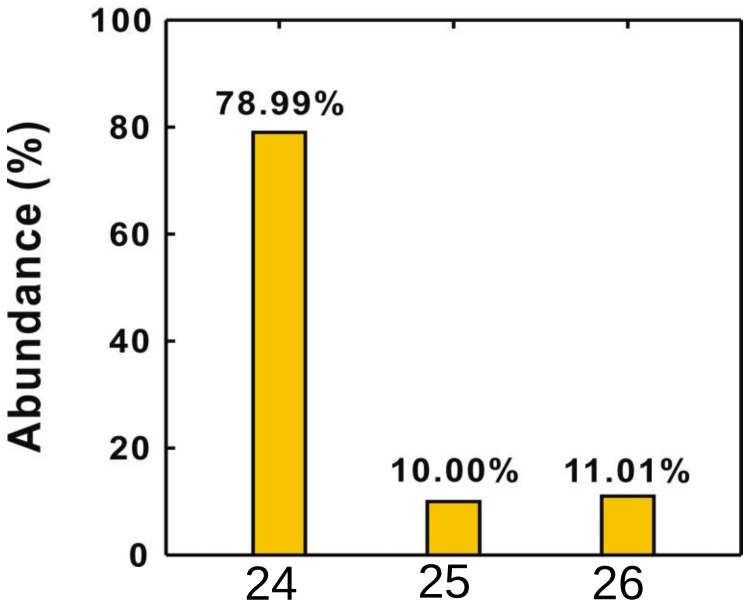
Lithophile → Mg on Earth is mainly associated with rocks



"Geochemistry" by Bill White

Mg isotopes

8% relative mass difference → Over 7‰ fractionation



$$\delta^{26}Mg(‰) = 1000 \times \left[\frac{\left({}^{26}Mg / {}^{24}Mg\right)_{sample}}{\left({}^{26}Mg / {}^{24}Mg\right)_{std}} - 1 \right]$$

Standard: DSM-3 (Galy et al., 2001)
Purified Mg metal provided by Dead Sea Magnesium Ltd

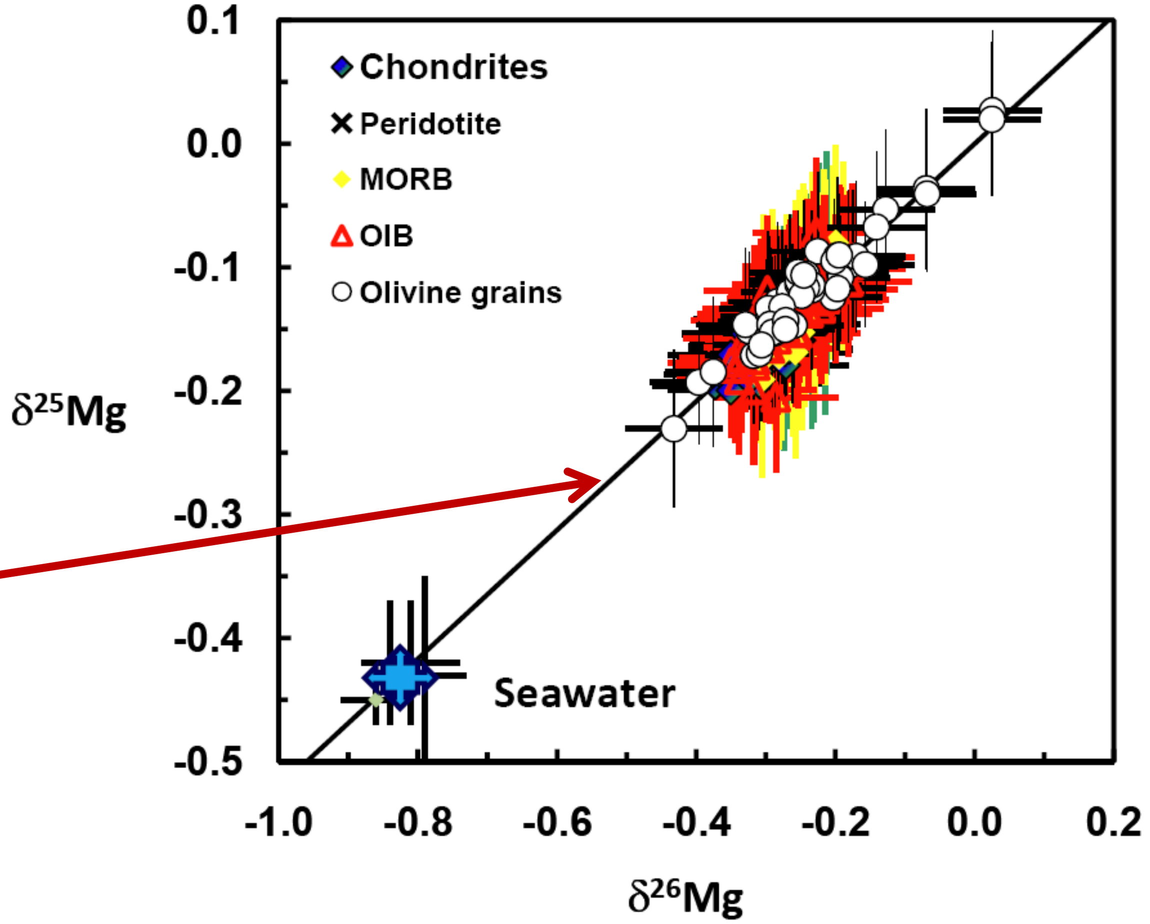
Mass-dependent fractionation

Terrestrial fractionations follow the mass-dependent line

Slope:

(25-24)/(26-24)= 0.5

$\delta^{25}\mathrm{Mg} = 0.516 \times \delta^{26}\mathrm{Mg}$



Teng et al. GCA 2010

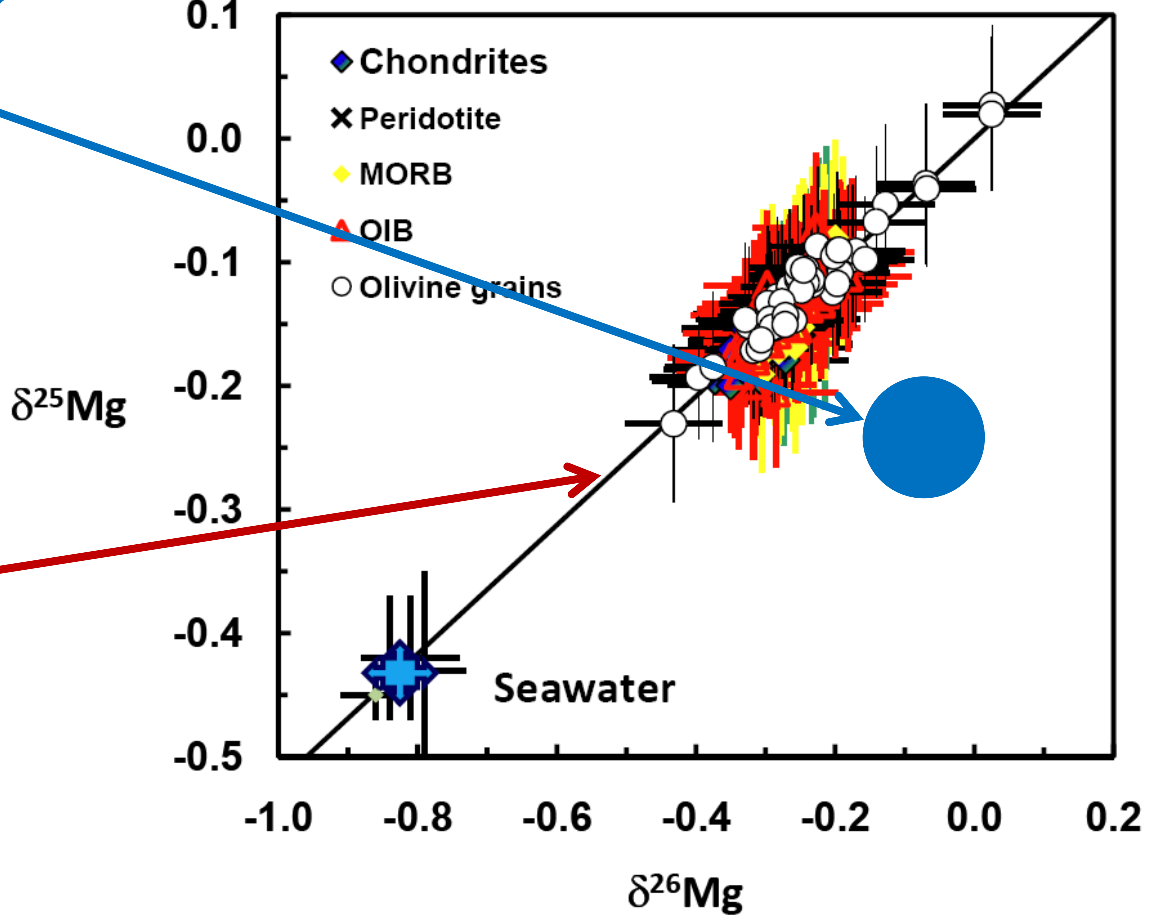
Radiogenic ^{26}Mg from decay of ^{26}Al

Radiogenic ^{26}Mg?

Slope:

(25-24)/(26-24)= 0.5

δ^{25}Mg = 0.516 x δ^{26}Mg



Teng et al. GCA 2010

How much ^{26}Al in the Earth today?

^{26}Al - ^{26}Mg (half life $t_{1/2}$ = 0.705 Myr)

Age of the Earth = 4.5 Ga = 4500 Myr

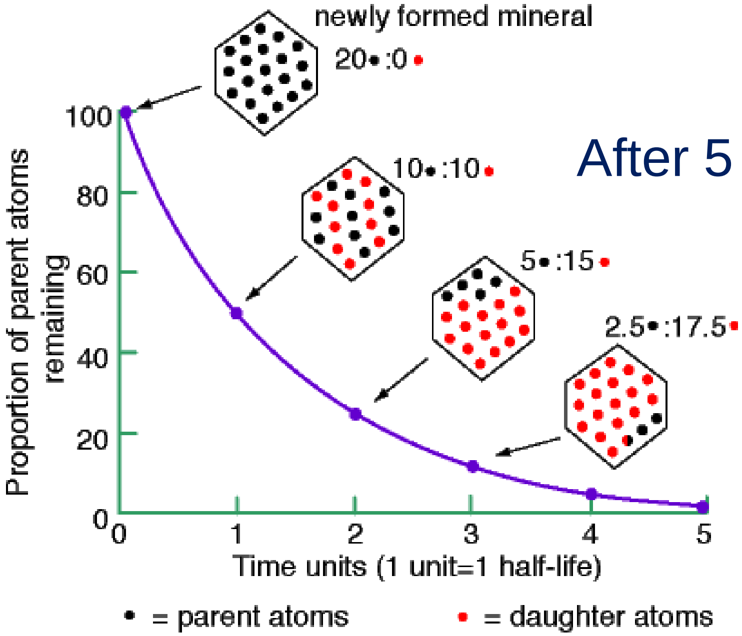
4500/0.705 = 6383

$$N(t) = N_0 \left(\frac{1}{2}\right)^{\frac{t}{t_{1/2}}}$$

$N(t)$ = quantity of the substance remaining
N_0 = initial quantity of the substance
t = time elapsed
$t_{1/2}$ = half life of the substance

Number of ^{26}Al alive today:

$N_{present} = (1/2)^{6383}$ x $N_{T=4.5\ Ga} = 0$



After 5 half-lives, radioactive (^{26}Al) isotopes are gone

Al-Mg system can only be used to date events in the early (< 5 Ma) solar system

Radiogenic ^{26}Mg and Al-Mg dating

Excess ^{26}Mg in the Allende Meteorite

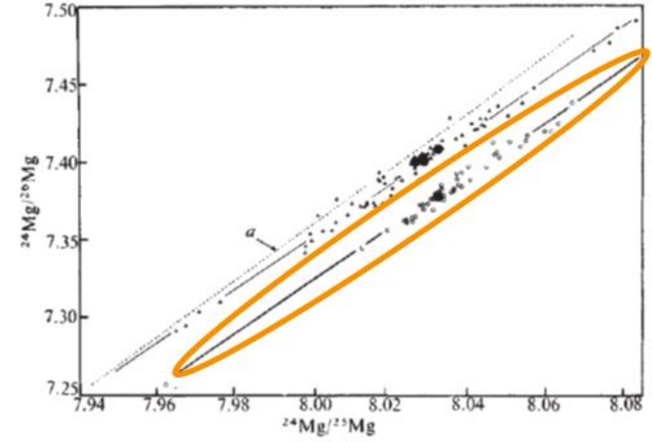
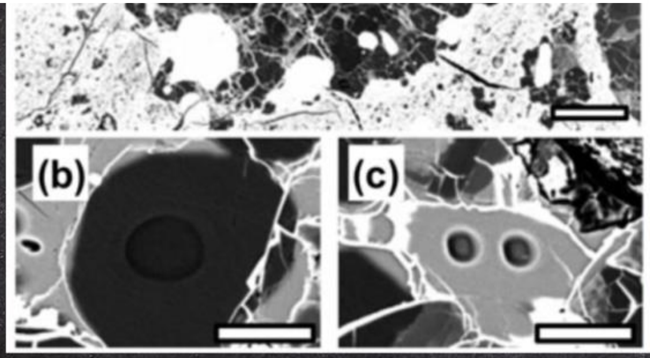


Fig. 2 ^{24}Mg/^{26}Mg against ^{24}Mg/^{25}Mg for the four runs (Table 2) of the anomalous chondrule 1 (open circles) compared with the three runs on Px 5415 (open triangles). *a*, One stage fractionation; solid circles, average for 'unfractionated' runs . The points for chondrule 1 define a separate fractionation line lower than the pyroxene line in ^{24}Mg/^{26}Mg but with the same mean ^{24}Mg/^{25}Mg. All other data in Table 2 fit the pyroxene line.

First discovery

(Gray and Compston Nature 1974)



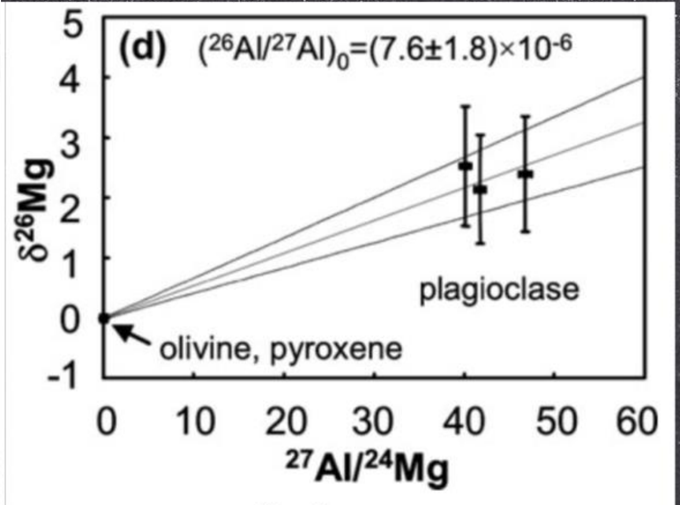


Fig. 1. An example of ^{26}Al-^{26}Mg dating of chondrules (after Ushikubo et al. 2010). a) Backscattered electron (BSE) image of a type I chondrule G73 in Acfer 094. A scale bar is 100 µm. BSE images of ion probe pits with high intensity beam on olivine (b) and with low intensity beam on plagioclase (c). Scale bars are 20 µm. d) The internal isochron of chondrule G73.

球粒的 $(^{26}\text{Al}/^{27}\text{Al})_0$ 越大，形成时间越早。

(Kita and Ushikubo MPS 2012)

$$\Delta t\ (\text{Myr}) = \ln\left[\frac{(^{26}\text{Al}/^{27}\text{Al})_{\text{CAI}}}{(^{26}\text{Al}/^{27}\text{Al})_{\text{Chondrule}}}\right] \times \frac{0.705}{\text{Ln}\ (2)}$$

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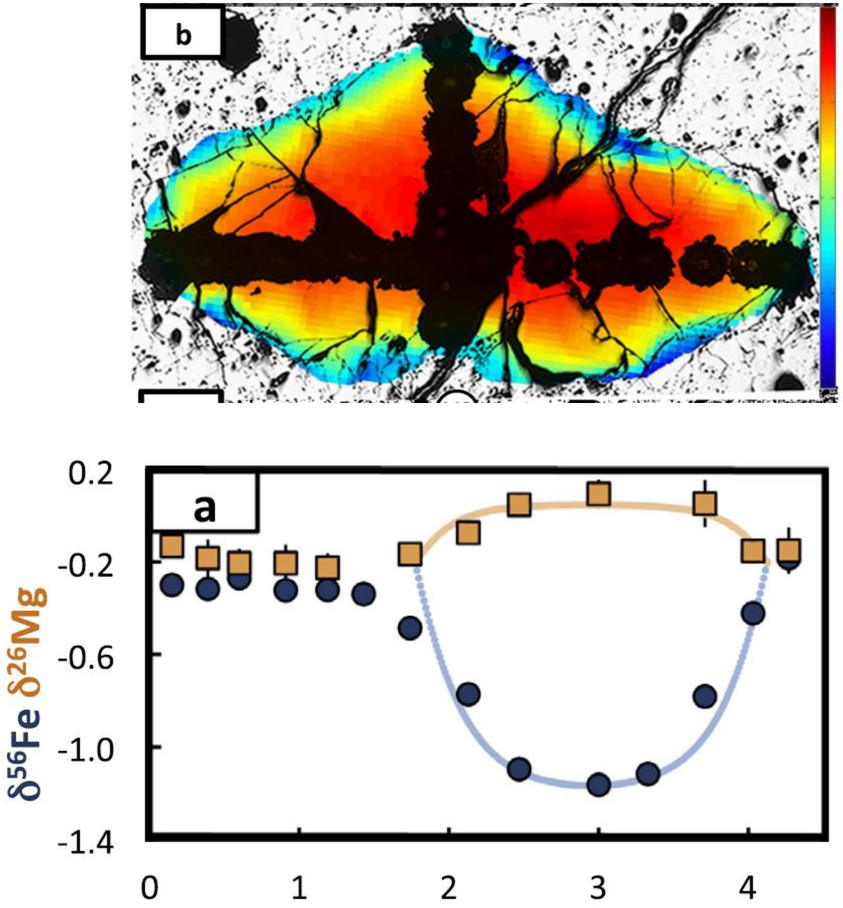
Methods for Mg isotope analysis

Solution method	**In situ method**
MC-ICP-MS	LA-MC-ICP-MS or SIMS
Introduced as solutions	Introduced as solids
Routine method	Spatial resolution
Better precision	Small sample size
Column chemistry	No purification
	Matrix-matched standard

Methods for Mg isotope analysis



Sio et al. GCA 2013

In situ method

LA-MC-ICP-MS or SIMS

Introduced as solids

Spatial resolution

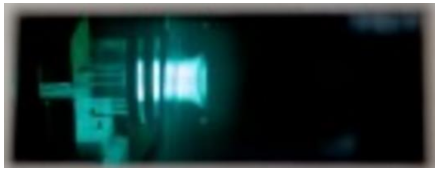
Small sample size

No purification

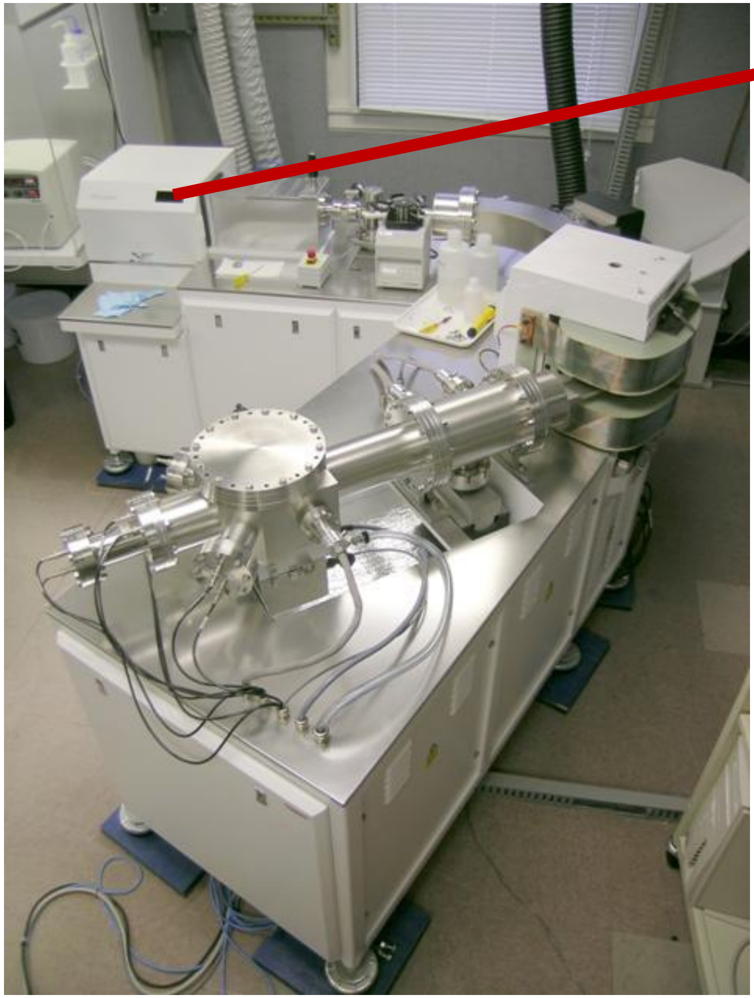
Matrix-matched standard

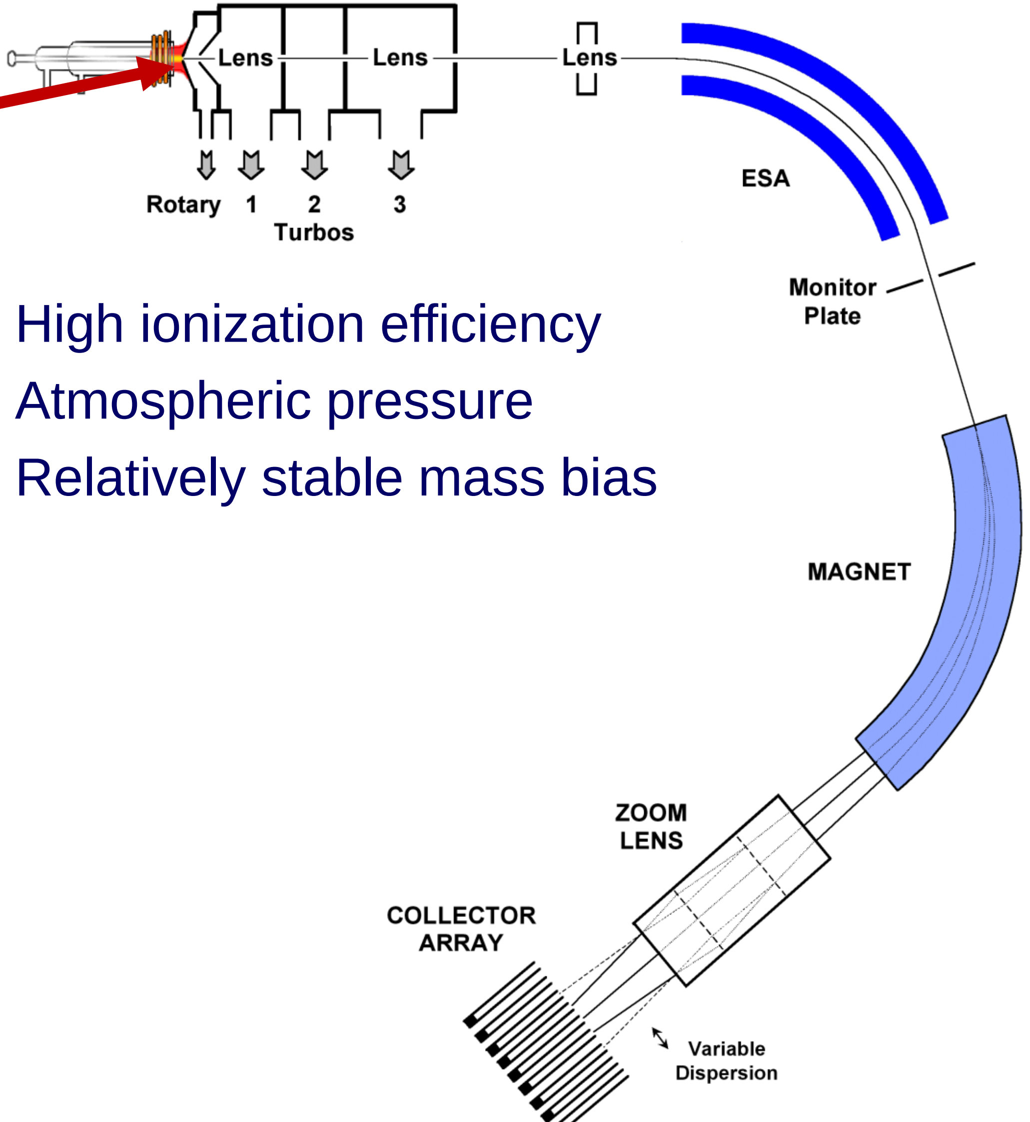
(李秋立老师报告)

MC-ICPMS: Ar plasma



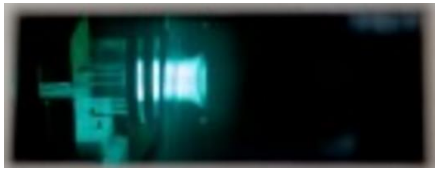
Ion source: Ar plasma (5000 – 10000° K)



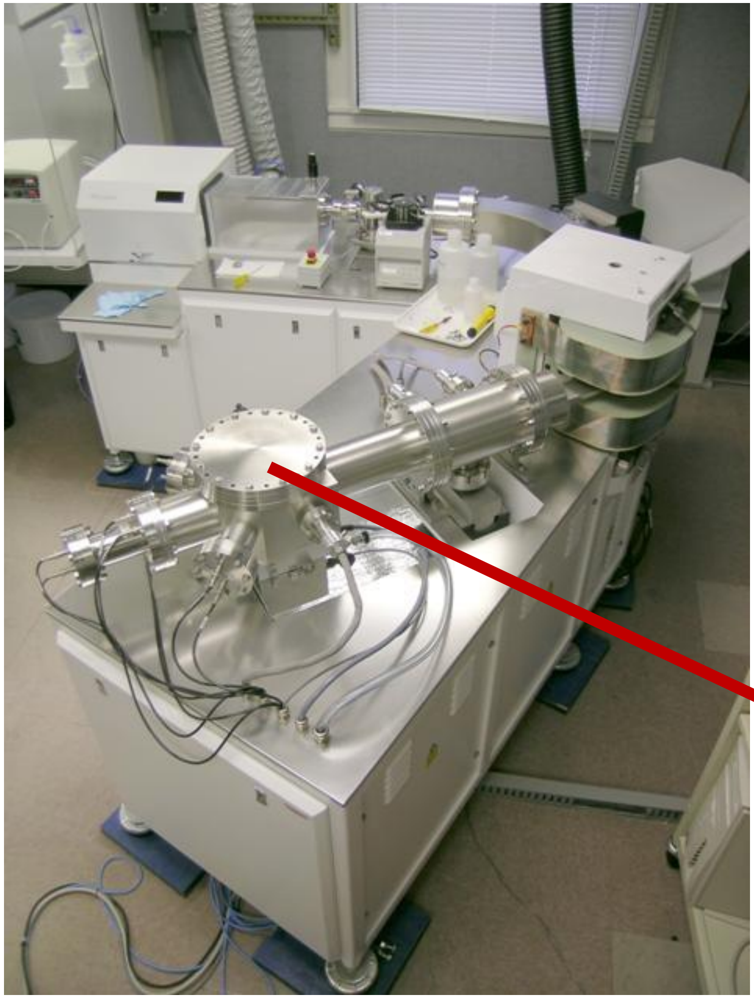


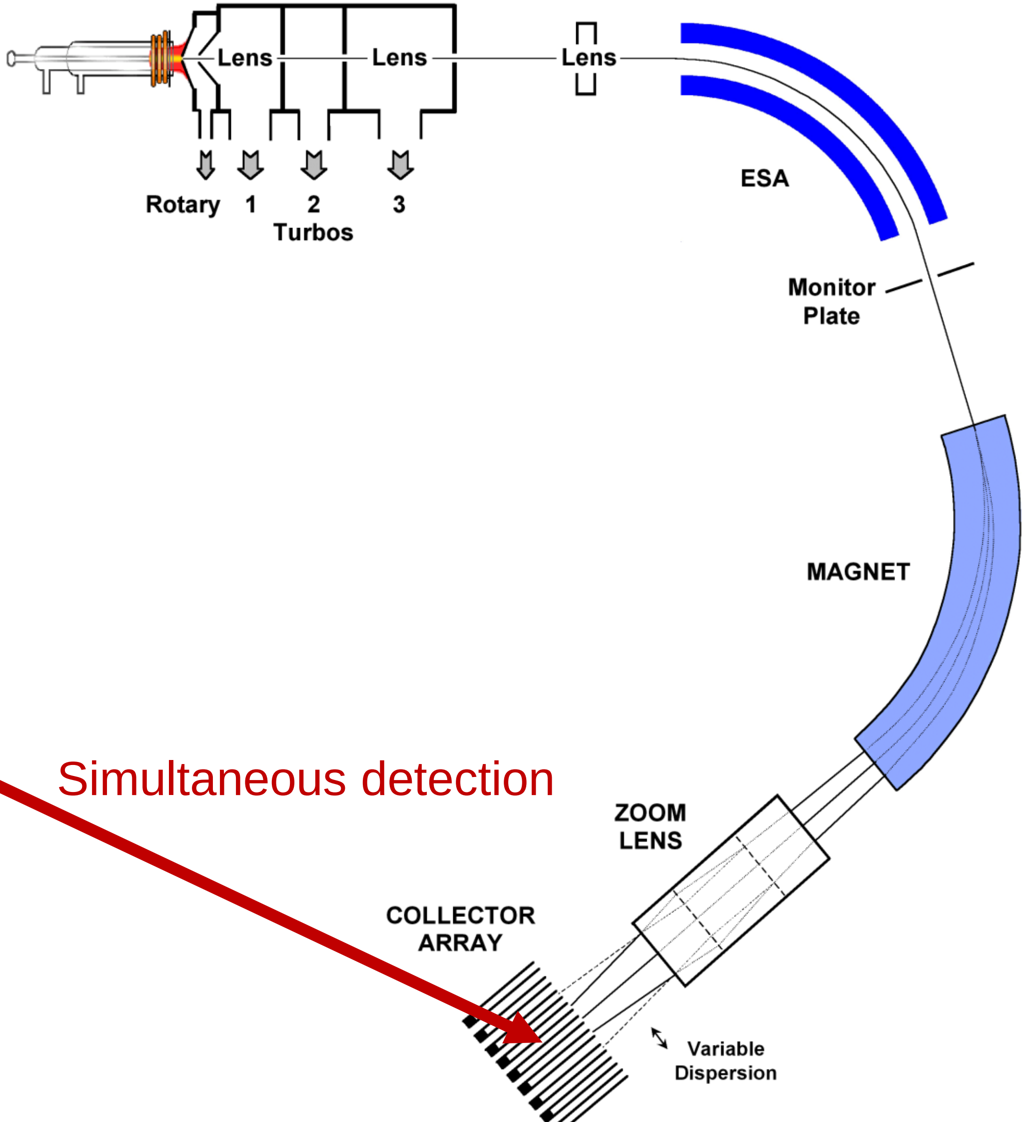
- High ionization efficiency
- Atmospheric pressure
- Relatively stable mass bias

MC-ICPMS: multi-collector array



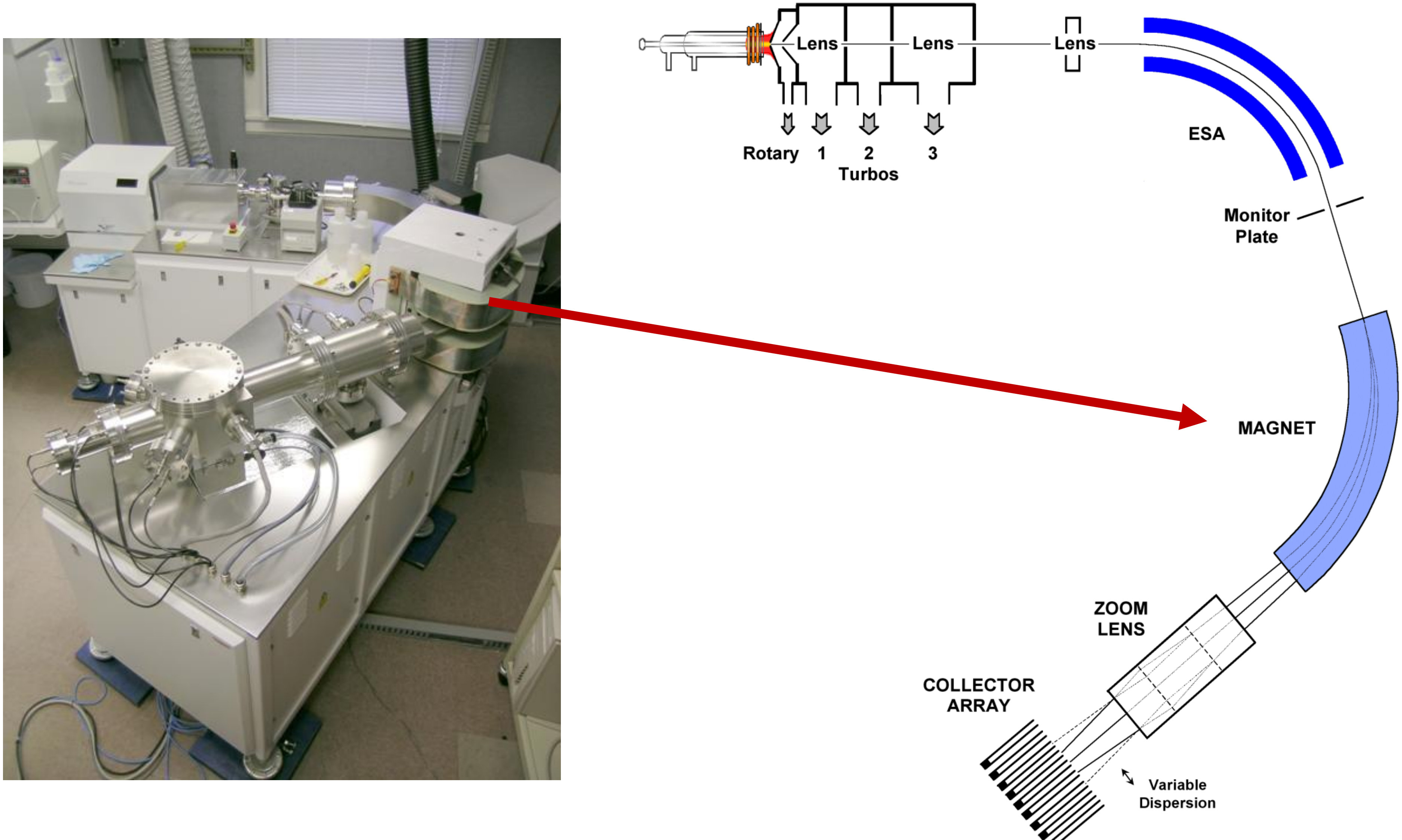
Ion source: Ar plasma (5000 – 10000° K)





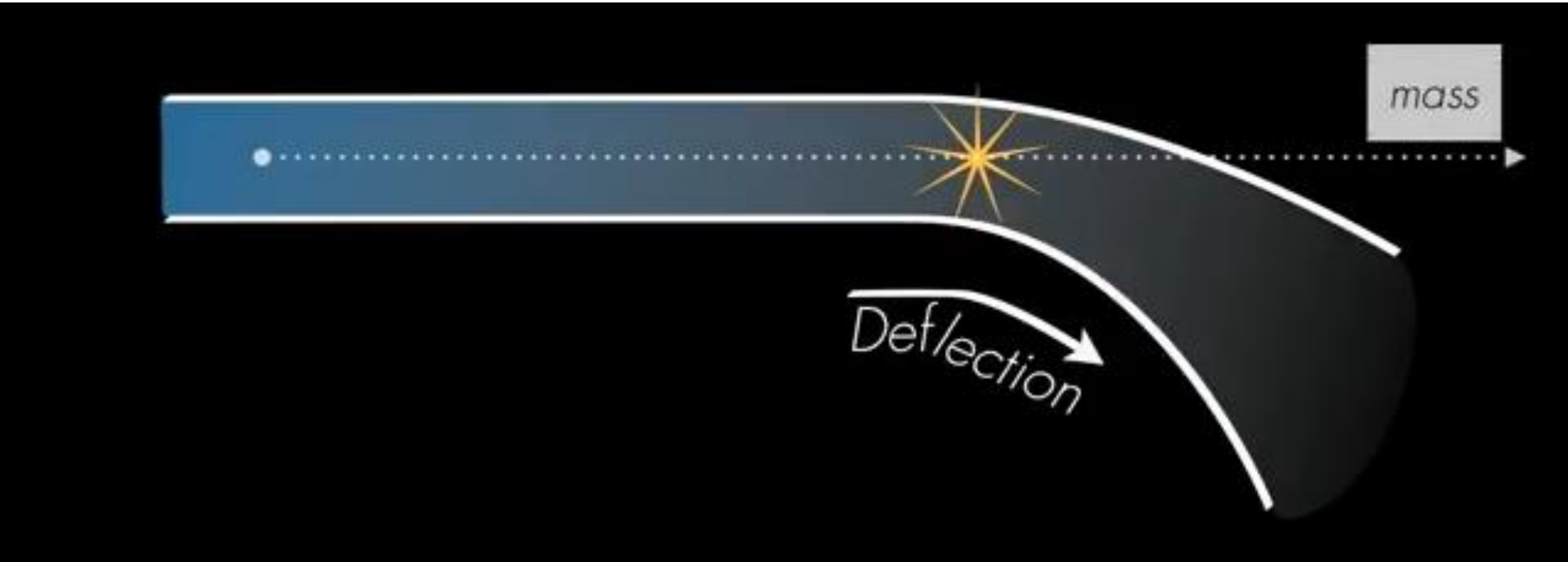
Simultaneous detection

MC-ICPMS: magnet



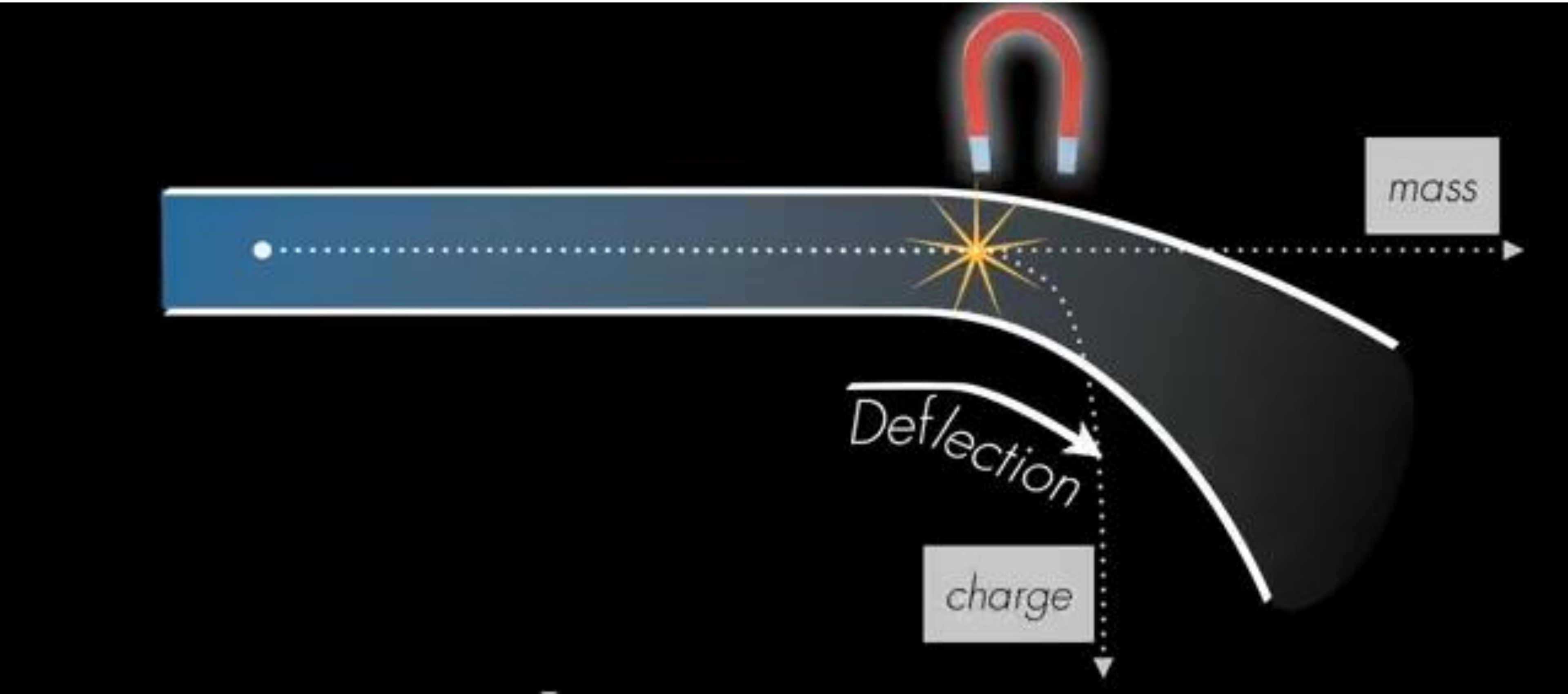
How does a MS work

- When we accelerate an ion, it would like to keep moving in a straight line.
- This tendency is called **momentum**.
- It is proportional to its **mass**.



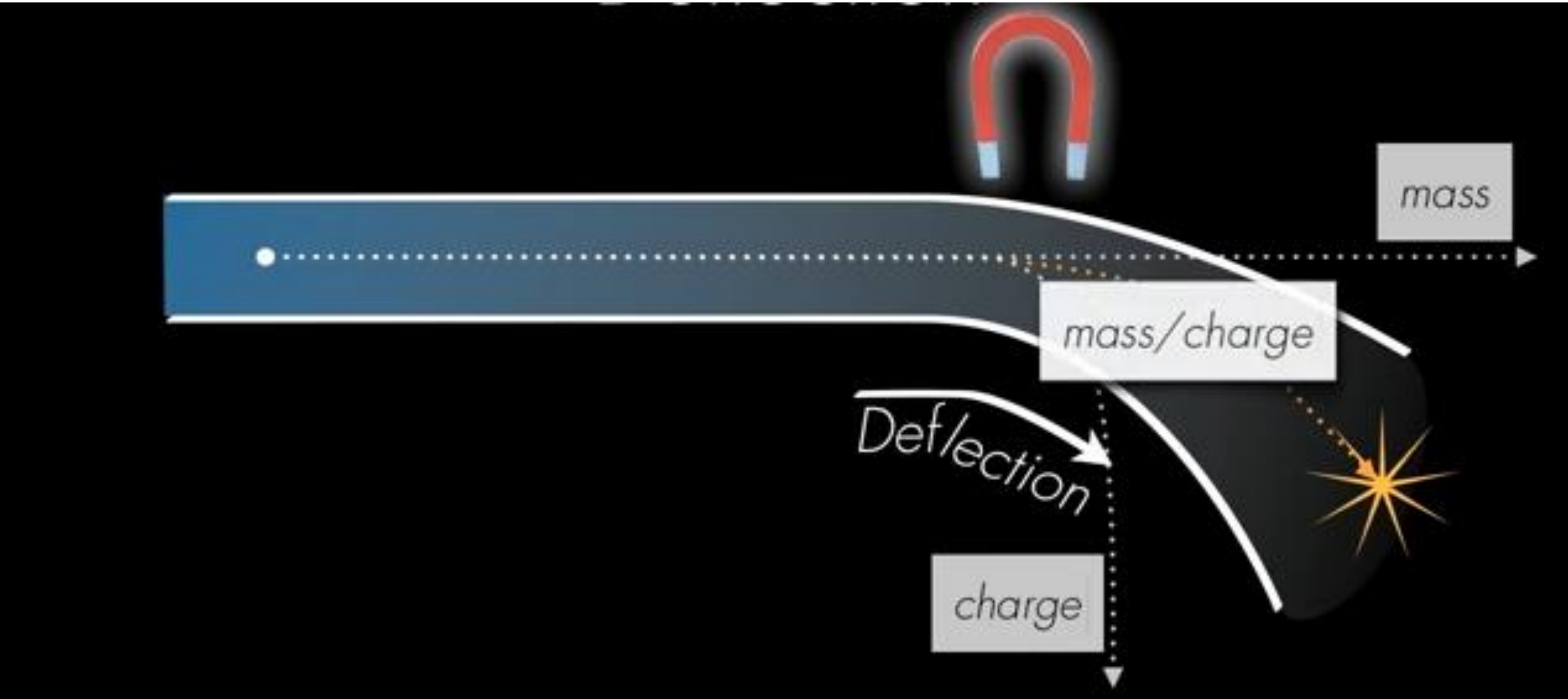
How does a MS work

- We use **magnets** to try to **deflect** the ions off their paths.
- The amount of force that the ion feels from the magnet is proportional to its **charge**.

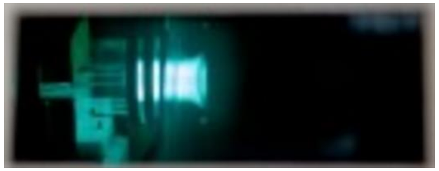


How does a MS work

- Therefore, the path that the ion actually takes is a result of its **mass/charge ratio**.
- Charge = +1, mass/charge ratio = mass

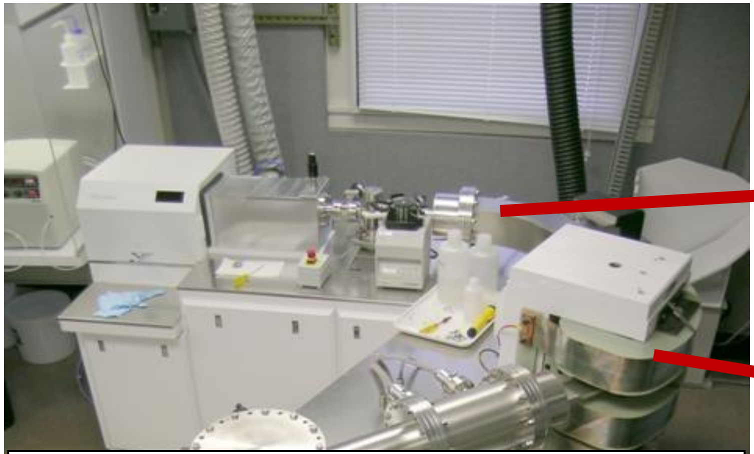


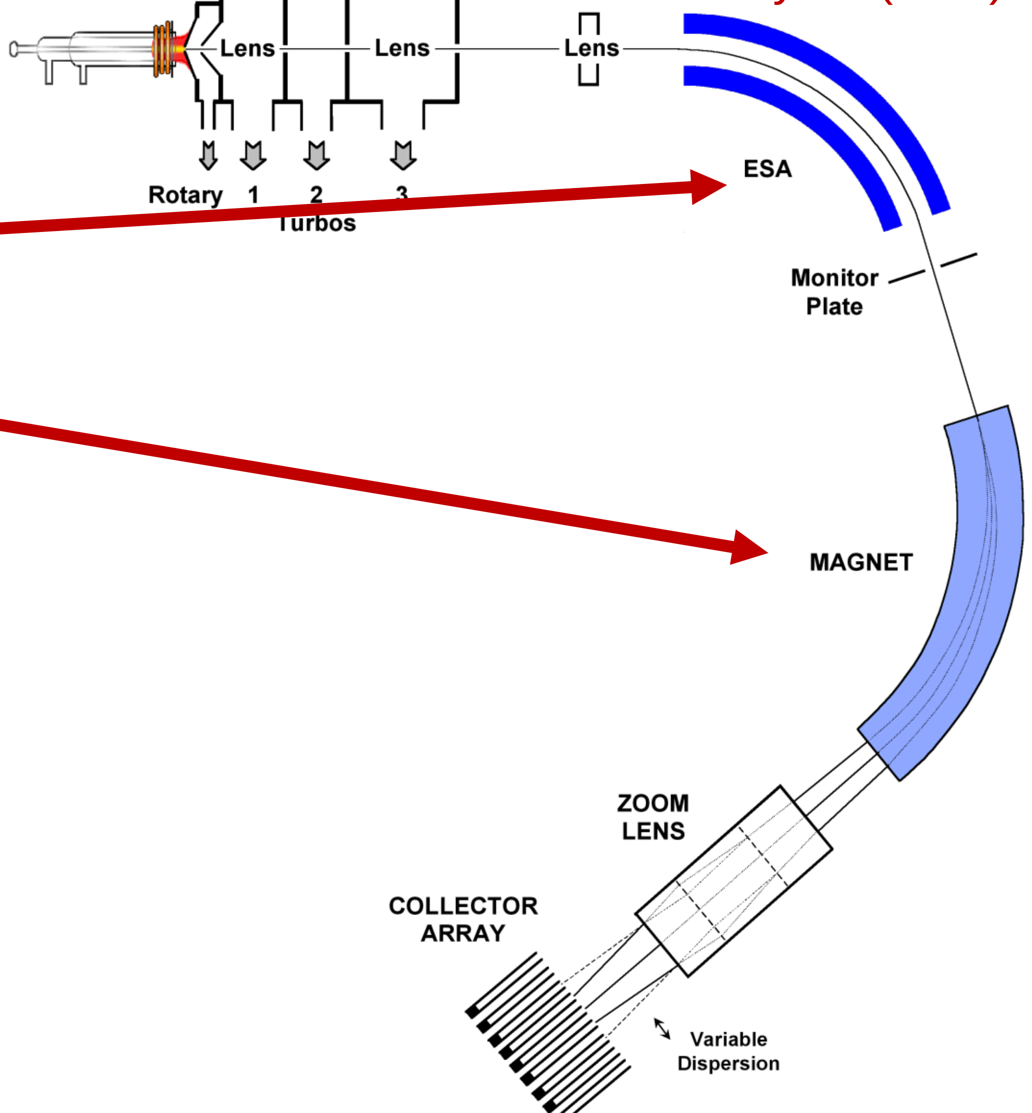
MC-ICPMS: double-focusing



Ion source: Ar plasma

Electrostatic analyzer (ESA)





Ions produced in Ar plasma:

- Energy spread (up to 30V)
- All directions

Results:

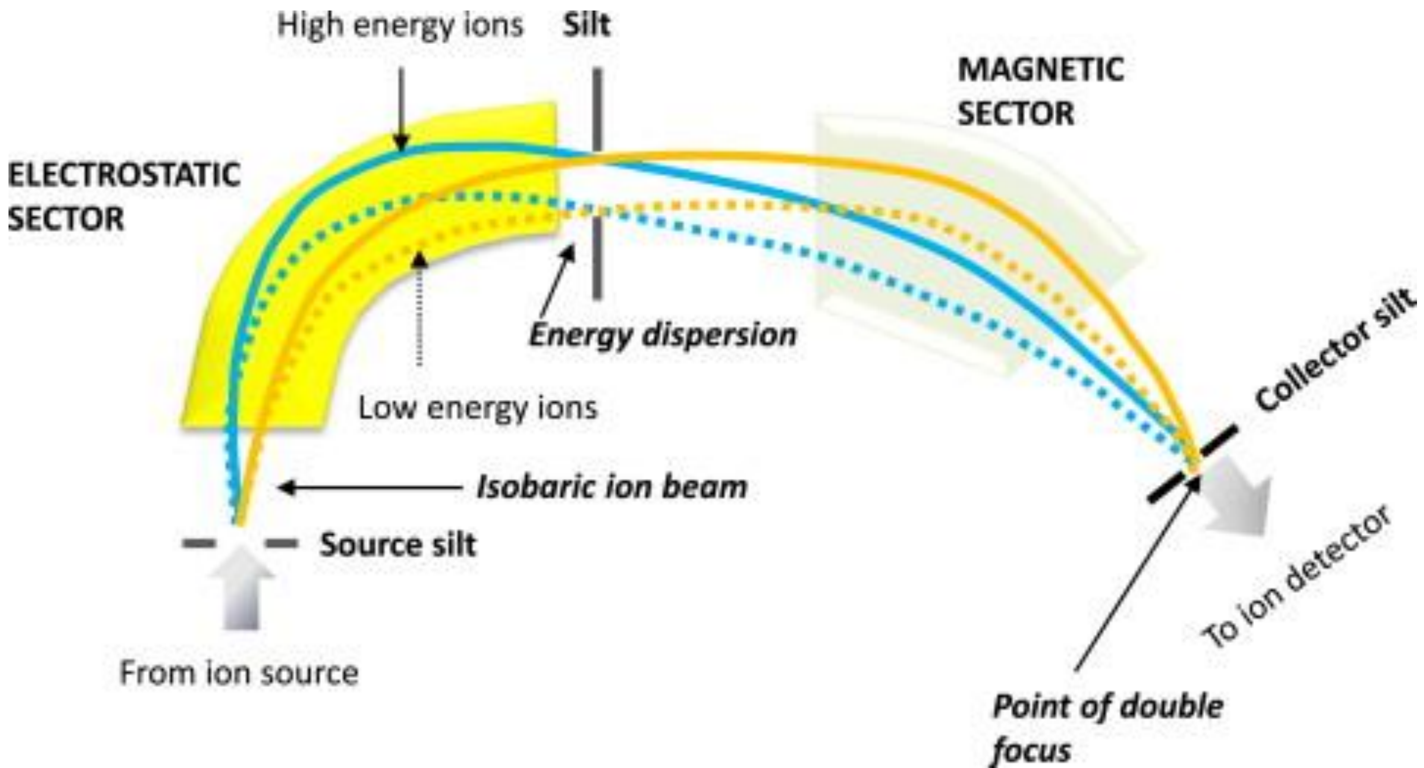
- Bad peak shape
- Loss of transmission
  i.e. low precision analysis

MC-ICPMS: double-focusing

Energy + angular focusing are needed for achieving high-precision isotopic analysis

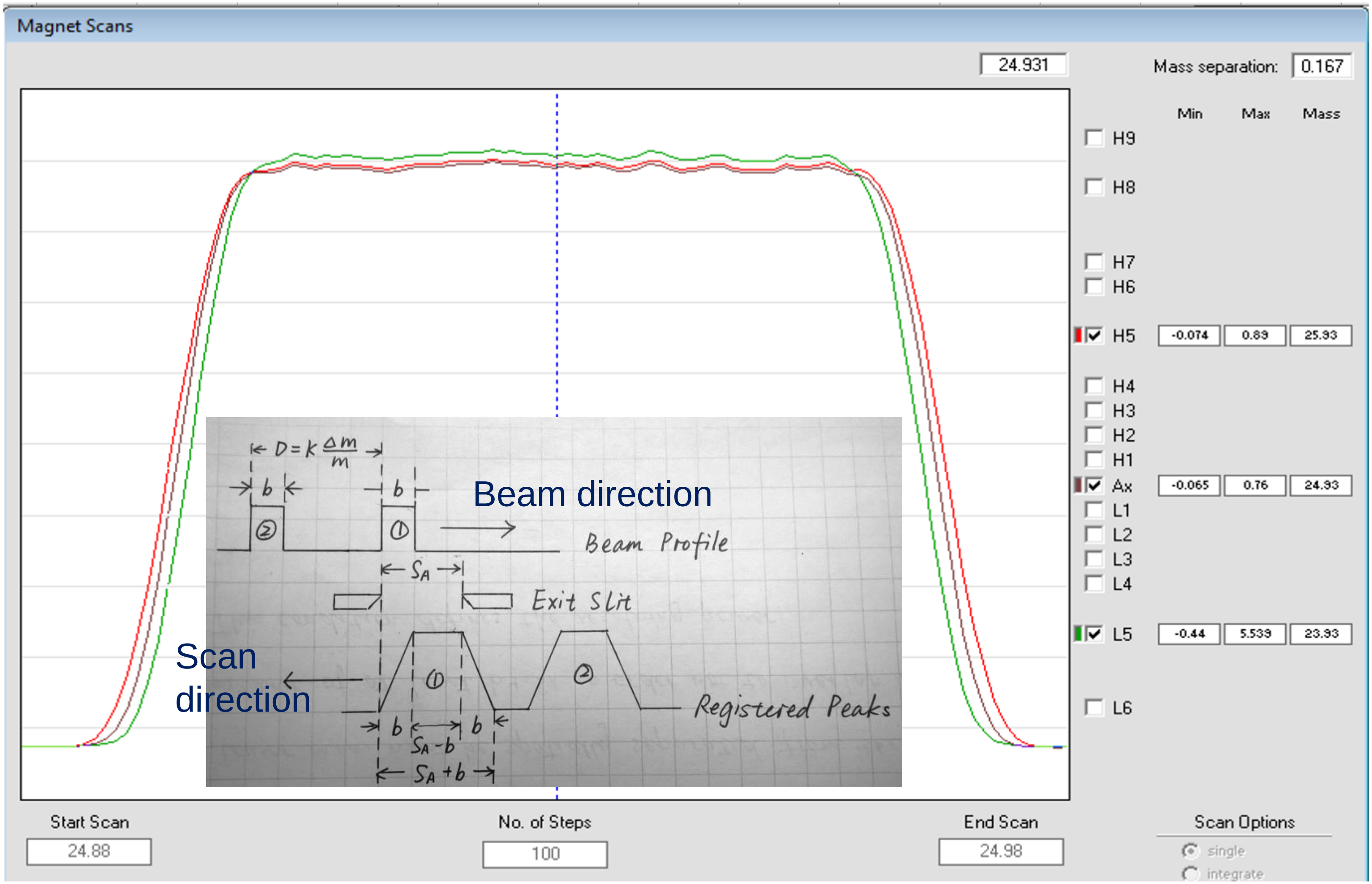
ESA: Energy focusing:
ions with the same energy follow the same path

Magnet: Angular focusing:
ions with same charge/mass ratio follow the same path



MC-ICPMS: flat-topped peaks

Guarantees a stable signal even if the magnetic field or the acceleration voltage is subjected to small fluctuations



Magnet Scans

24.931

Mass separation: 0.167

	Min	Max	Mass
☐ H9			
☐ H8			
☐ H7			
☐ H6			
☑ H5	-0.074	0.89	25.93
☐ H4			
☐ H3			
☐ H2			
☐ H1			
☑ Ax	-0.065	0.76	24.93
☐ L1			
☐ L2			
☐ L3			
☐ L4			
☑ L5	-0.44	5.539	23.93
☐ L6			

Start Scan: 24.88

No. of Steps: 100

End Scan: 24.98

Scan Options
● single
○ integrate

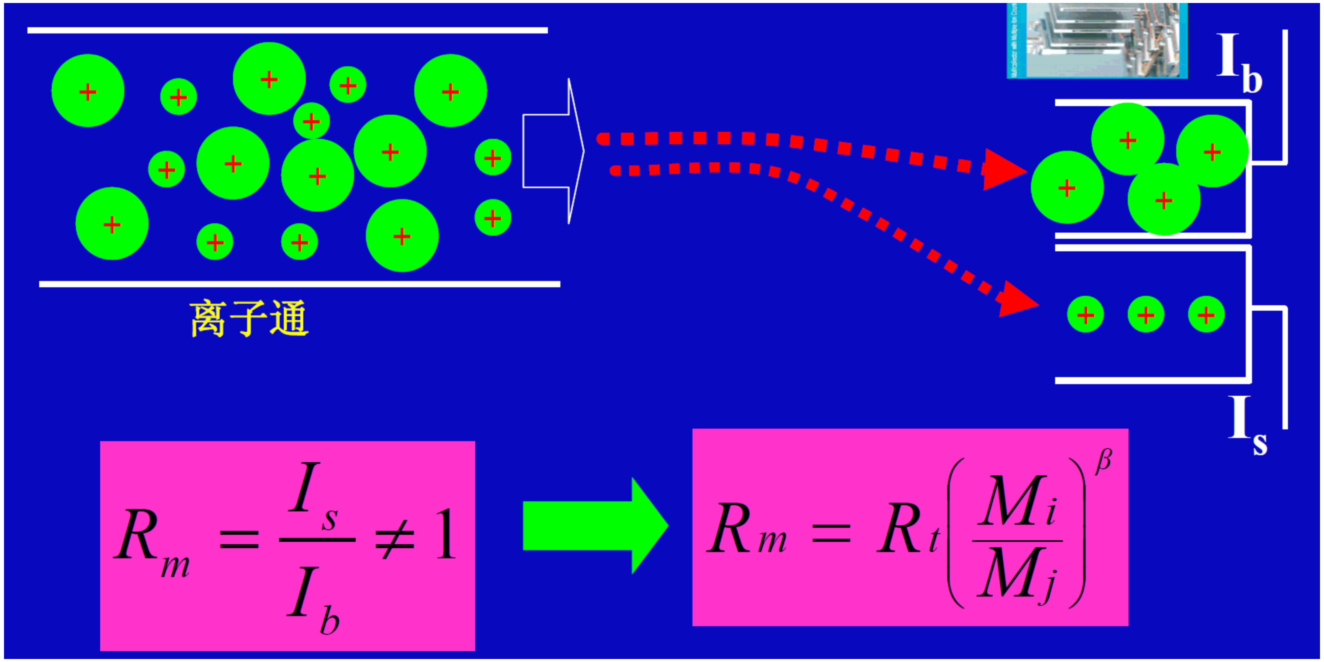
Beam direction

Scan direction

Instrumental fractionation

Mass-dependent ion transmission efficiency (Mass Bias)

light ions are driven off the beam center more than heavy ones



$$R_m = \frac{I_s}{I_b} \neq 1$$

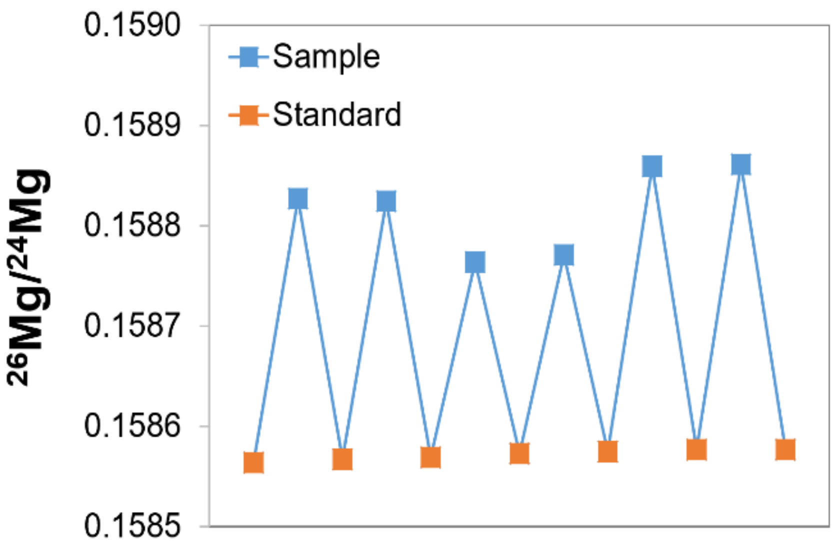
$$R_m = R_t \left(\frac{M_i}{M_j} \right)^{\beta}$$

杨岳衡老师课件

Correction for instrumental fractionation

Standard-sample-bracketing

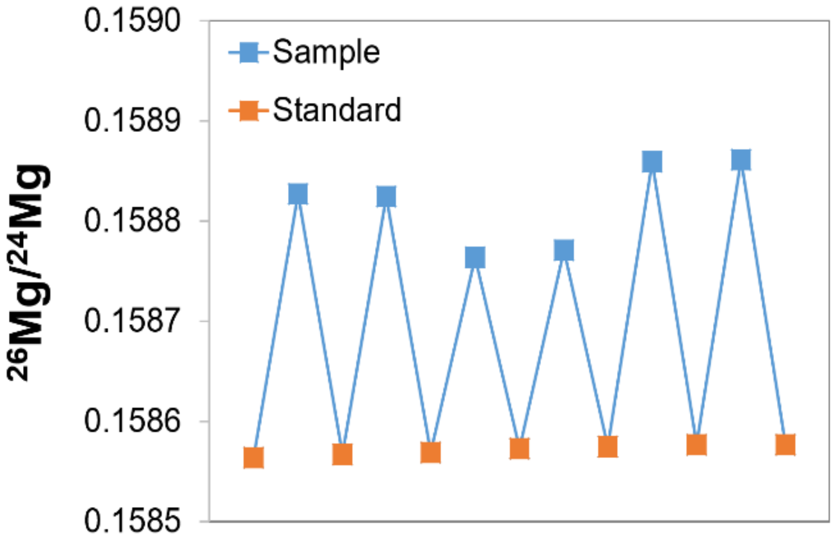
- Standard-sample-standard are measured sequentially

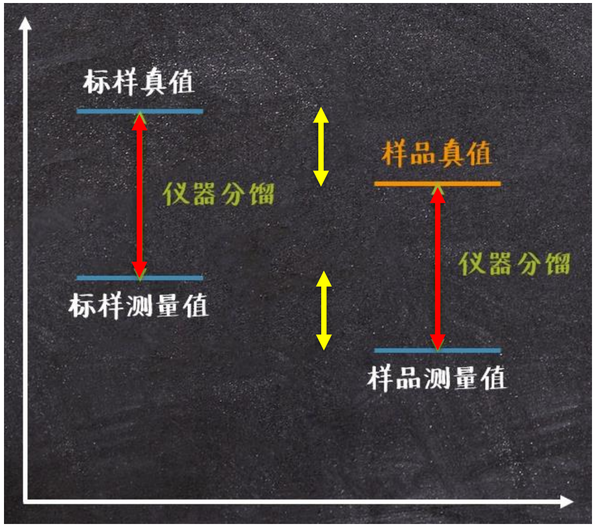


Correction for instrumental fractionation

Standard-sample-bracketing

- Standard-sample-standard are measured sequentially
- Instrumental mass bias changes smoothly within a short time period.
- Sample and standard have the same instrumental mass bias.



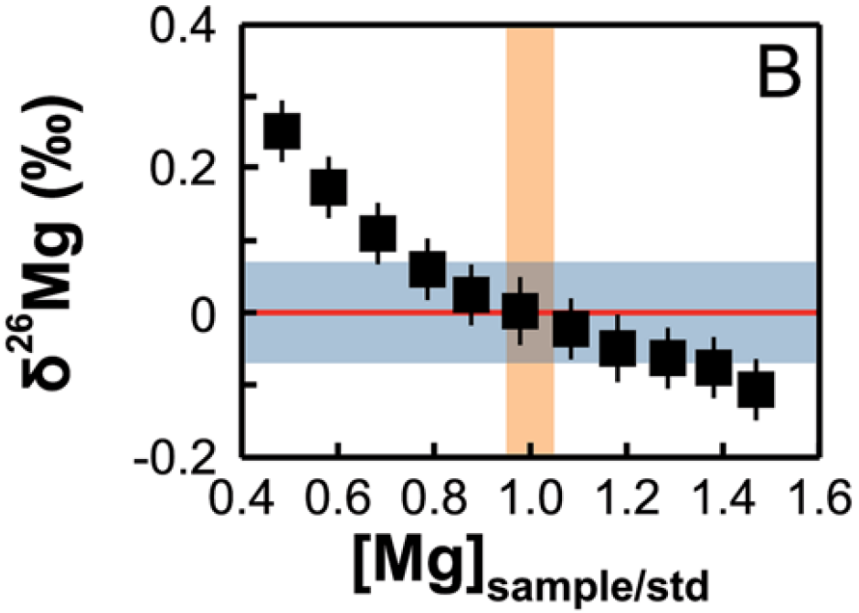


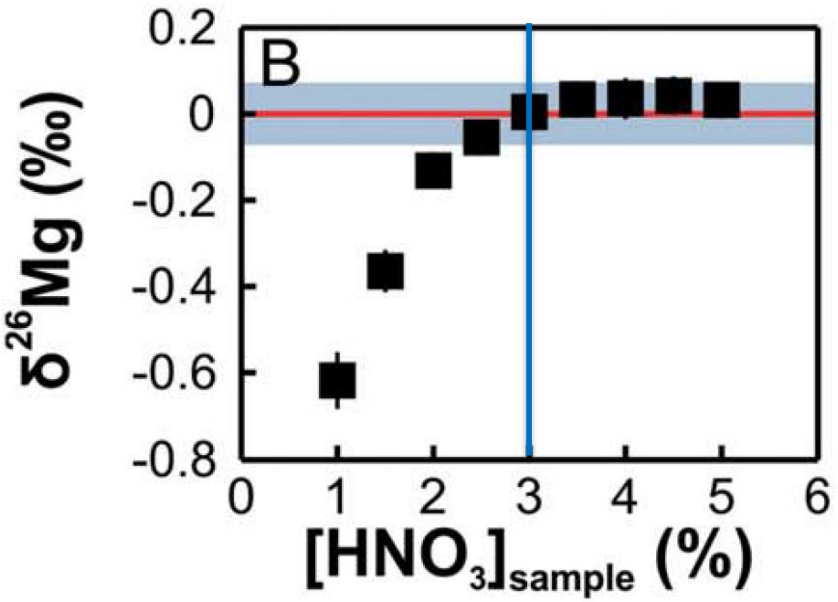
$$\delta^{X}\mathrm{Mg}_{\mathrm{sample}_i} = 10^3 \times \left\{ \frac{(^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{sample}_i}}{\frac{(^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{calibrator}_i} + (^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{calibrator}_{i+1}}}{2}} - 1 \right\} \quad (1)$$

$$\delta^{X}\mathrm{Mg}_{\mathrm{calibrator}_i} = 10^3 \times \left\{ \frac{(^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{calibrator}_i}}{\frac{(^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{calibrator}_{i-1}} + (^{X}\mathrm{Mg}/^{24}\mathrm{Mg})_{\mathrm{calibrator}_{i+1}}}{2}} - 1 \right\} \quad (2)$$

Matching Mg and acid concentration

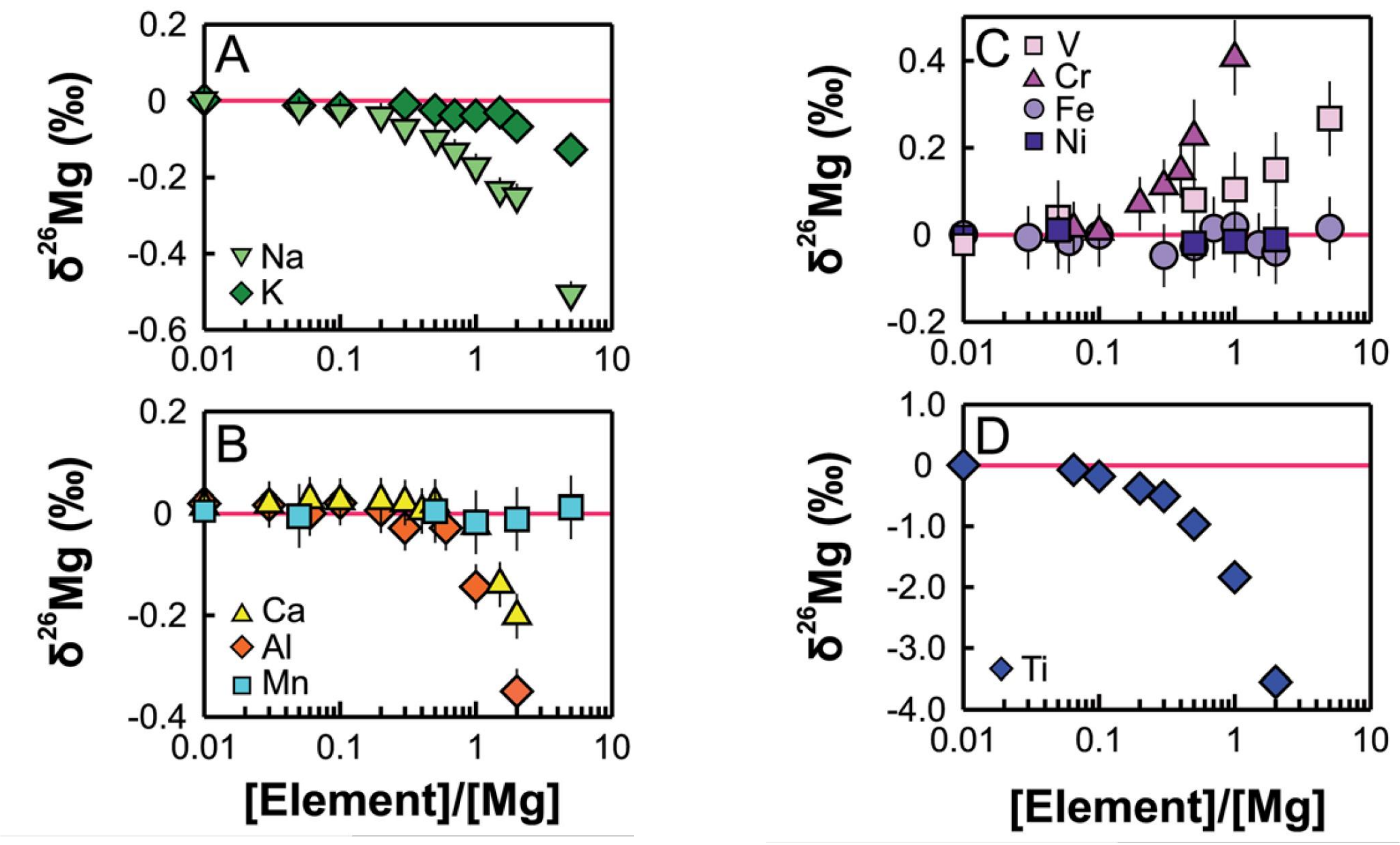
- Mg concentration is recommended to match within 5%
- Diluting sample and standard using the same batch of 3% nitric acid





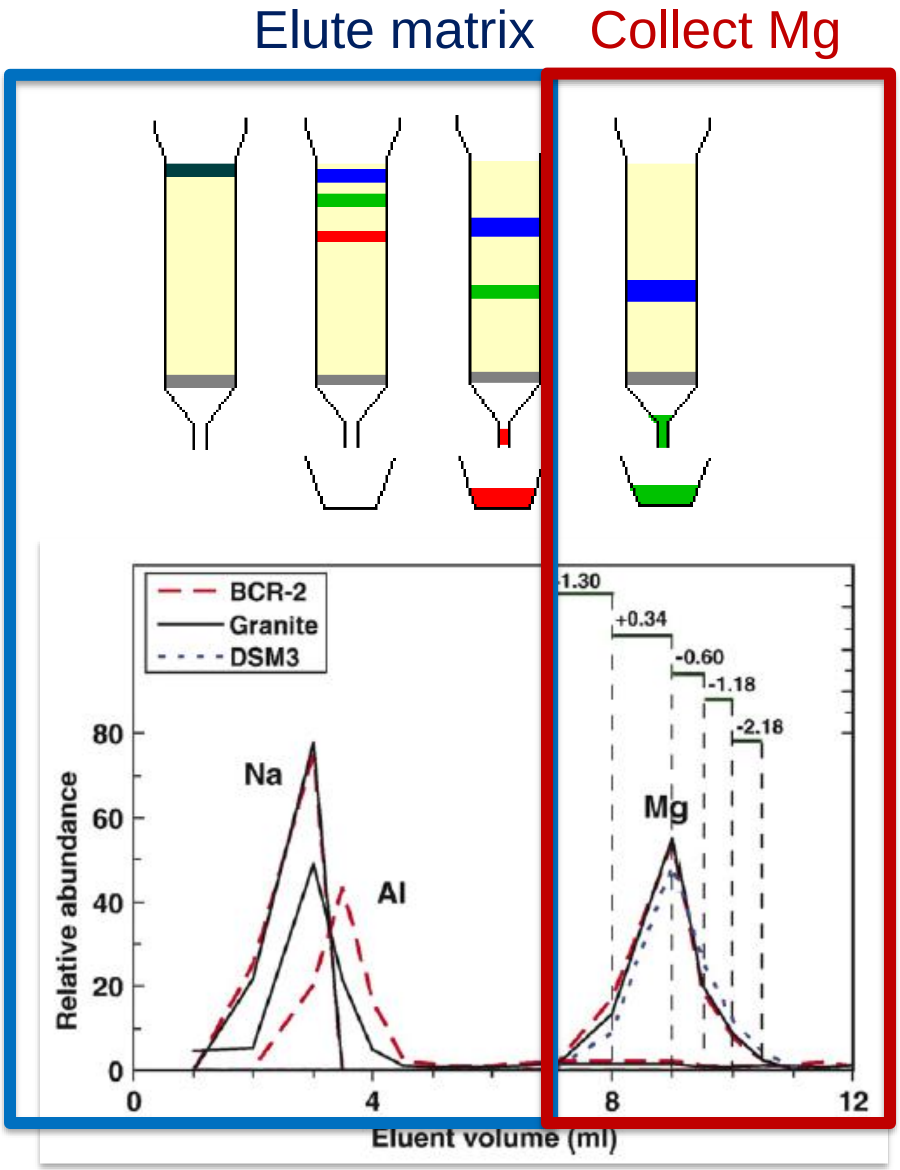
Hu & Teng, JAAS, 2019

Matrix effects

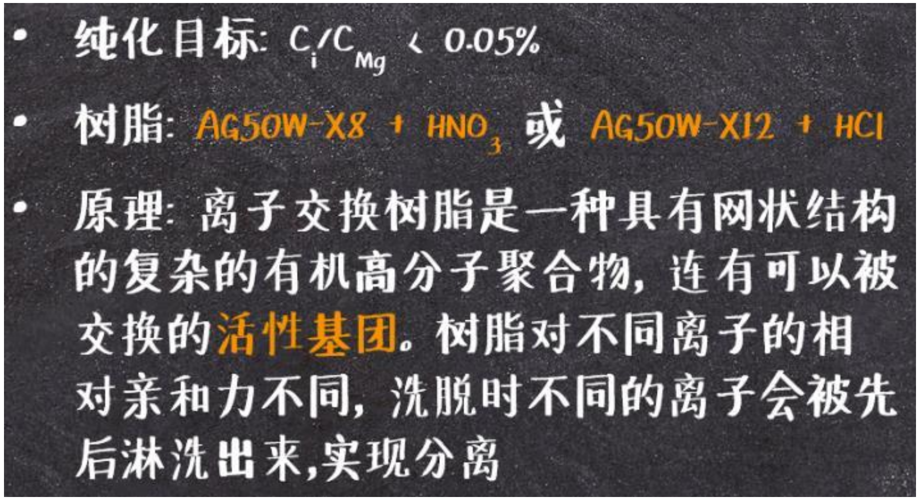


Hu & Teng, JAAS, 2019

Removing matrix elements



离子交换柱



- 纯化目标: $C_i/C_{Mg} < 0.05\%$
- 树脂: AG50W-X8 + HNO_3 或 AG50W-X12 + HCl
- 原理: 离子交换树脂是一种具有网状结构的复杂的有机高分子聚合物，连有可以被交换的活性基团。树脂对不同离子的相对亲和力不同，洗脱时不同的离子会被先后淋洗出来,实现分离

$$R^-H^+ + M^+ = R^-M^+ + H^+$$

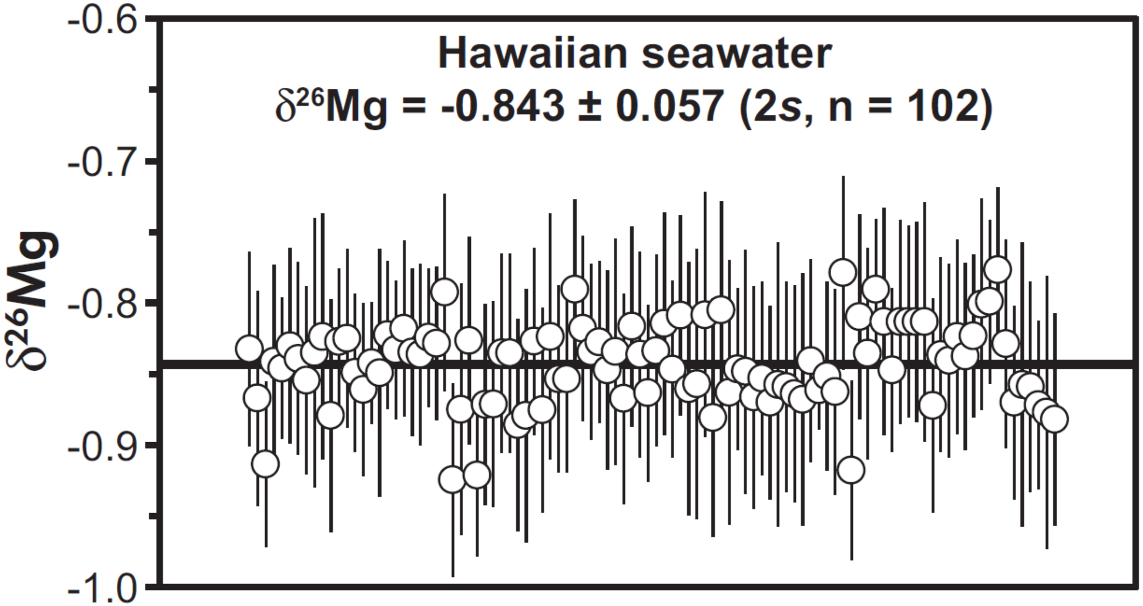
Collection interval should cover the entire Mg peak

Teng et al. EPSL 2007

Analytical precision

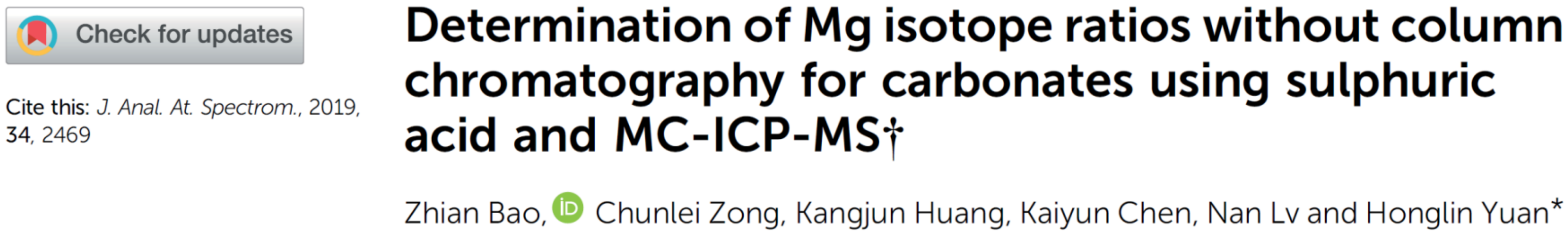
- **内部精度**: 单次分析（例如一组40个测定数据）数据结果的重复性，一般δ^{26}Mg内部精度可达 0.02‰，体现了仪器的稳定性，反应了分析方法的潜力
- **外部精度**: 同一样品多次分析（例如几个月的时间内重复分析几十次）数据结果的重复性，目前溶液法测量δ^{26}Mg外部精度可达 0.06‰，反应整个分析流程的重现性

Measurements of seawater over four-year period



Teng et al. GGR 2015

Additional methods



Check for updates

Cite this: *J. Anal. At. Spectrom.*, 2019, **34**, 2469

Determination of Mg isotope ratios without column chromatography for carbonates using sulphuric acid and MC-ICP-MS†

Zhian Bao, Chunlei Zong, Kangjun Huang, Kaiyun Chen, Nan Lv and Honglin Yuan*

Reacts carbonate with H_2SO_4 to remove Ca as $CaSO_4$

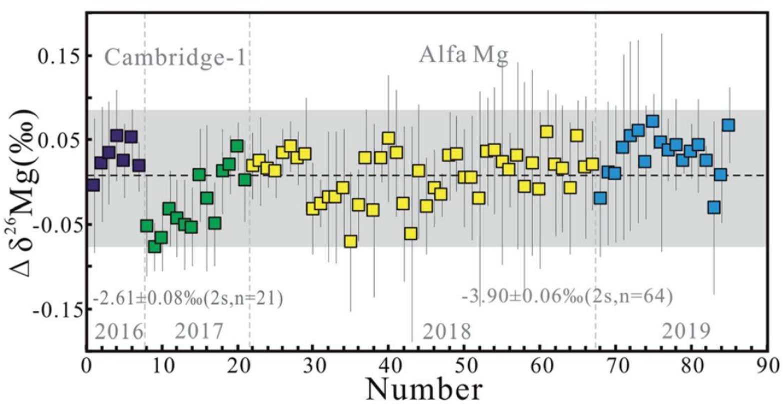


Fig. 5 Long-term reproducibility of the δ^{26}Mg measurement of Cambridge-1 and pure Alfa Mg solutions. The dark blue and green

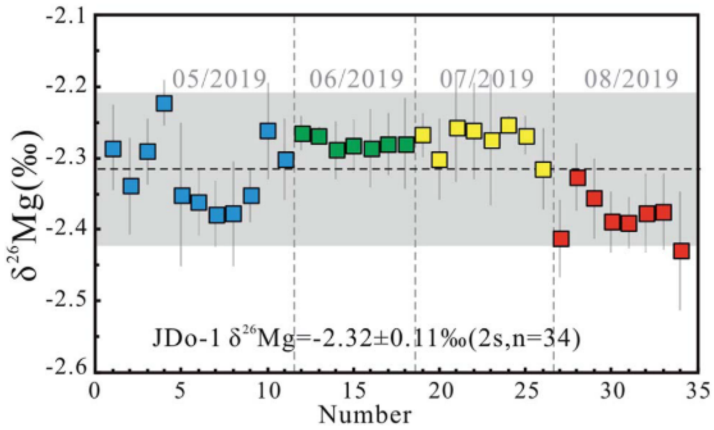
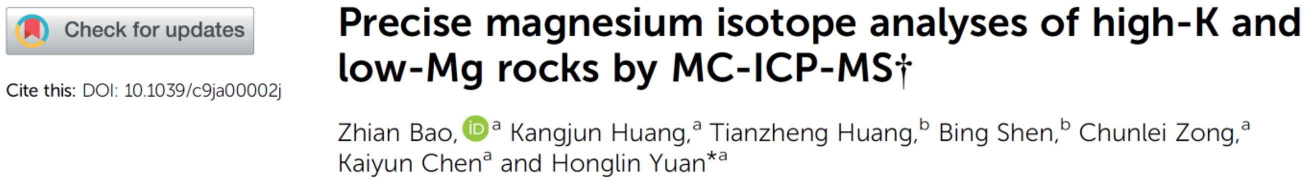


Fig. 6 Long-term reproducibility of the δ^{26}Mg measurement of JDo-1. The long-term reproducibility was better than 0.11‰ (2SD). Errors

Additional methods



Check for updates

Cite this: DOI: 10.1039/c9ja00002j

Precise magnesium isotope analyses of high-K and low-Mg rocks by MC-ICP-MS†

Zhian Bao,[a] Kangjun Huang,[a] Tianzheng Huang,[b] Bing Shen,[b] Chunlei Zong,[a]
Kaiyun Chen[a] and Honglin Yuan*[a]

International Journal of Mass Spectrometry 448 (2020) 116268

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International Journal of Mass Spectrometry

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

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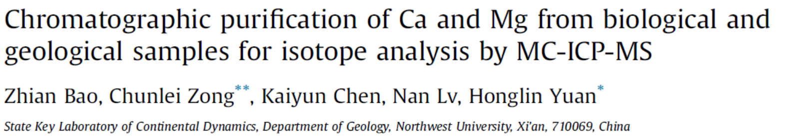

Chromatographic purification of Ca and Mg from biological and geological samples for isotope analysis by MC-ICP-MS

Zhian Bao, Chunlei Zong**, Kaiyun Chen, Nan Lv, Honglin Yuan*

State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an, 710069, China

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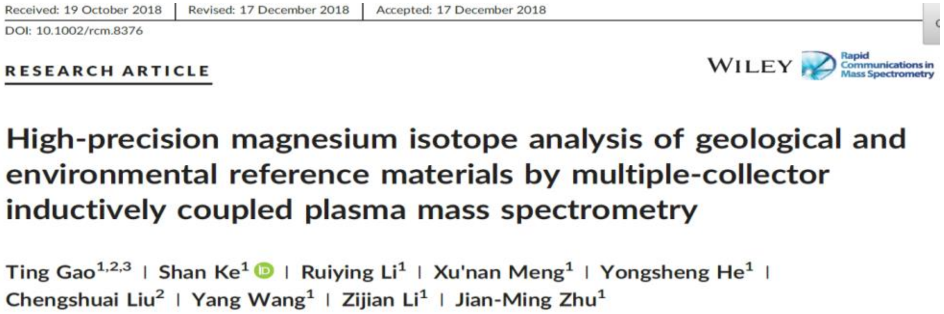


Received: 19 October 2018 | Revised: 17 December 2018 | Accepted: 17 December 2018

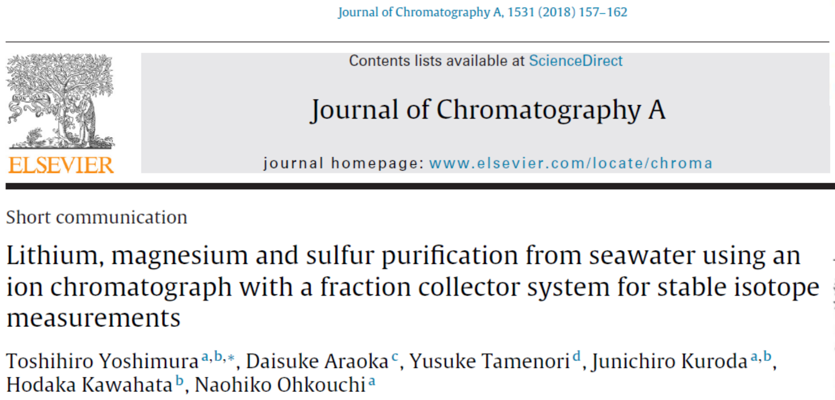
DOI: 10.1002/rcm.8376

RESEARCH ARTICLE

WILEY Rapid Communications in Mass Spectrometry

High-precision magnesium isotope analysis of geological and environmental reference materials by multiple-collector inductively coupled plasma mass spectrometry

Ting Gao[1,2,3] | Shan Ke[1] | Ruiying Li[1] | Xu'nan Meng[1] | Yongsheng He[1] |
Chengshuai Liu[2] | Yang Wang[1] | Zijian Li[1] | Jian-Ming Zhu[1]



Journal of Chromatography A, 1531 (2018) 157–162

Contents lists available at ScienceDirect

Journal of Chromatography A

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

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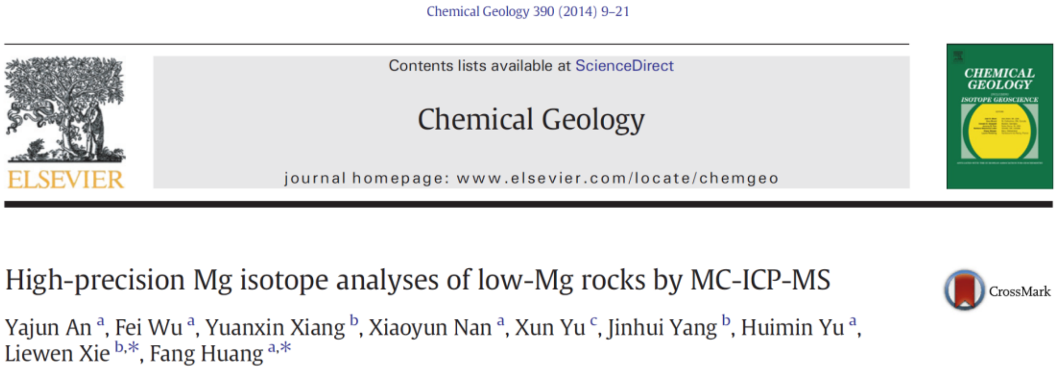
Short communication

Lithium, magnesium and sulfur purification from seawater using an ion chromatograph with a fraction collector system for stable isotope measurements

Toshihiro Yoshimura[a,b,*], Daisuke Araoka[c], Yusuke Tamenori[d], Junichiro Kuroda[a,b],
Hodaka Kawahata[b], Naohiko Ohkouchi[a]



Chemical Geology 390 (2014) 9–21

Contents lists available at ScienceDirect

Chemical Geology

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

ELSEVIER

CrossMark

High-precision Mg isotope analyses of low-Mg rocks by MC-ICP-MS

Yajun An[a], Fei Wu[a], Yuanxin Xiang[b], Xiaoyun Nan[a], Xun Yu[c], Jinhui Yang[b], Huimin Yu[a],
Liewen Xie[b,*], Fang Huang[a,*]

Outline

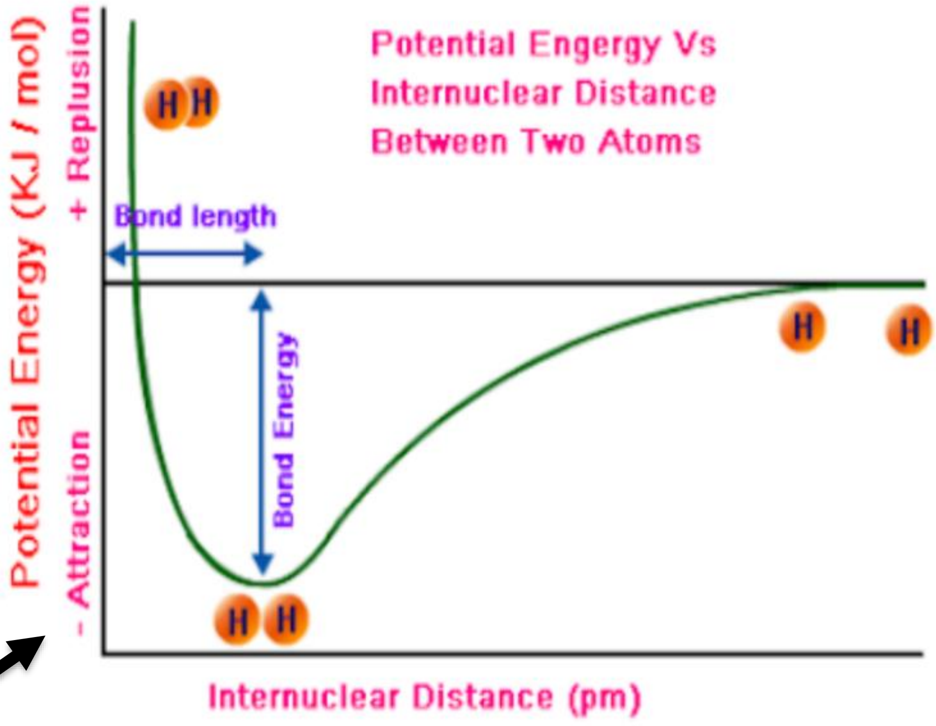
1. Introduction to Mg and Mg isotopes
2. Analytical methods for Mg isotopes
3. Mechanisms of Mg isotope fractionation
4. Mg isotopic compositions of major reservoirs
5. Mg isotope studies in chemical weathering
6. Mg isotope studies in subduction recycling

Isotope fractionation

同位素分馏是指同位素在物理，化学，生物等反应过程中以不同比例分配于不同物质（相）之中的现象。

Isotopic fractionations occur due to:

- Differences in bond energies (equilibrium)
- Reaction rates (kinetics)



$$\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}$$

Equilibrium isotope fractionation

Vibrational energy of molecules

$$E_n = h\nu(n+½)$$

h: Planck's constant

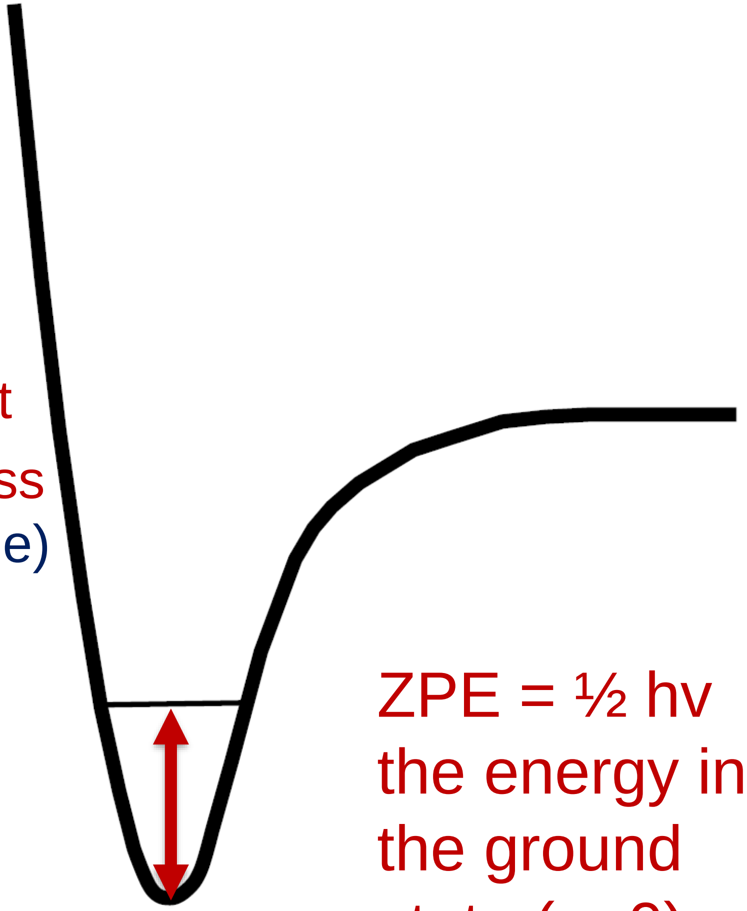
Vibrational frequency

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Spring constant

Reduced mass (see next slide)

Zero-point energy differences drive typical equilibrium stable isotope fractionations.

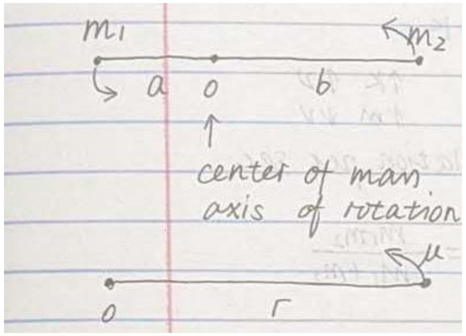


ZPE = ½ hv the energy in the ground state (n=0)

Reduced mass

The "effective" inertial mass appearing in the two-body problem.

It allows the two-body problem to be solved as if it were a one-body system.



Same moment of inertia $\boxed{I = mr^2}$

转动惯量

$m_1 a = m_2 b$

$\Rightarrow m_1 a + m_1 b = m_2 b + m_1 b$

$\Rightarrow m_1 (a+b) = b\,(m_1+m_2)$

$\Rightarrow m_1 r = b\,(m_1+m_2)$

$\Rightarrow b = m_1 r/(m_1+m_2)$ likewise, $a = m_2 r/(m_1+m_2)$

$$I = m_1 a^2 + m_2 b^2 = m_1\left(\frac{m_2 r}{m_1+m_2}\right)^2 + m_2\left(\frac{m_1 r}{m_1+m_2}\right)^2 = r^2\left[\frac{m_1 m_2^2 + m_2 m_1^2}{(m_1+m_2)^2}\right] = \boxed{r^2\left[\frac{m_1 m_2}{m_1+m_2}\right]}$$

$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}}$$

$$\frac{1}{\mu} = \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{m_1} + \frac{1}{m_2}$$

Case 1: let $m_1 = m_2$, then $\mu = m^2/2m = m/2$ (Max μ)

Case 2: let $m_2 \gg m_1$, then $\mu \approx m_1 m_2/m_2 = m_1$ (Min μ)

Reduced mass

*Equilibrium **isotope fractionation***

At a given k, bonds with heavy isotopes have lower vibrational frequencies

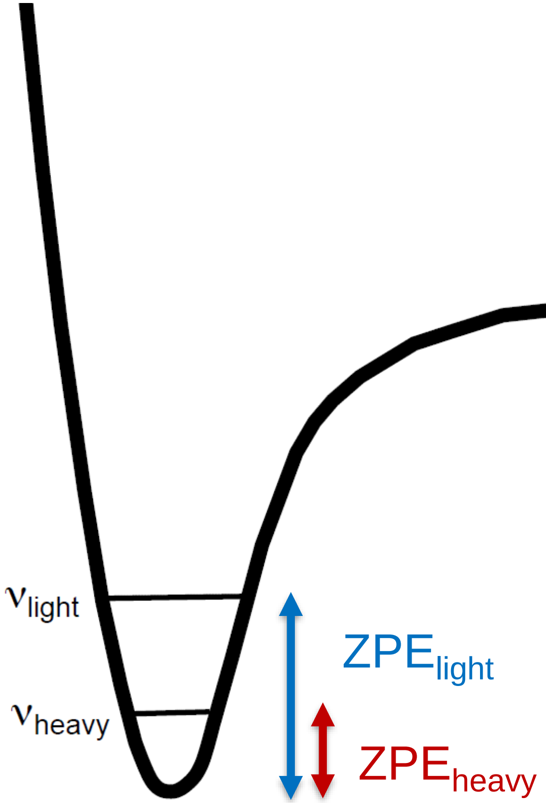
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$\Delta ZPE = ZPE_{heavy} - ZPE_{light}$
$= \frac{1}{2} h(\nu_{heavy} - \nu_{light})$

$$\nu_{heavy} - \nu_{light} =$$

$$\frac{1}{2\pi}\sqrt{k}\left(\frac{1}{\sqrt{\mu_{heavy}}} - \frac{1}{\sqrt{\mu_{light}}}\right) < 0$$

$\Delta ZPE < 0$



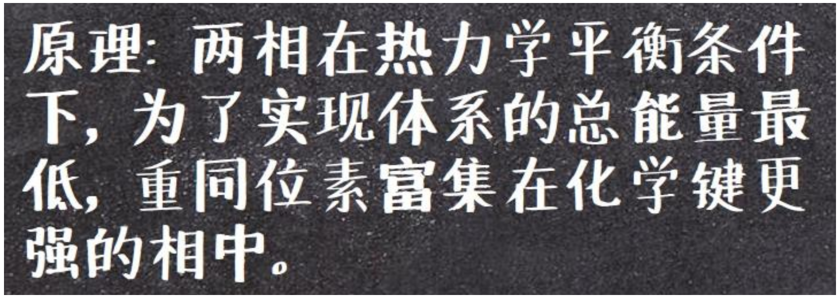
Substitution of a light isotope by a heavy isotope leads to a decrease in ZPE

Equilibrium isotope fractionation

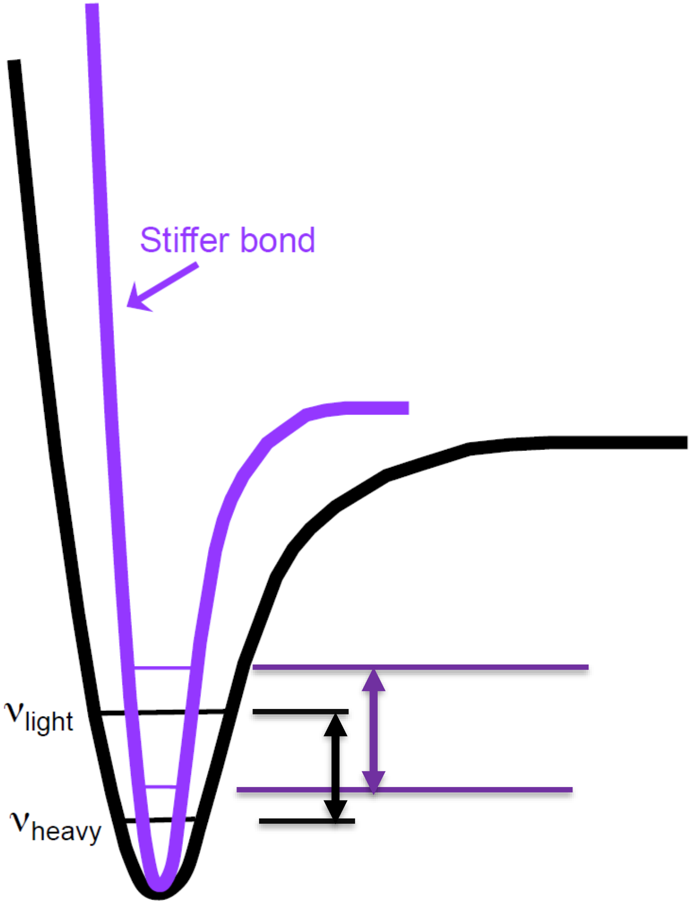
Substitution of a light isotope by a heavy isotope lowers more energy in stiffer bonds (with higher k)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\nu_{heavy} - \nu_{light} = \frac{1}{2\pi}\sqrt{k}\left(\frac{1}{\sqrt{\mu_{heavy}}} - \frac{1}{\sqrt{\mu_{light}}}\right)$$



原理：两相在热力学平衡条件下，为了实现体系的总能量最低，重同位素富集在化学键更强的相中。



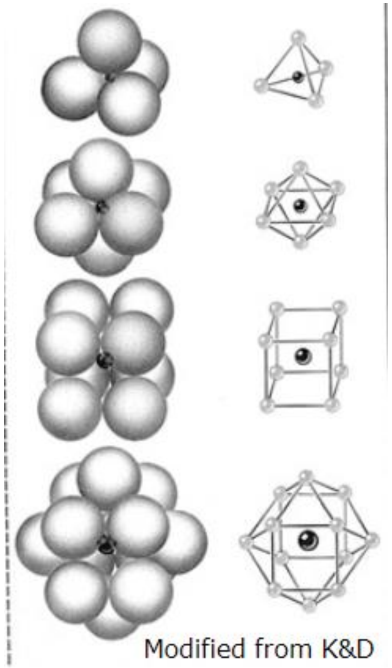
$|\Delta ZPE_{stiff}| > |\Delta ZPE_{soft}|$

Equilibrium isotope fractionation

Stiffer bonds concentrates the heavy isotopes

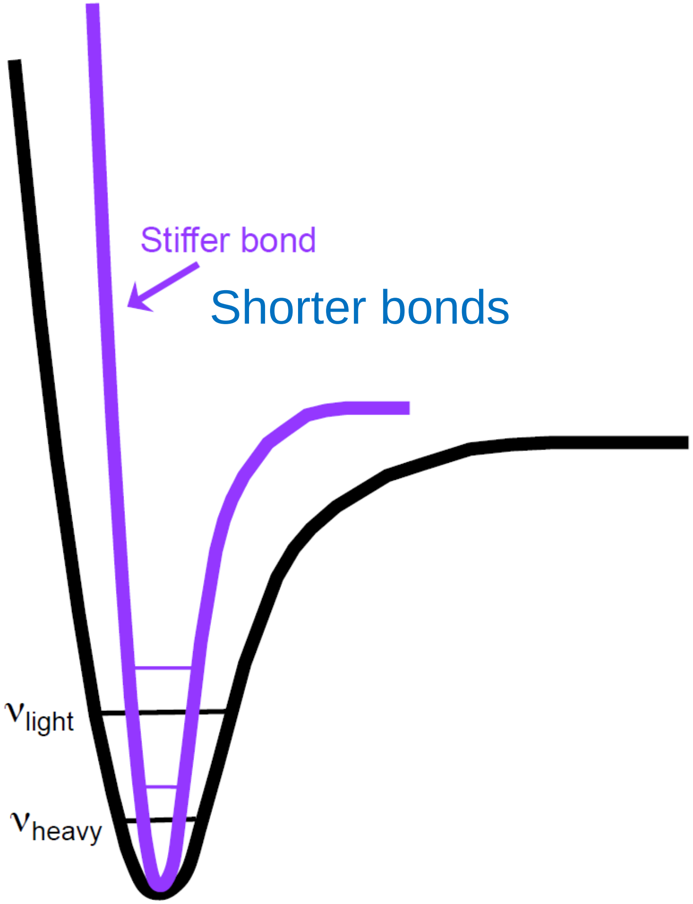
- Shorter bonds
- Higher oxidation state
  (Mg only occurs as Mg^{2+} in minerals)
- Lower coordination number

A cation's coordination number (CN) is the number of anions with which it is in contact



Bond lengths increase with increasing CN

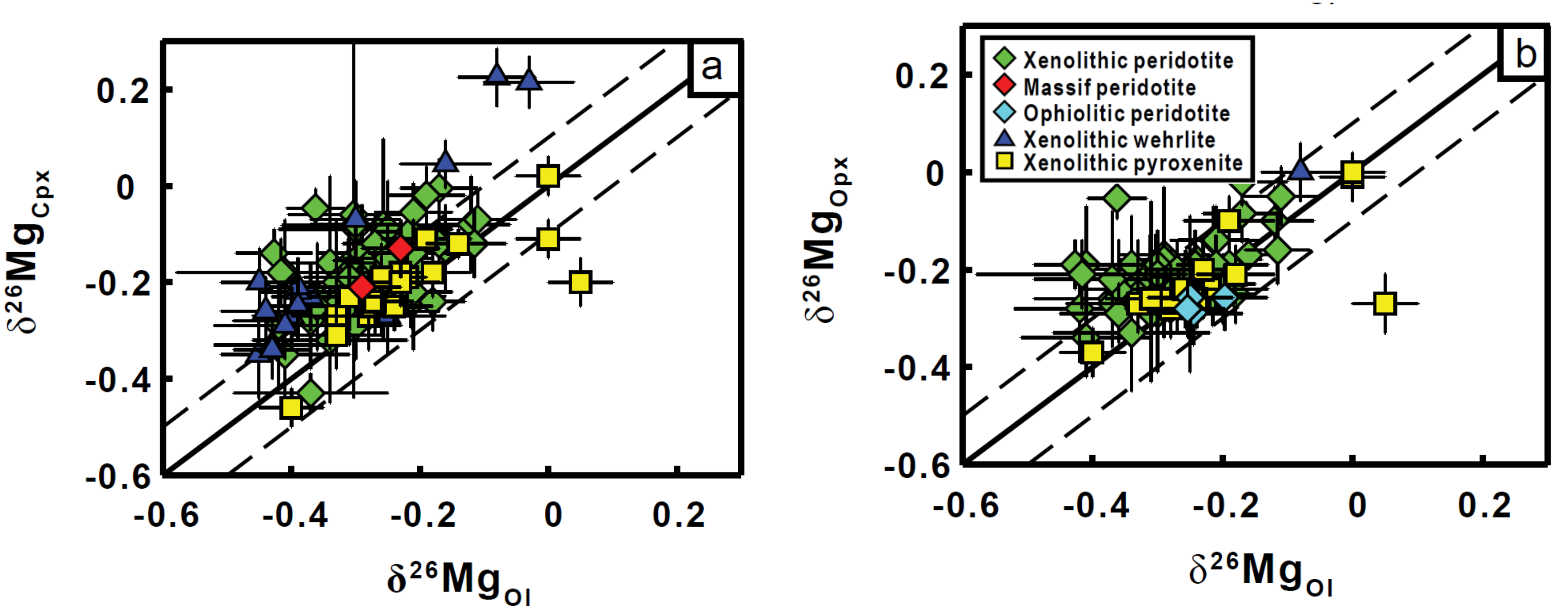
Thus shorter bonds are associated with lower CN



Equilibrium Mg isotope fractionation

In most rock-forming minerals (Ol, Opx, Cpx, Hbl, Bt), coordination number of Mg is 6.

Hence limited inter-mineral fractionation is expected.



Teng RiMG 2017

Equilibrium Mg isotope fractionation

In most rock-forming minerals (Ol, Opx, Cpx, Hbl, Bt), coordination number of Mg is 6.

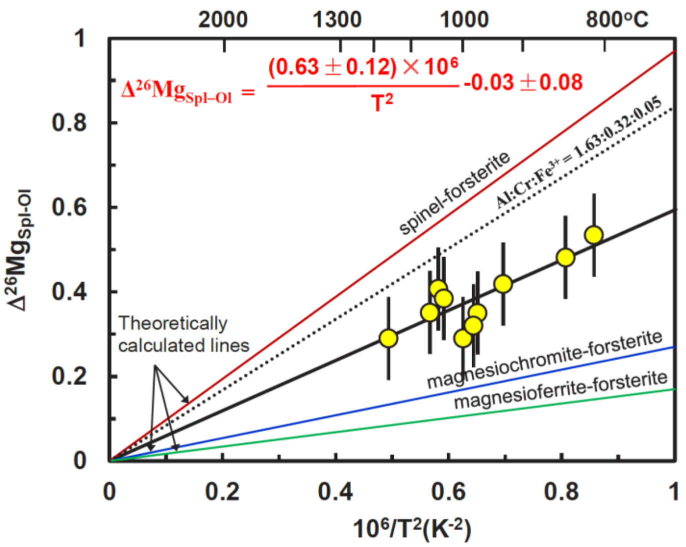
Hence limited inter-mineral fractionation is expected.

Coordination of Mg is not 6 in two important rock-forming minerals:

Spinel (CN=4) and Garnet (CN=8)

Large fractionation is expected when these two minerals are present, and can be used as geothermometers.

Mg isotope geothermometers

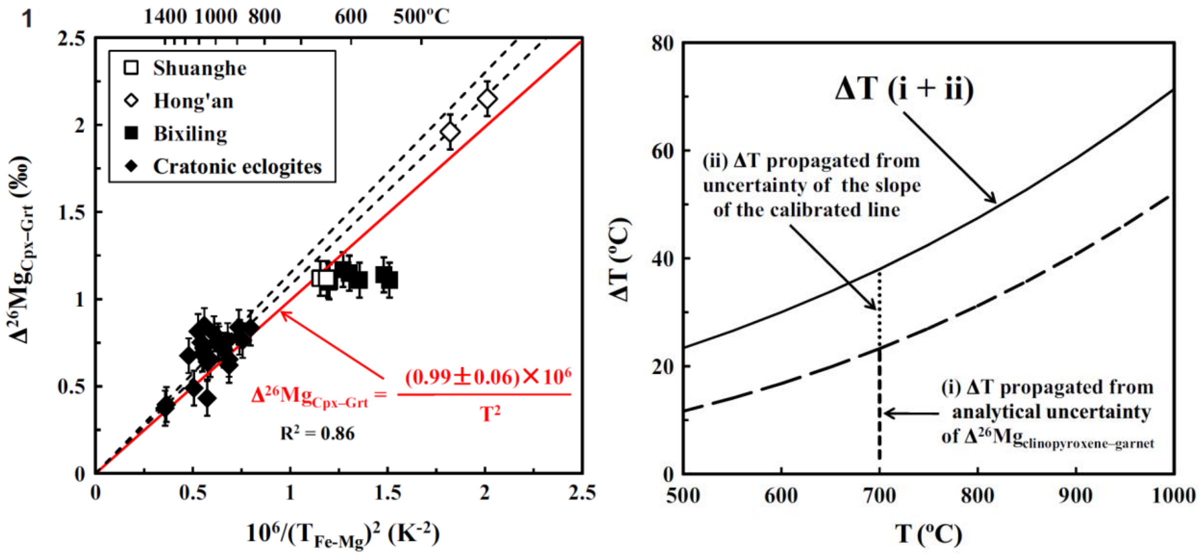


Cpx-Spl thermometer

(Liu et al. EPSL 2011)

Cpx-Grt thermometer

(Li et al. CMP 2016)



More precise T estimates than elemental geothermometer because Mg isotopes are measured with high precisions (2SD ~ 0.06 ‰)

Kinetic fractionation of isotopes (diffusion)

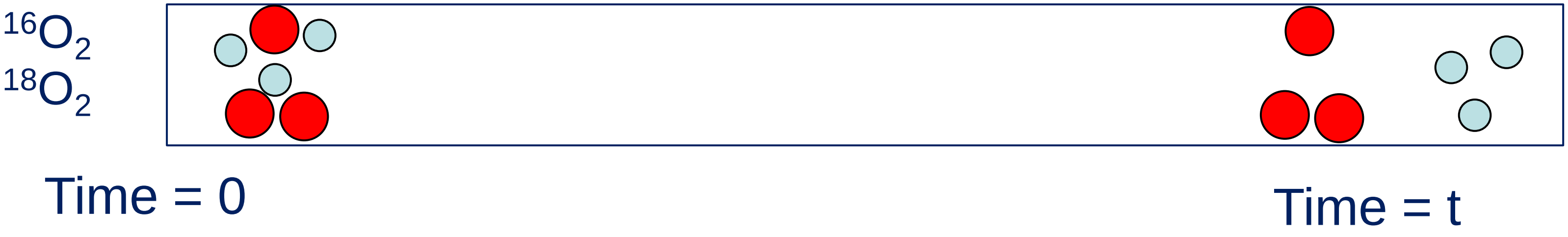
Lighter isotopes diffuse faster than heavy ones

At the same T, same kinetic energy $KE_{ave} = ½\, m_i v_i^2$

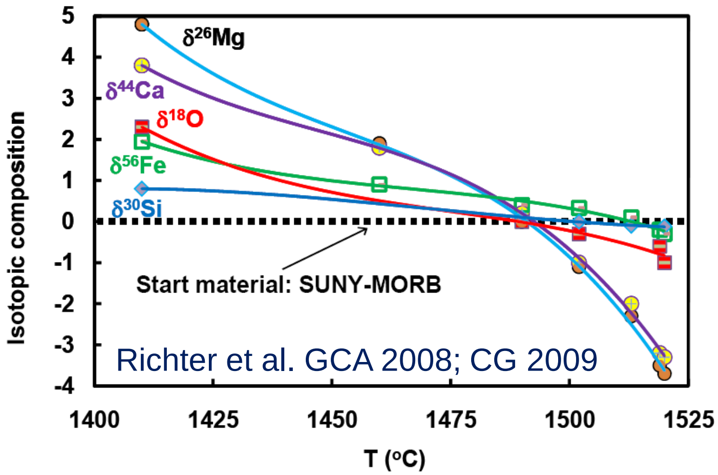
The velocity ratio for two isotopes: $v_2/v_1=(m_1/m_2)^{0.5}$

$^{16}O_2$ diffuses $\sqrt{}36/32 = 1.06$ times faster than $^{18}O_2$

Let $^{16}O_2$ and $^{18}O_2$ diffuse through a tube; their different diffusivity will separate them, i.e., isotope fractionation.



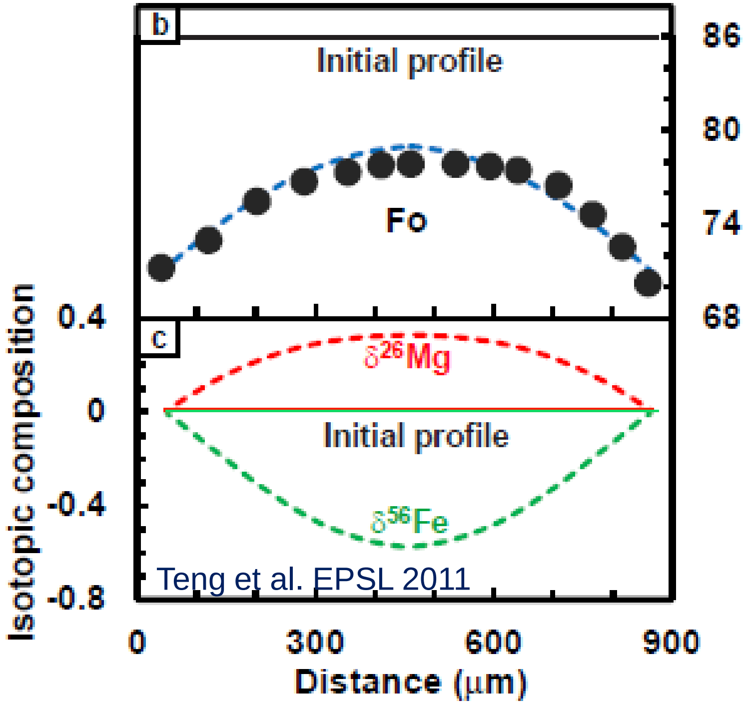
Kinetic fractionation of Mg isotopes



Richter et al. GCA 2008; CG 2009

Thermal or Soret diffusion

- Lighter isotopes are concentrated at the cold end along a temperature gradient
- Different isotope systems are positively correlated
- Haven't been observed in natural samples yet



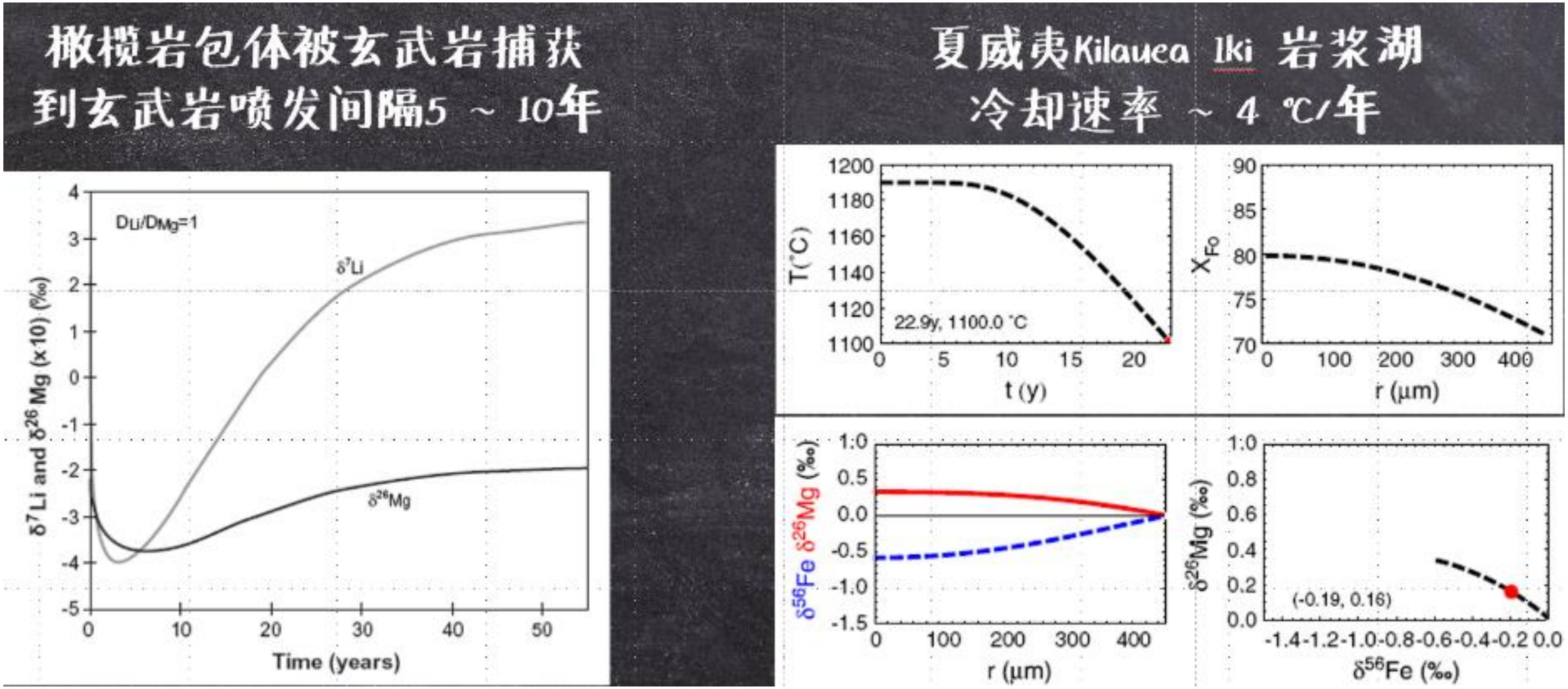
Teng et al. EPSL 2011

Chemical diffusion

Fe-Mg inter-diffusion

- δ^{26}Mg and δ^{56}Fe are negatively correlated
- Can be used to distinguish diffusion zoning (large fractionation) from growth zoning (limited fractionation)

Mg isotope *geospeedometers*



橄榄岩包体被玄武岩捕获
到玄武岩喷发间隔5 ~ 10年

夏威夷Kilauea Iki 岩浆湖
冷却速率 ~ 4 ℃/年

Pogge von Strandmann et al. GCA 2011

Teng et al. EPSL 2011

Outline

1. Introduction to Mg and Mg isotopes
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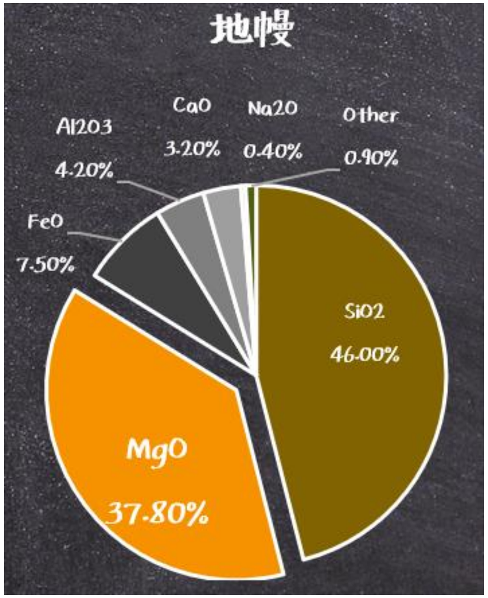
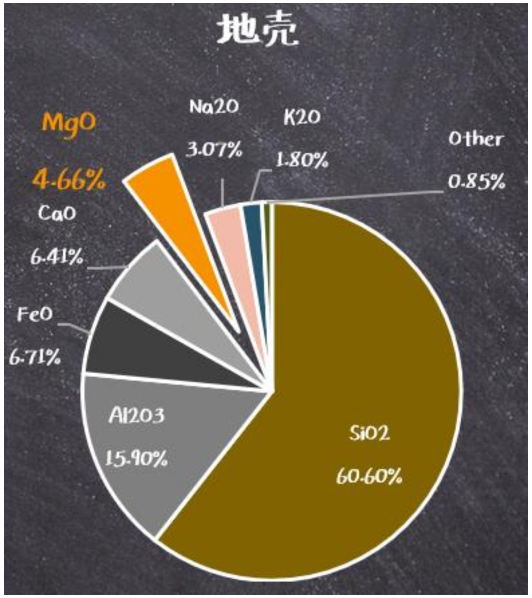
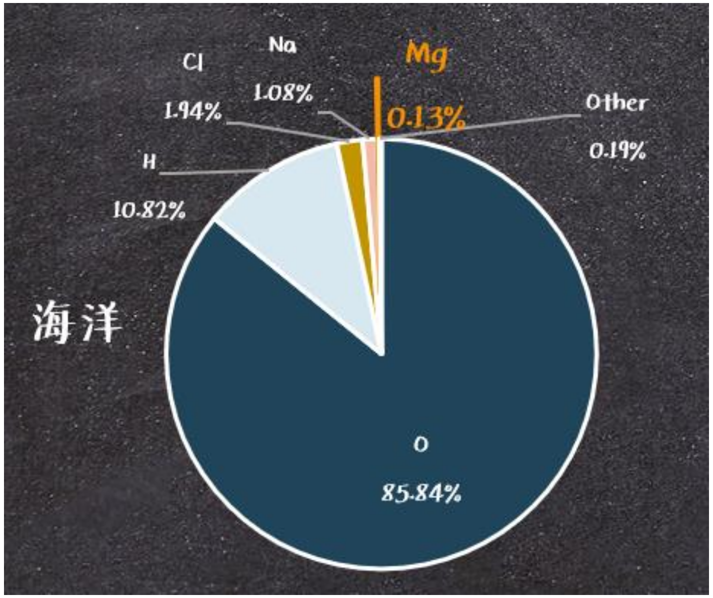
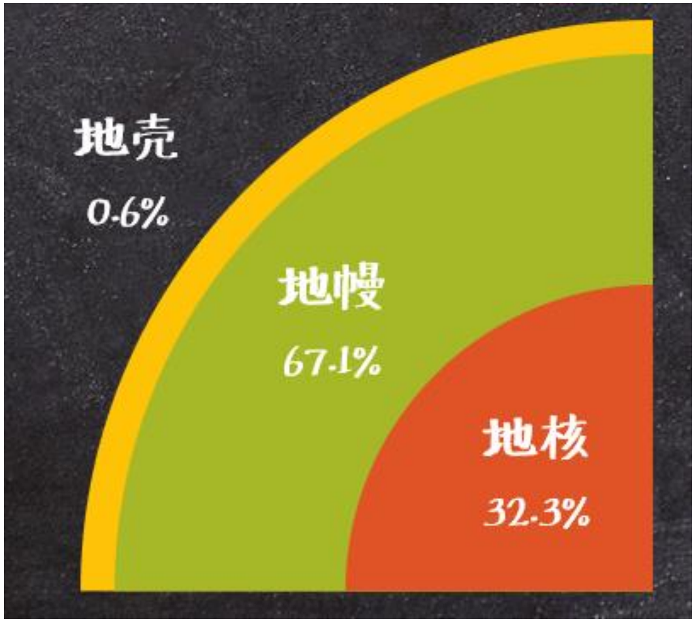
Major terrestrial Mg reservoirs









- Highly heterogeneous Mg distribution
- The mantle contains 99.89% of terrestrial Mg

Terrestrial distribution of Mg

Oceanic crust
MgO = 8 wt.%

Mantle
MgO = 38 wt.%

Continental crust
MgO = 5 wt.%

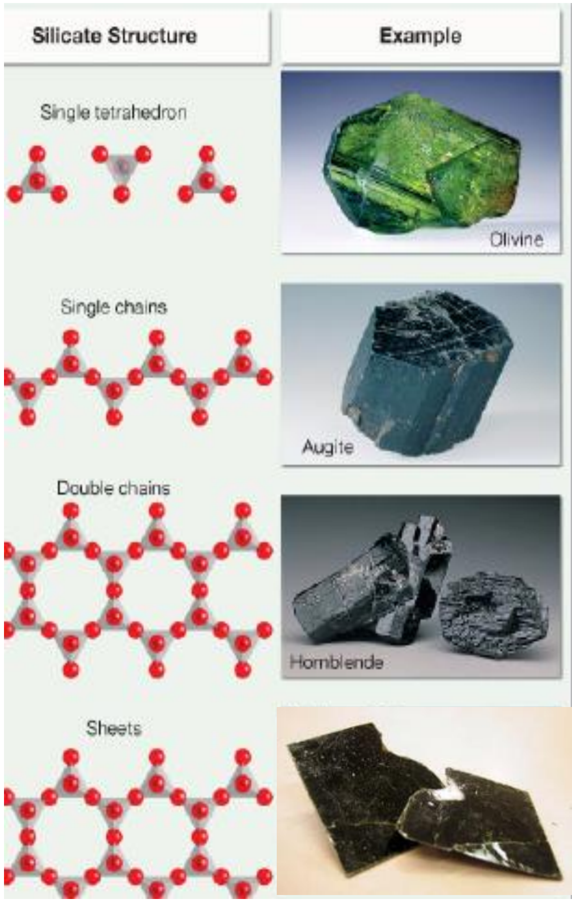
Olivine
$(Mg,Fe)_2SiO_4$

Pyroxene
$(Ca,Mg,Fe)_2Si_2O_6$

Amphibole
Na-Ca-Mg-Fe-Al

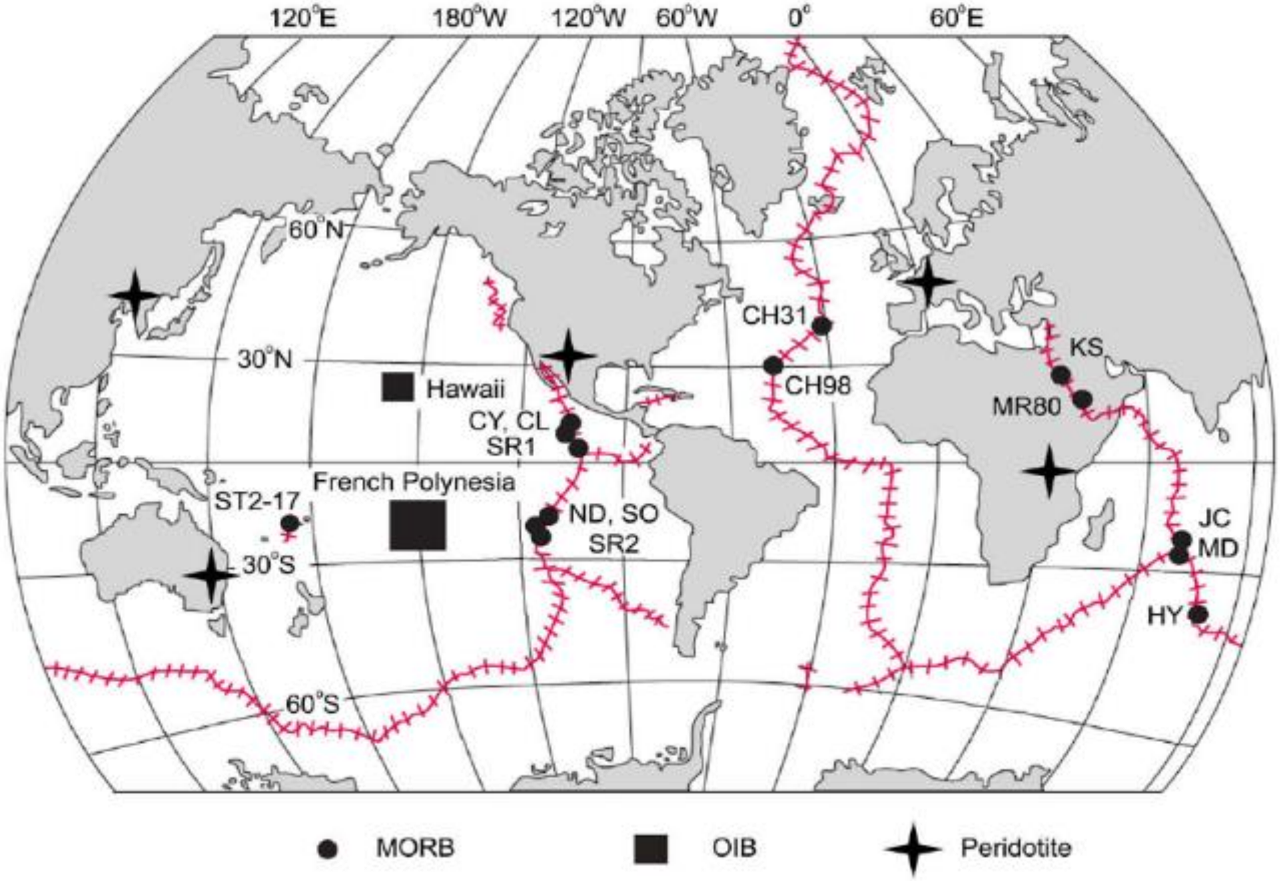
Biotite
$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$

Mafic minerals



Samples of the Mantle

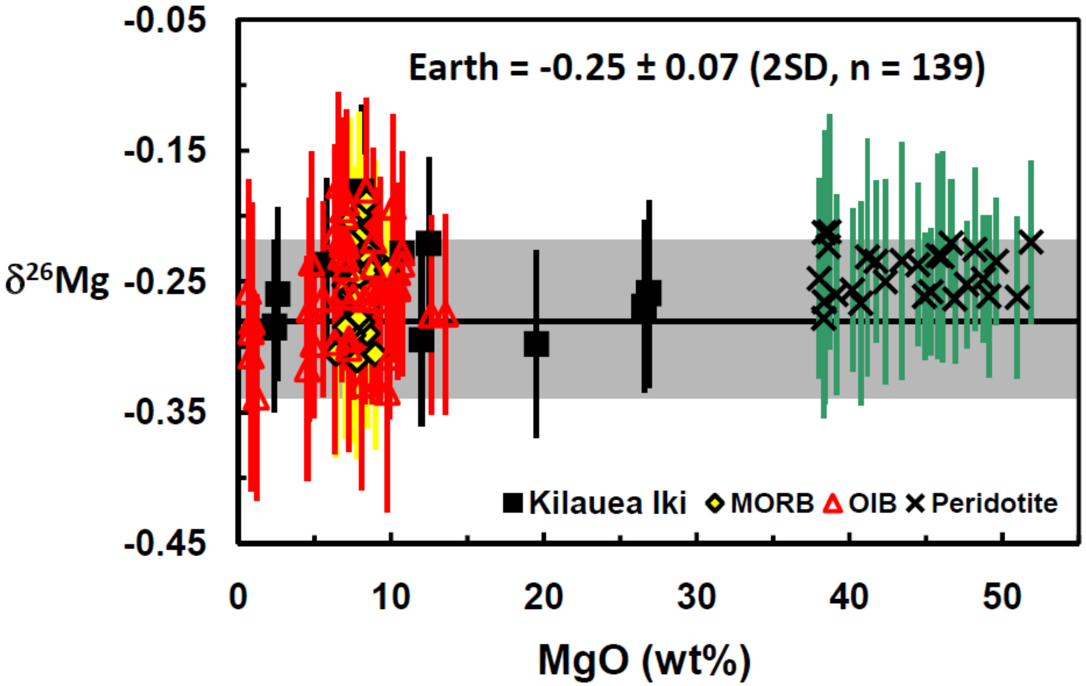
Globally distributed, chemically diverse peridotite xenoliths and oceanic basalts (n = 139)



Teng et al., GCA 2010

Homogeneous δ^{26}Mg in the Mantle

$\delta^{26}\mathrm{Mg}_{\mathrm{peridotite}} = \delta^{26}\mathrm{Mg}_{\mathrm{OIB}} = \delta^{26}\mathrm{Mg}_{\mathrm{MORB}}$



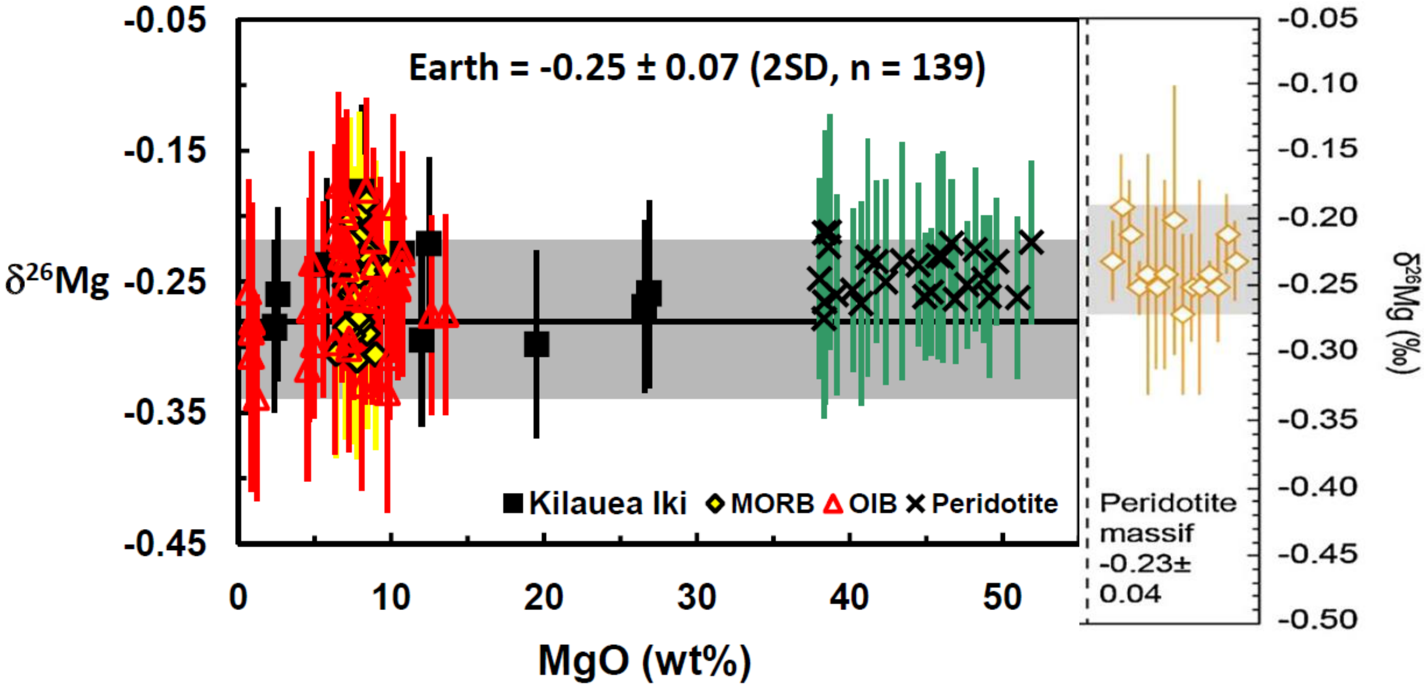
- The mantle has an overall homogeneous δ^{26}Mg at -0.25‰
- Mantle partial melting does not fractionate Mg isotopes
- Magmatic differentiation does not fractionate Mg isotopes

(except for when significant amounts of oxides are removed)

Teng et al., GCA 2010

Homogeneous δ^{26}Mg in the Mantle

$\delta^{26}\mathrm{Mg}_{\text{peridotite}} = \delta^{26}\mathrm{Mg}_{\text{OIB}} = \delta^{26}\mathrm{Mg}_{\text{MORB}}$



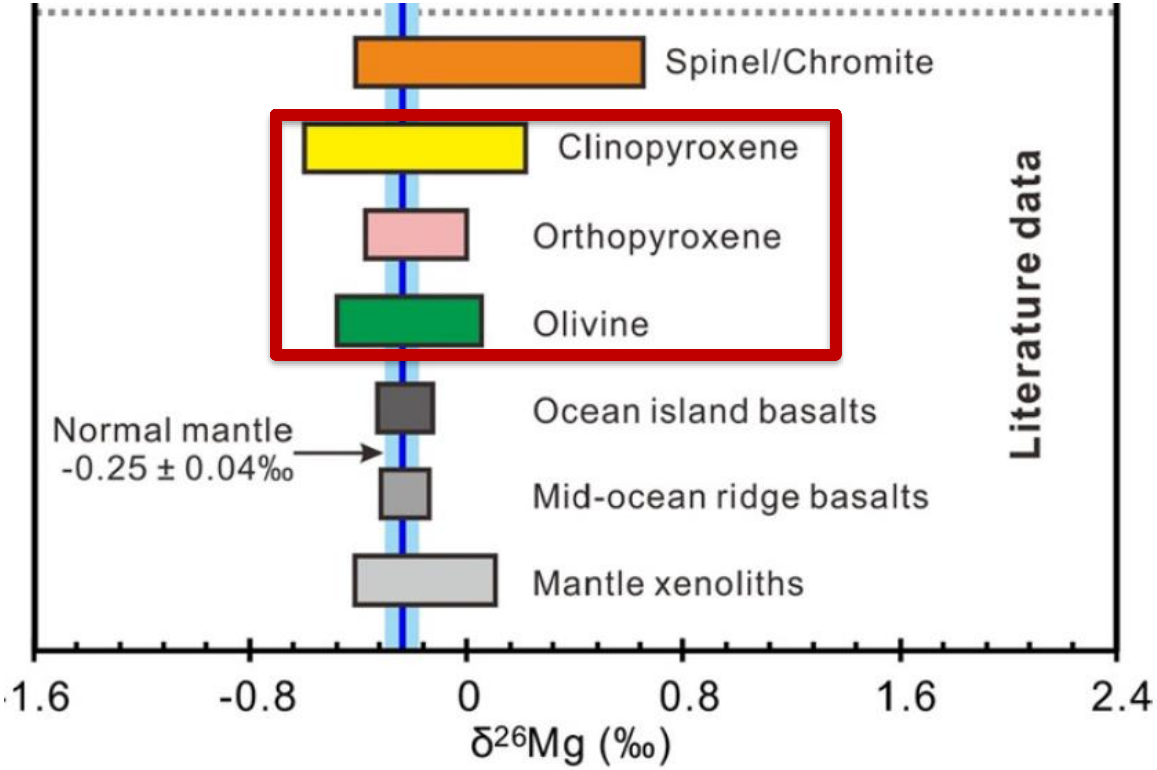
Peridotite xenoliths and massif peridotites have similar δ^{26}Mg values

Teng et al., 2010 GCA; Lai et al GCA 2015

Equilibrium **Mg isotope fractionation**

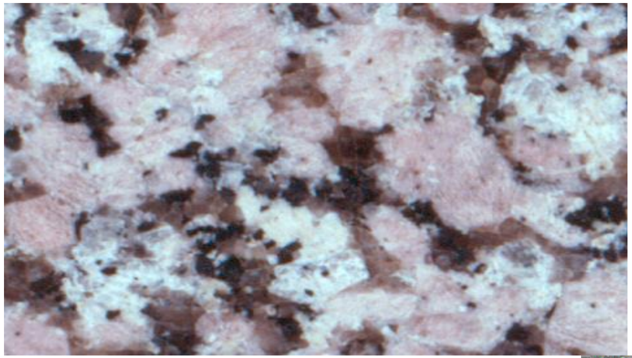
In most rock-forming minerals (Ol, Opx, Cpx, Hbl, Bt), coordination number of Mg is 6.

Hence limited inter-mineral fractionation is expected.



Chen et al. EPSL 2018

Samples of the continental crust



Granite

A major igneous rock type in UCC

Derived from glacial outwash & desert regions

Produced mainly by mechanical abrasion

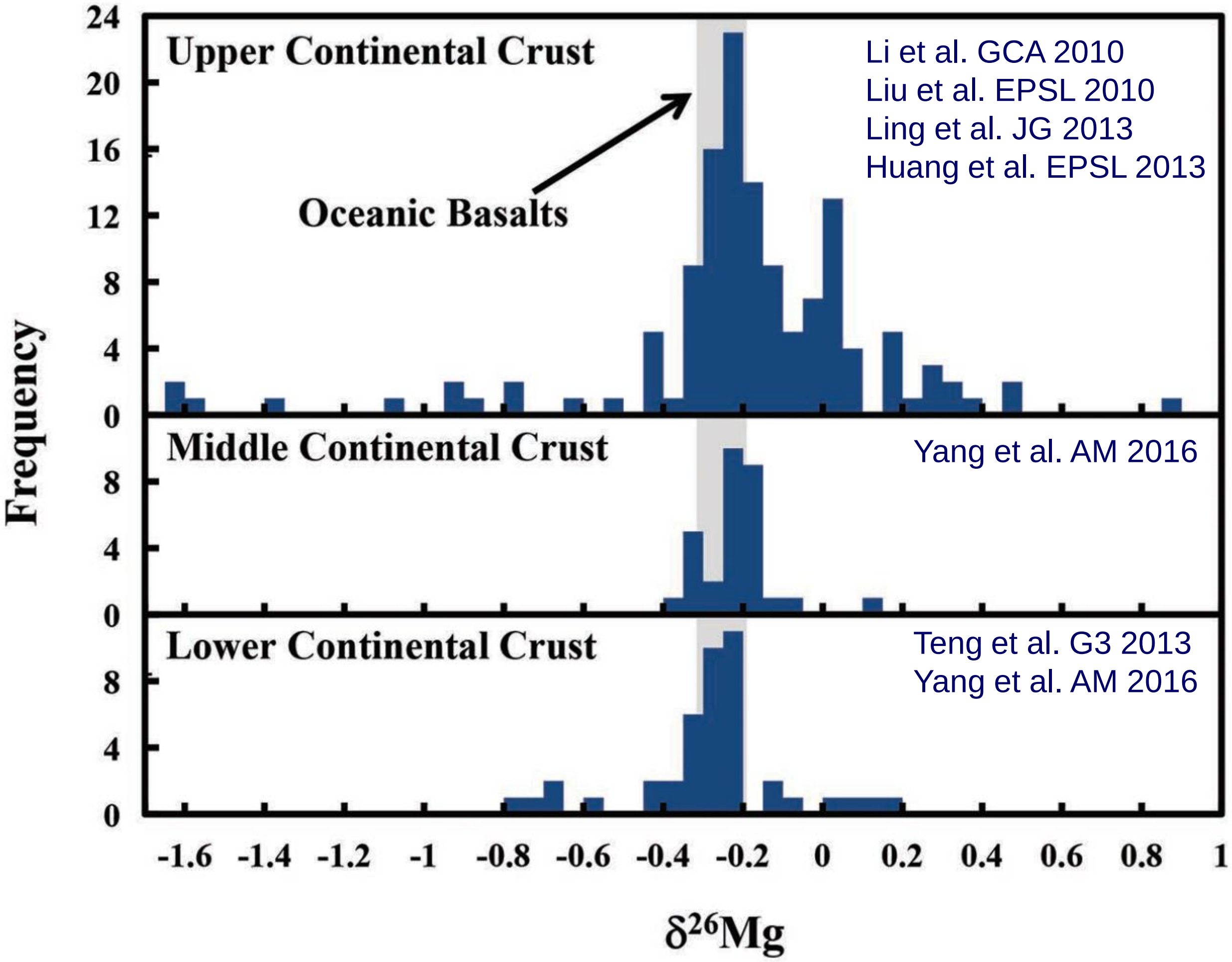
Loess

Wind-blown rock flour (predominantly silt-sized)

Shale

Fine-grained sedimentary rocks
Deposited in water (fluid-rock interaction)
Produced by complex processes (e.g. diagenesis)
Generally underwent higher degrees of weathering

Heterogeneous *δ^{26}Mg in continental crust*



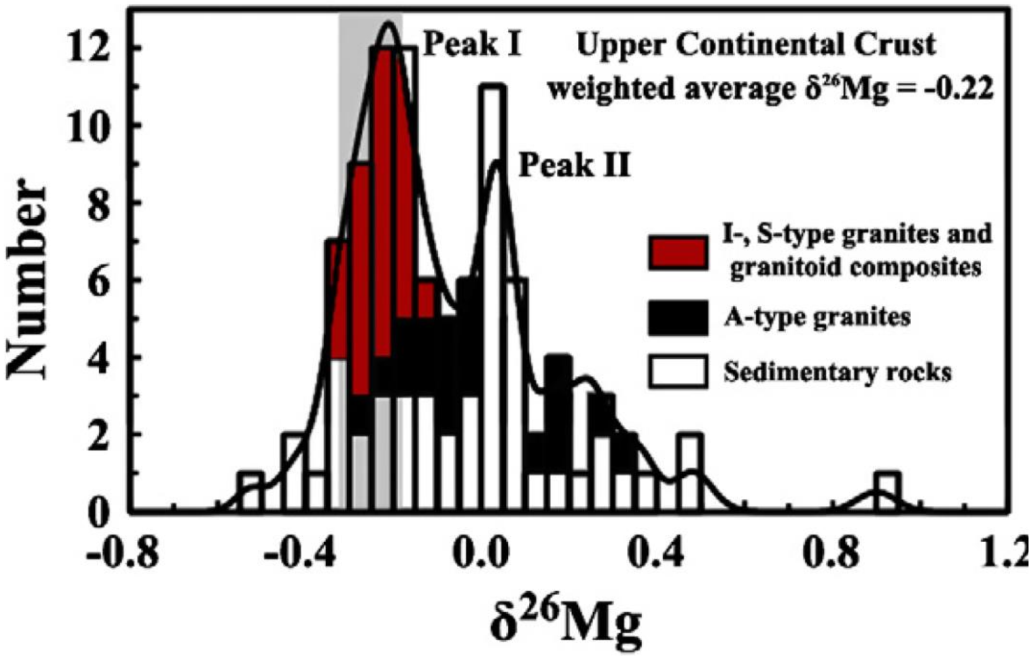
Li et al. GCA 2010
Liu et al. EPSL 2010
Ling et al. JG 2013
Huang et al. EPSL 2013

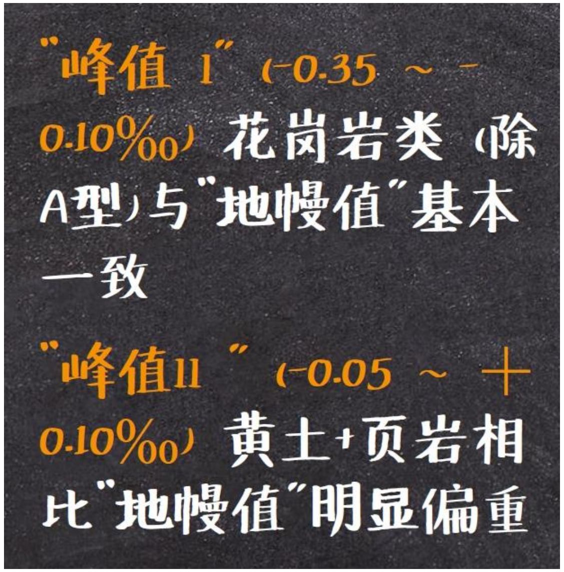
Yang et al. AM 2016

Teng et al. G3 2013
Yang et al. AM 2016

Compiled by Yang et al. AM 2016

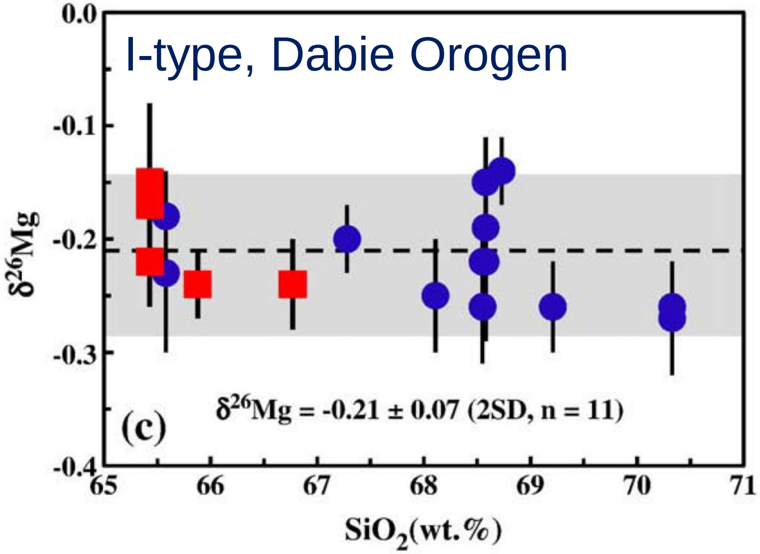
δ^{26}Mg in upper continental crust





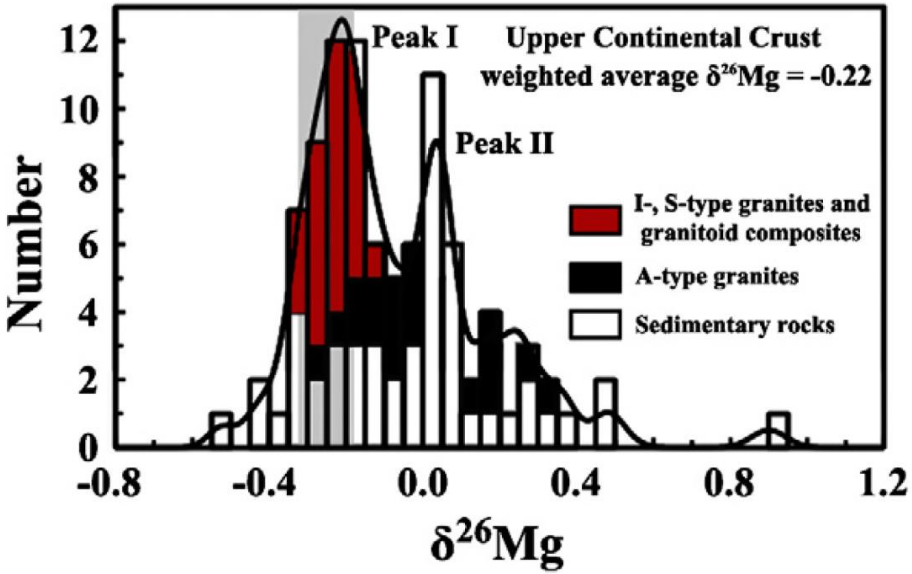
“峰值 I”（-0.35 ~ -0.10‰）花岗岩类（除A型）与“地幔值”基本一致

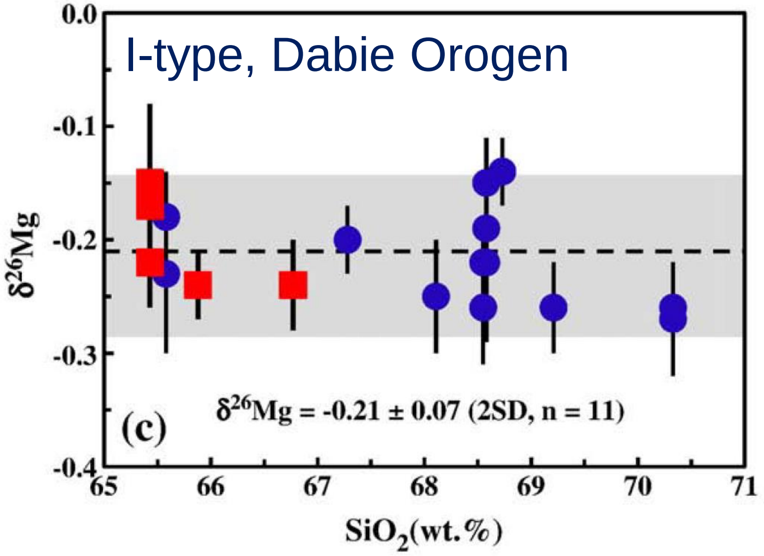
“峰值II”（-0.05 ~ +0.10‰）黄土+页岩相比“地幔值”明显偏重

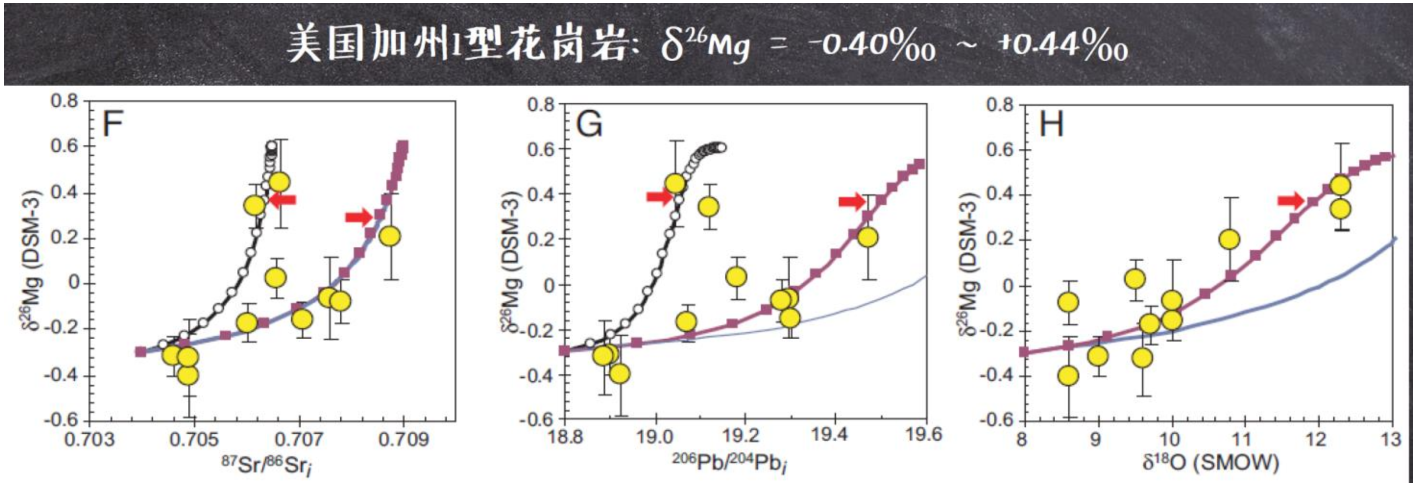


Li et al. GCA 2010; Liu et al EPSL 2010

δ^{26}Mg in granite



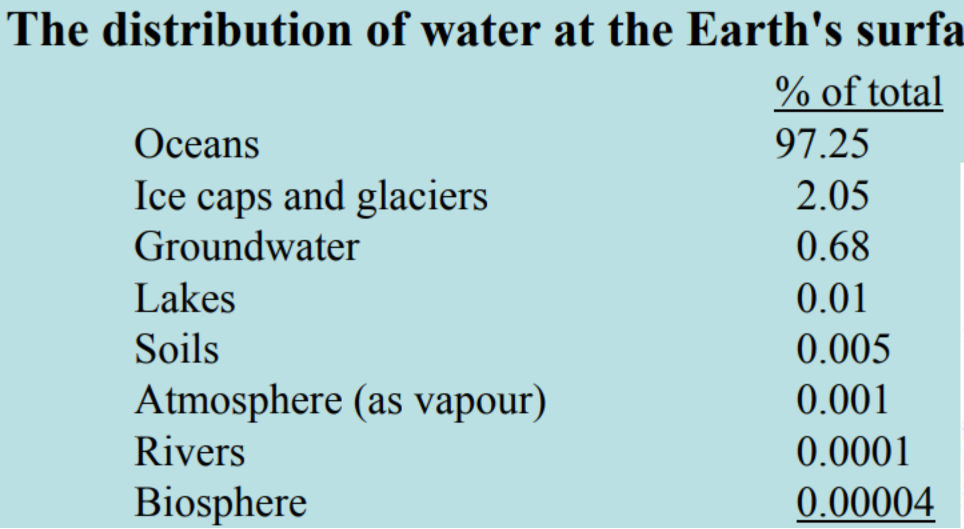

I-type, Dabie Orogen


美国加州I型花岗岩: δ^{26}Mg = -0.40‰ ~ +0.44‰

Shen et al. PNAS 2009; Li et al. GCA 2010; Liu et al EPSL 2010

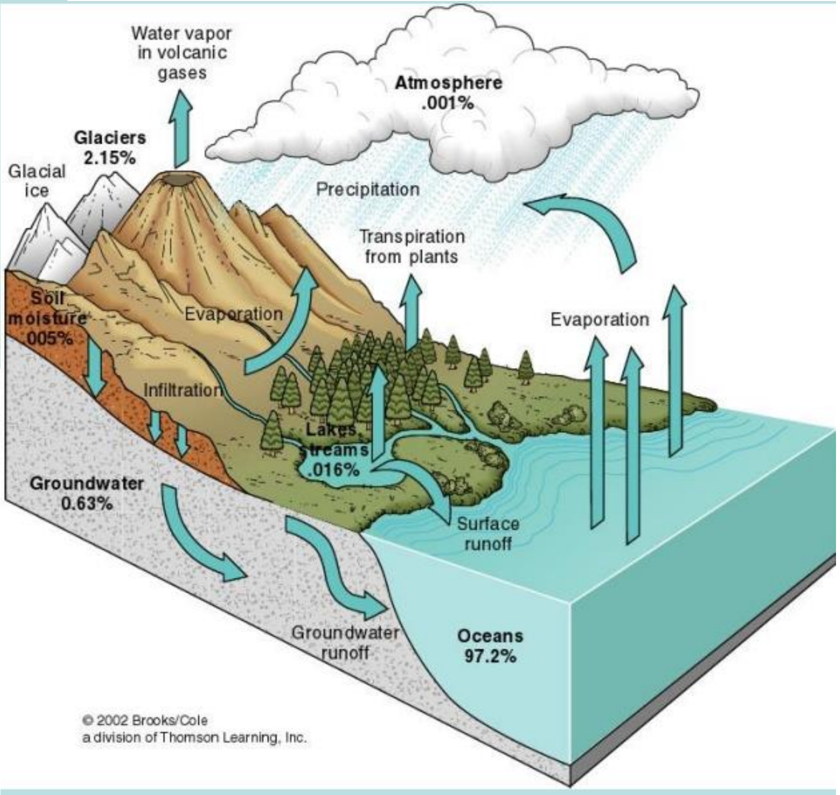
Samples of the hydrosphere

The oceans are the largest water body in the hydrosphere



The distribution of water at the Earth's surface

	% of total
Oceans	97.25
Ice caps and glaciers	2.05
Groundwater	0.68
Lakes	0.01
Soils	0.005
Atmosphere (as vapour)	0.001
Rivers	0.0001
Biosphere	0.00004



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Residence time and mixing time

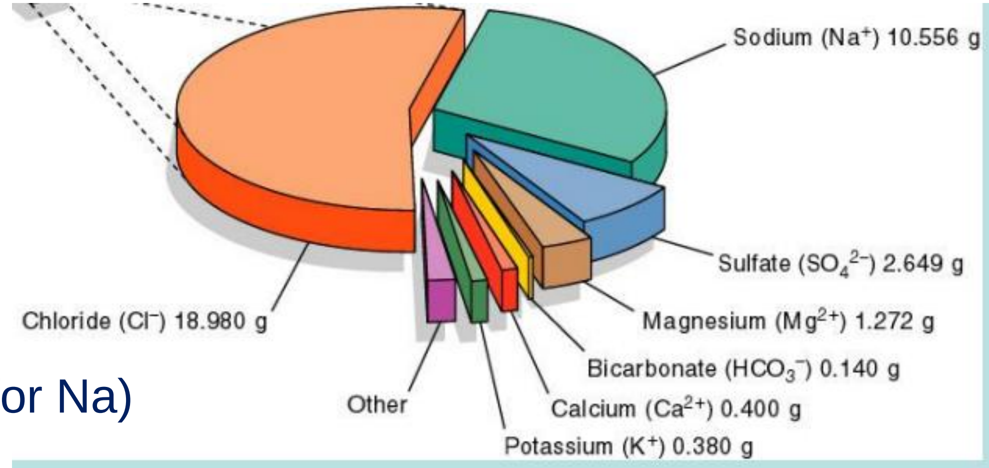
Residence time is the average time an element spends in a reservoir. It is also the length of time it takes to replace the amount in a reservoir.

Residence time (in years) of an element in the ocean = *Amount of Mg in the ocean* / *Amount of Mg being added to (or removed from) the ocean each year*

In general, higher concentration means longer residence time

Mixing time of the oceans: **~ 1000 years**

Residence times range from < 50 years (for Fe) to > 50 million years (for Na)



Mg residence time in the oceans

Mg^{2+} in the oceans: 5.3×10^{-2} moles/kg

Mg^{2+} in rivers: 1.6×10^{-4} moles/kg

Ocean volume: 1.37×10^{21} liters

World average river runoff rate: 3.6×10^{16} liters/year

Residence time of Mg in the oceans

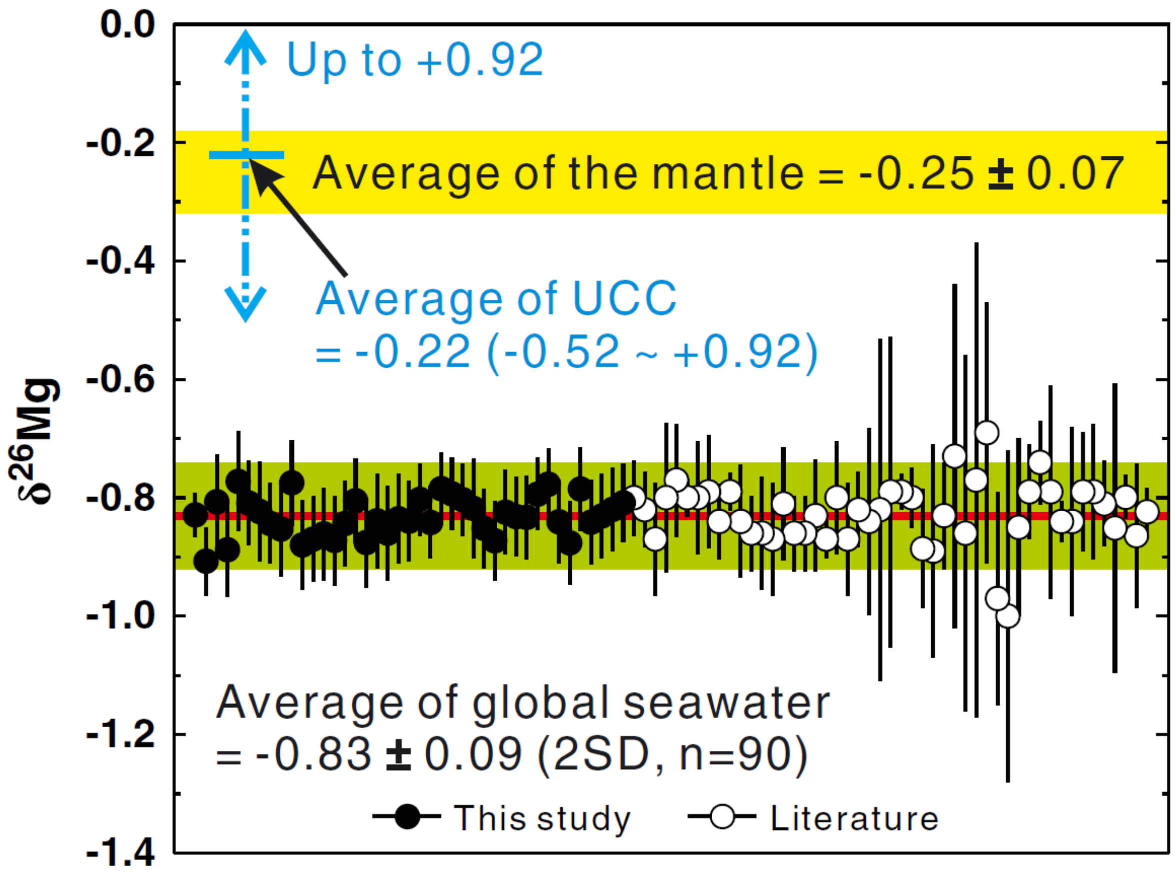
$= (1.37 \times 10^{21} \times 5.3 \times 10^{-2})/(3.6 \times 10^{16} \times 1.6 \times 10^{-4}) =$ **12.6 Ma**

12.6 Ma >> mixing time of the ocean (1000 years)

→ Uniform Mg concentration in the oceans ***(well mixed)***

Homogeneous δ^{26}Mg in seawater

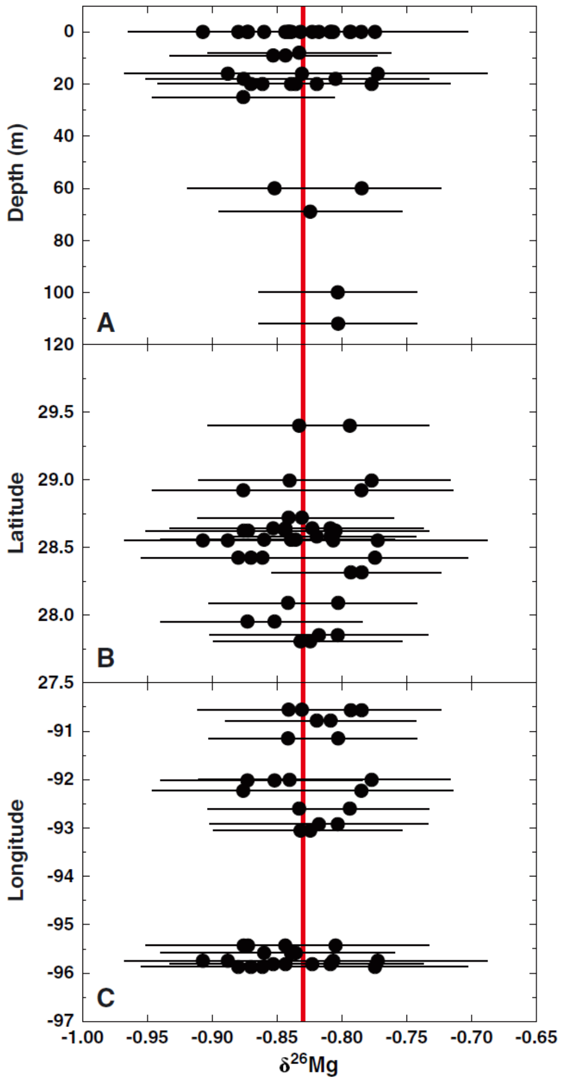
Reflecting the long residence time of Mg (13 Ma)

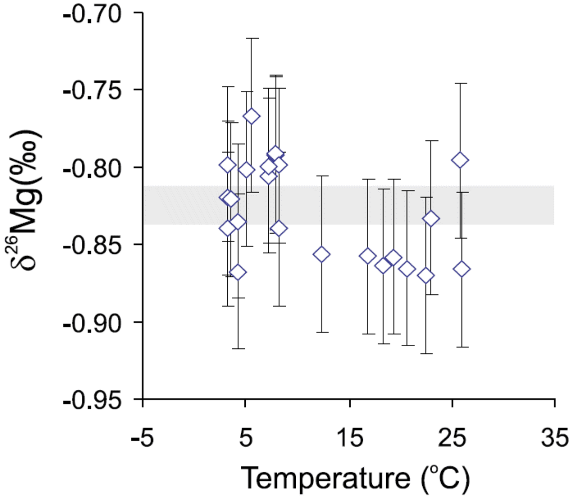


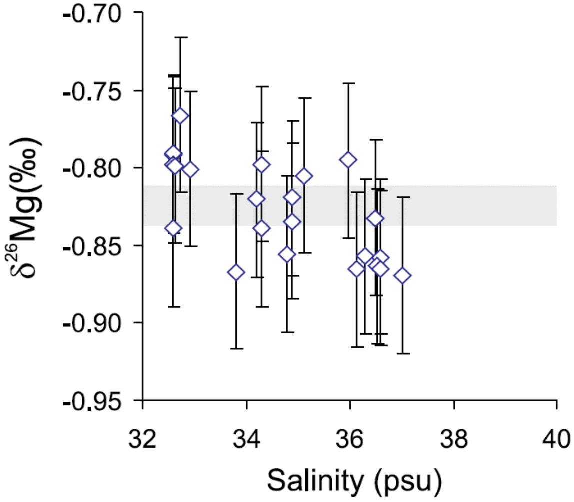
Ling et al. RCM 2011

Homogeneous δ^{26}Mg in seawater

No variation with location, depth, temperature, or salinity



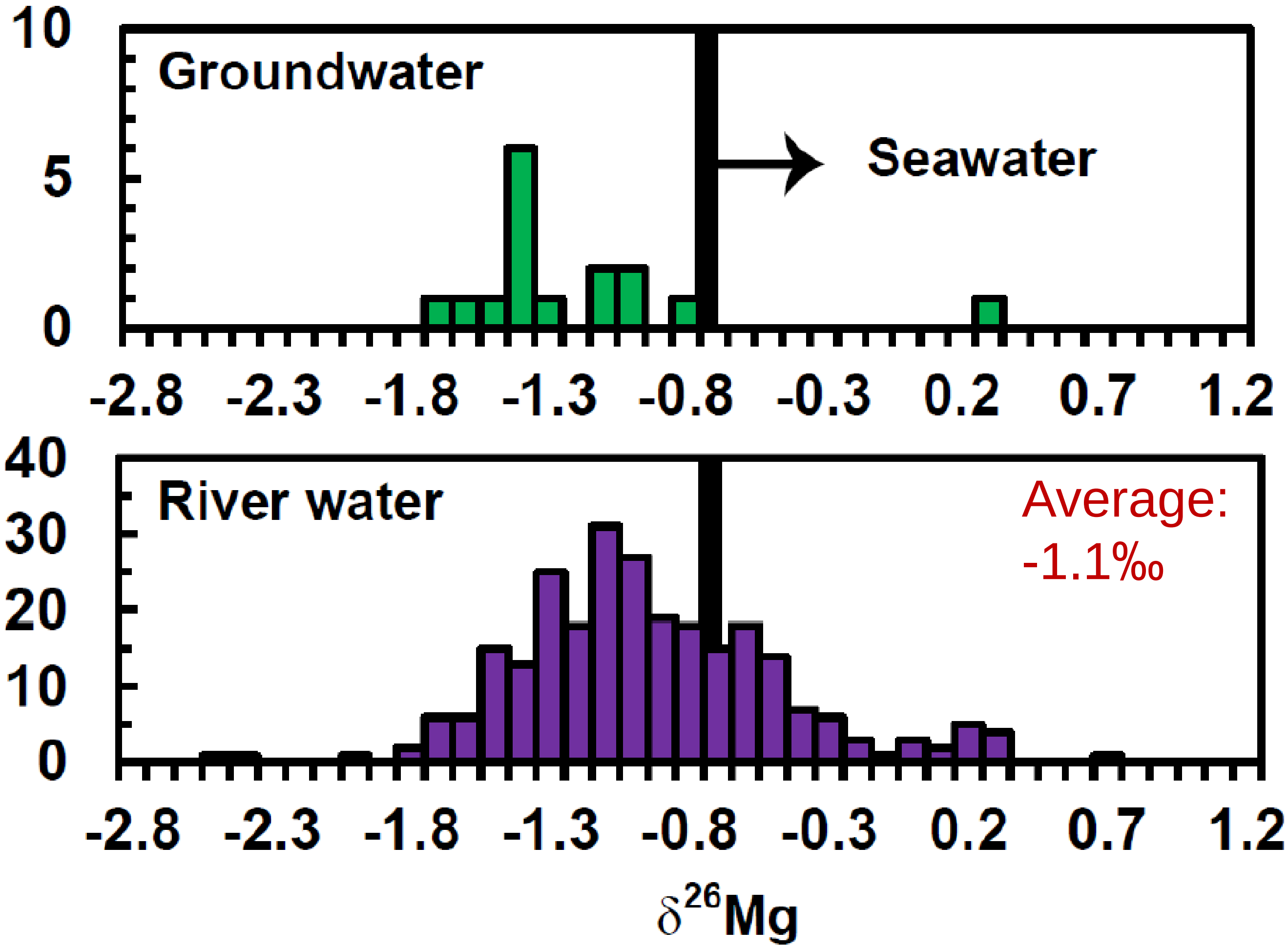




Foster et al. G3 2010; Ling et al. RCM 2011

Heterogeneous δ^{26}Mg in rivers

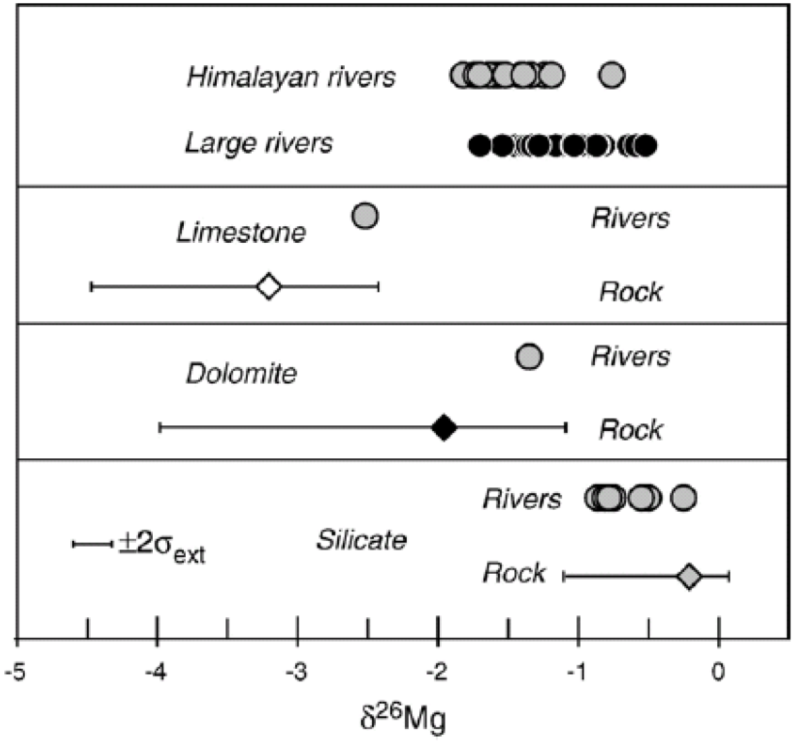
On average lighter than seawater



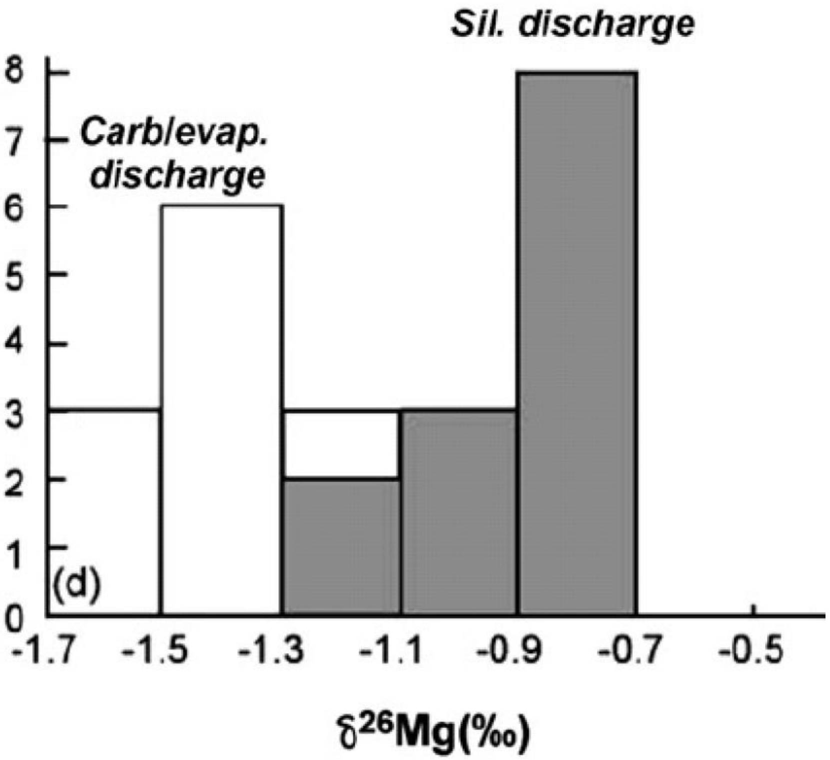
Compiled by Teng RiMG 2017

Bedrock control on riverine δ^{26}Mg

Rivers flowing over carbonate bedrocks are isotopically lighter than those flowing over silicate rivers



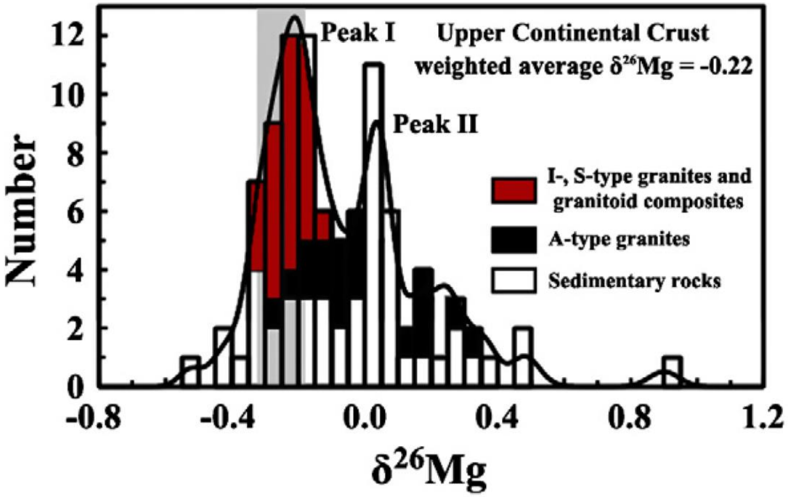
Tipper et al. EPSL 2006

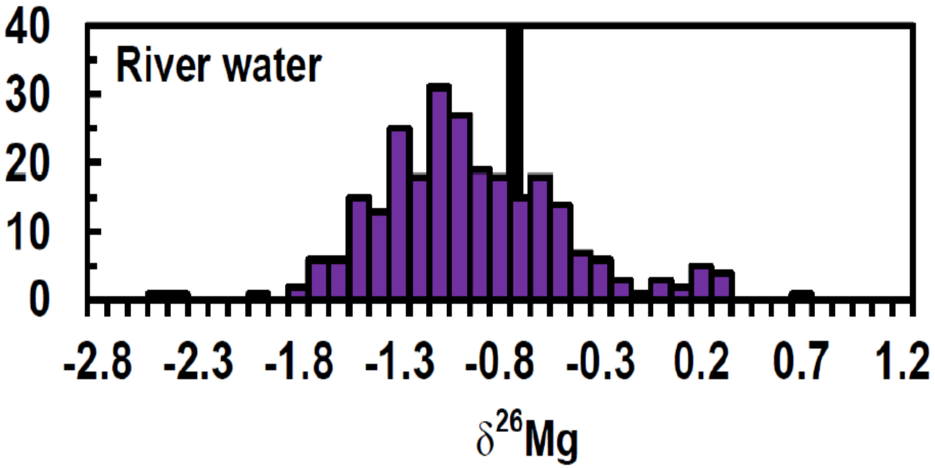


Brenot et al. GCA 2008

Summary

1. The ***mantle*** and ***oceanic crust*** have *homogeneous* δ^{26}Mg at -0.25‰
2. The ***continental crust*** has highly *heterogeneous* δ^{26}Mg, yet the average of -0.22‰ is similar to the mantle
3. Siliclastic sedimentary rocks are on average higher than the mantle
4. ***Seawater*** has a *uniform* δ^{26}Mg at -0.83‰, lighter than mantle
5. ***Rivers*** have *heterogeneous* δ^{26}Mg, averaging at -1.1‰

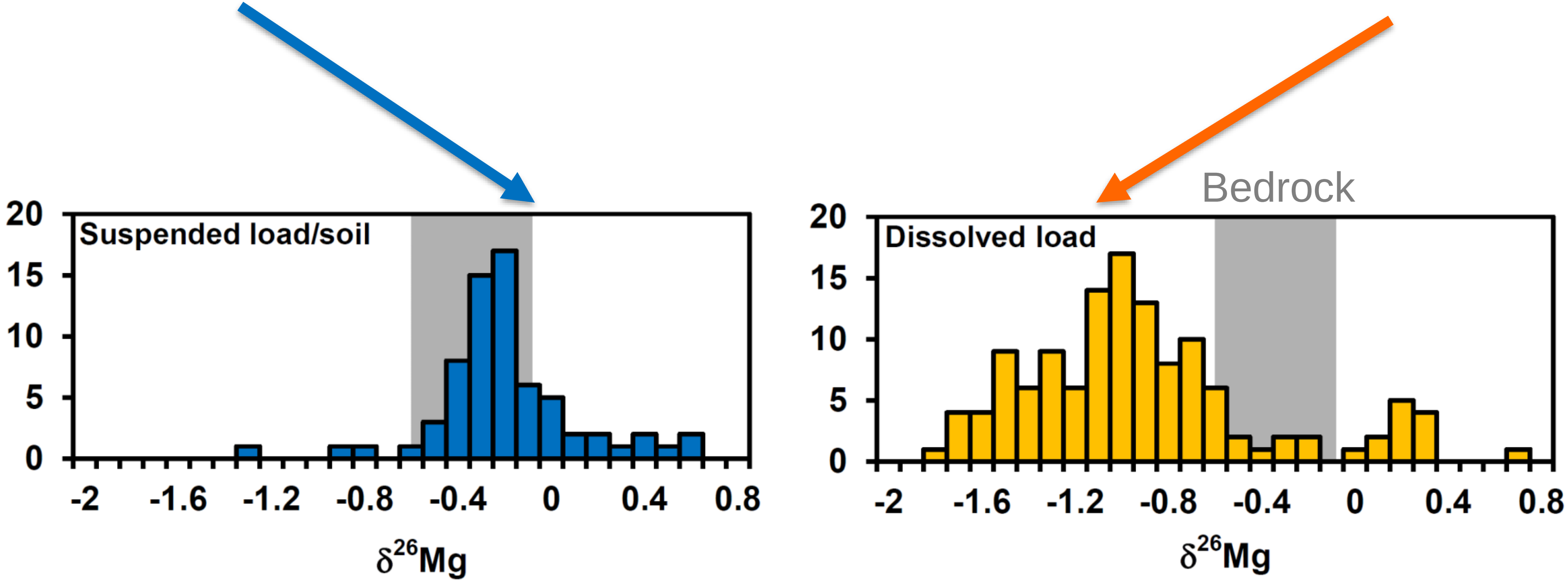




What drives Mg isotopic variation on surface?

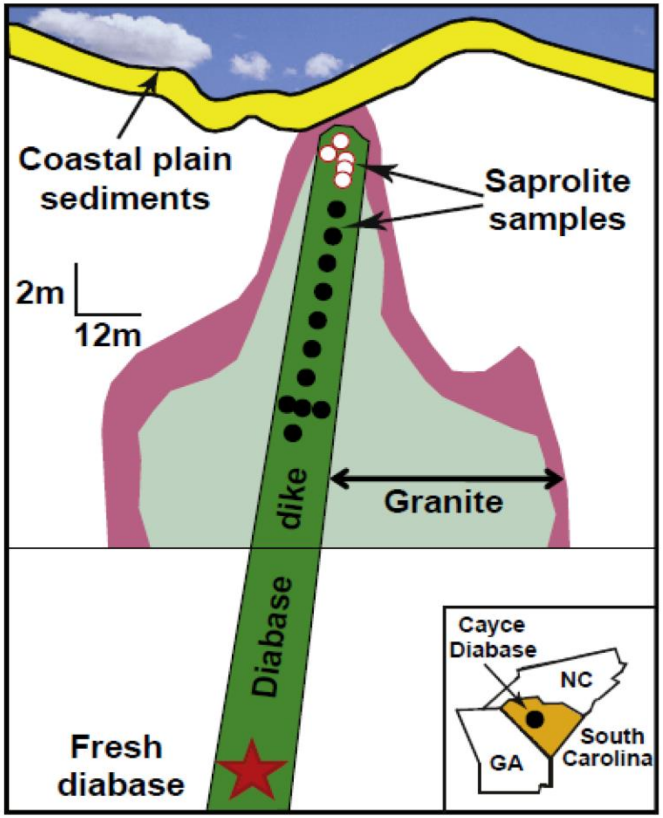
Chemical weathering?

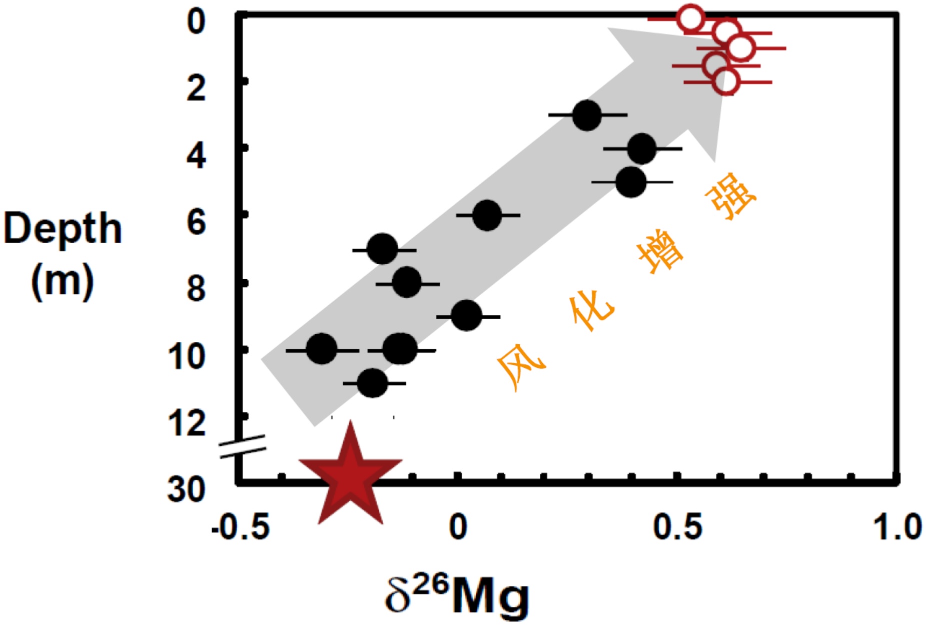
Soils/sediments are isotopically complementary to dissolved Mg in rivers



Teng RiMG 2017

Mg isotope fractionation during chemical weathering





Weathered residuals preferentially retain heavy Mg

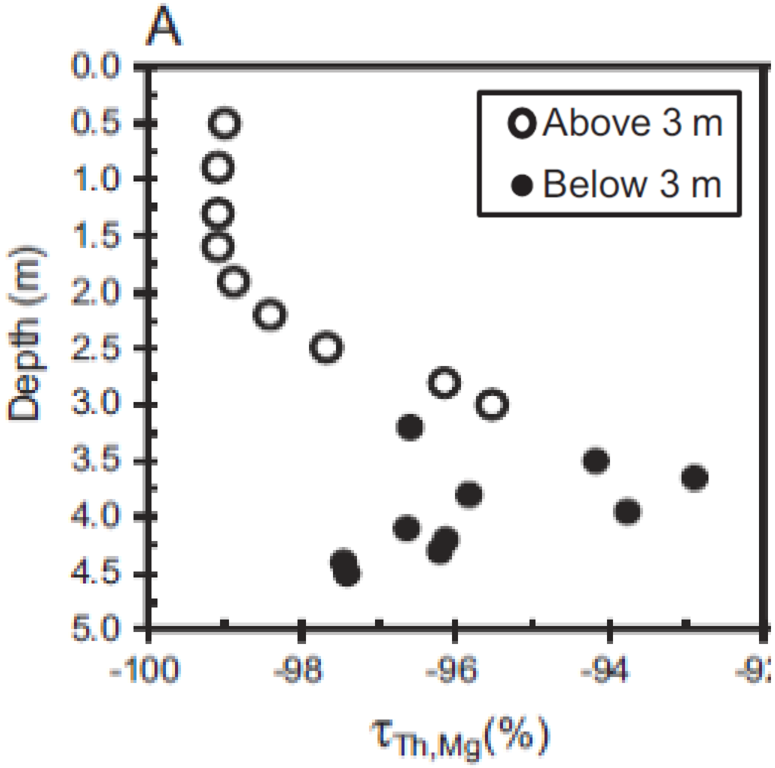
Releasing light Mg to the hydrosphere

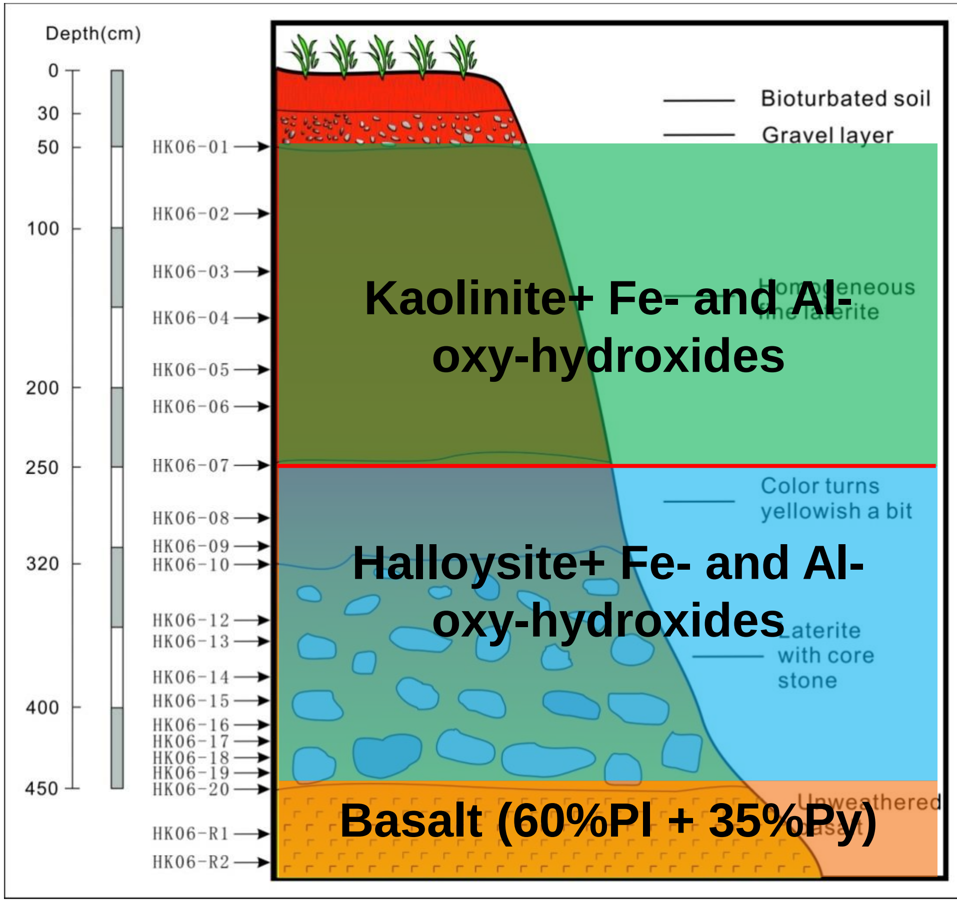
Teng et al. 2010 EPSL

Mg isotope fractionation during chemical weathering

- Extreme weathering
- >90% Mg was lost

Location: Hainan Island, China





Kaolinite+ Fe- and Al-oxy-hydroxides

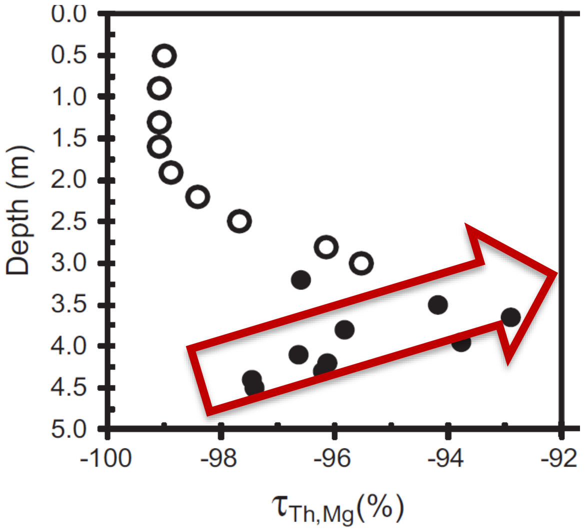
Halloysite+ Fe- and Al-oxy-hydroxides

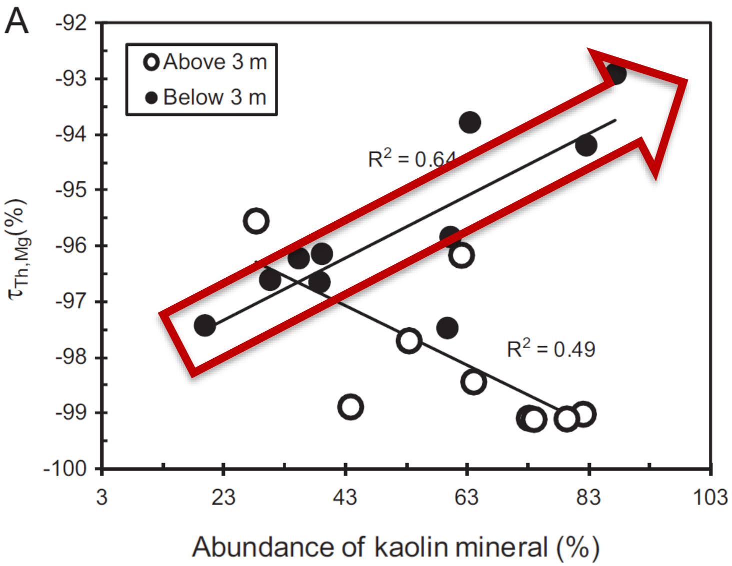
Basalt (60%Pl + 35%Py)

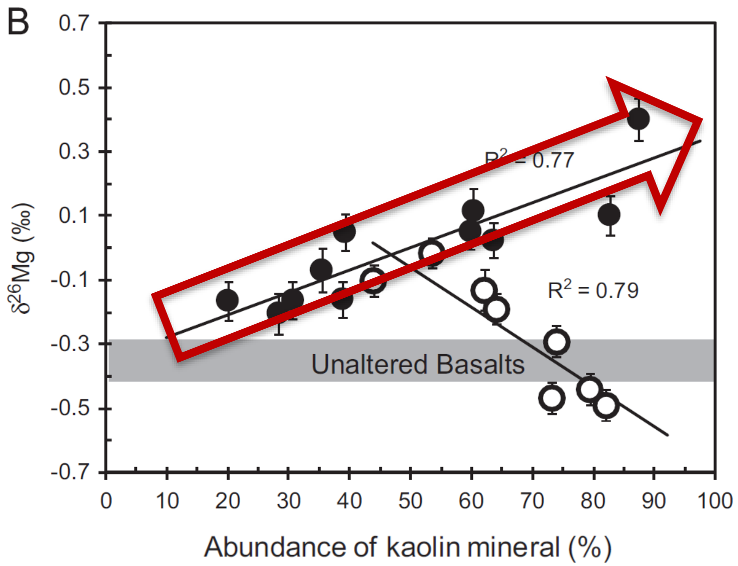
Huang et al. EPSL 2012

Mg isotope fractionation during chemical weathering

Adsorption of heavy Mg onto kaolinites

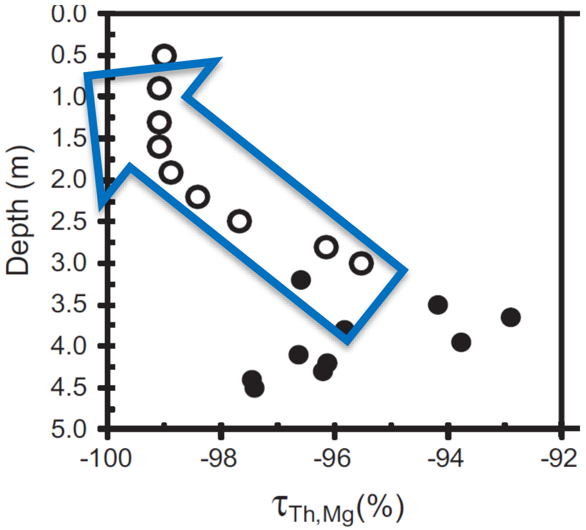






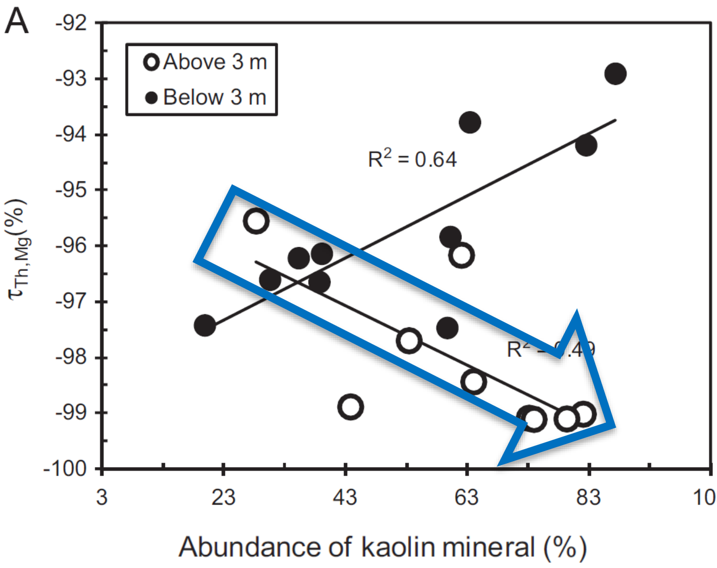
Huang et al. EPSL 2012

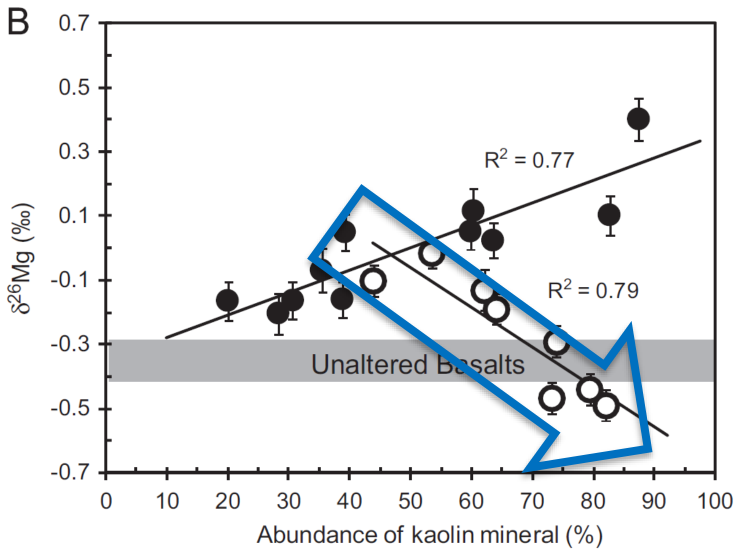
Mg isotope fractionation during chemical weathering



Adsorption of heavy Mg onto kaolinites

Desorption of heavy Mg via cation exchange



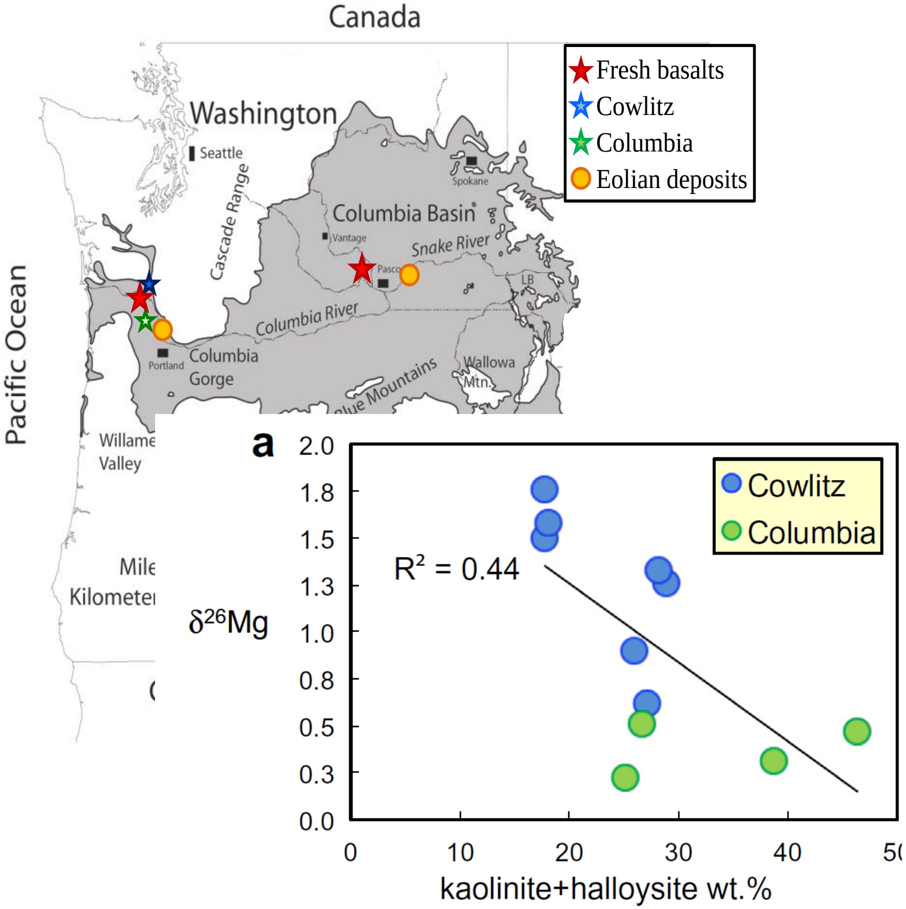


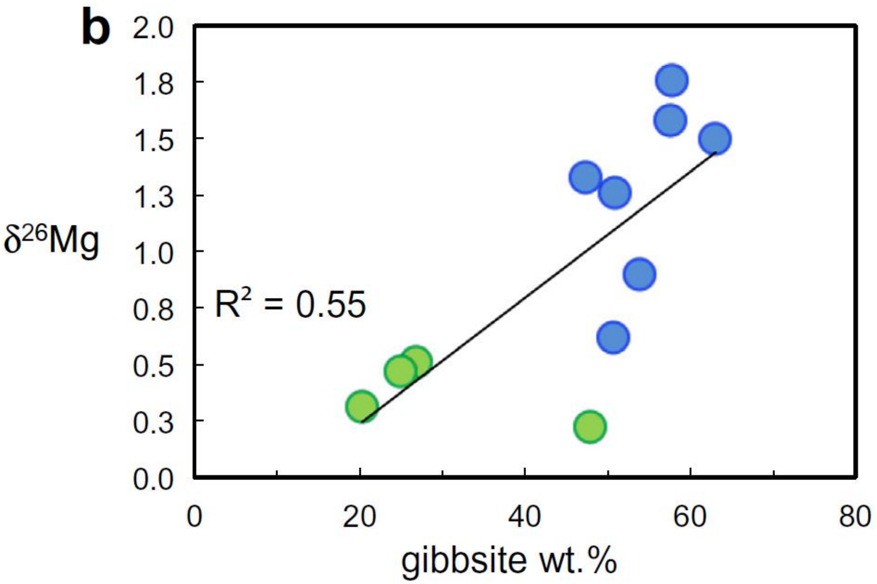
Huang et al. EPSL 2012

Mg isotope fractionation during chemical weathering

Bauxite cores from Columbia River Basalts

- δ^{26}Mg is mainly controlled by gibbsite, rather than kaolin minerals
- δ^{26}Mg in saprolite is sensitive to secondary mineralogy

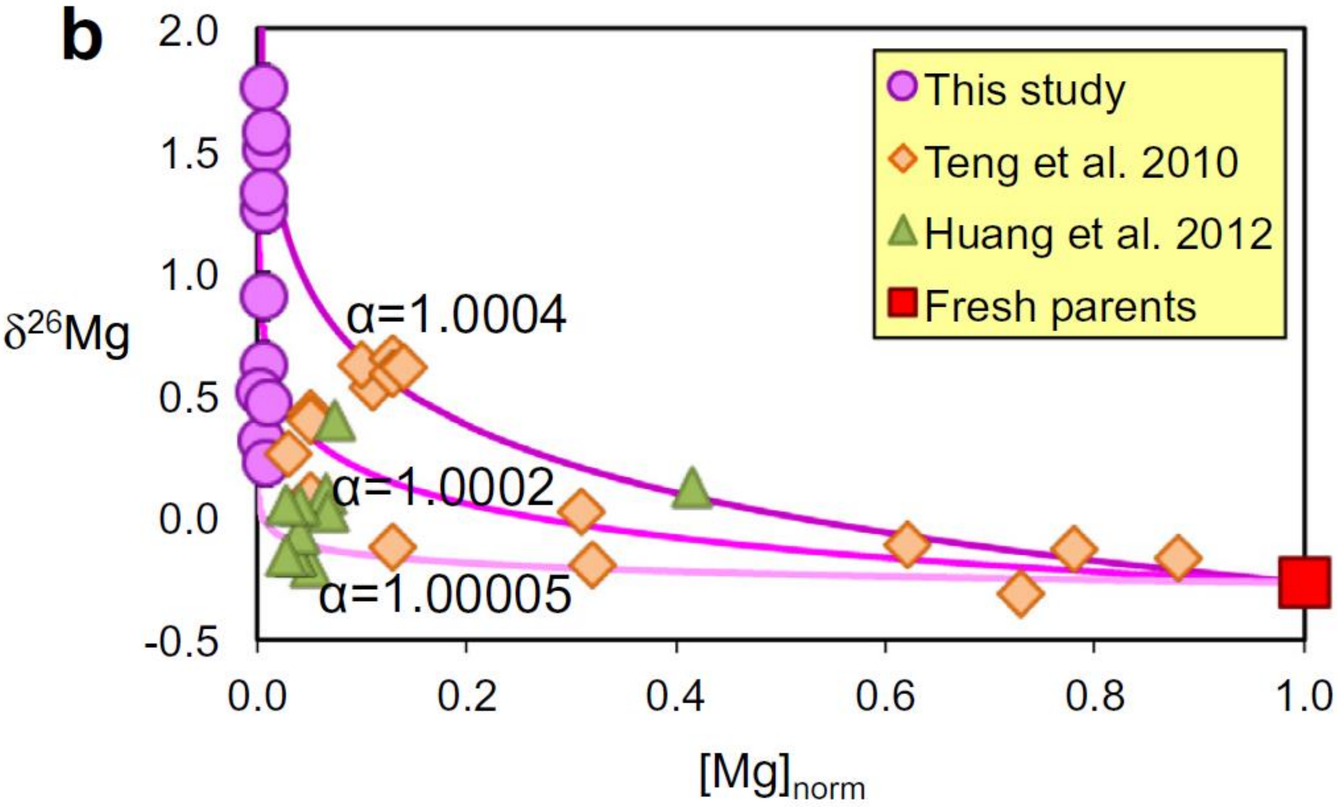




Liu et al. GCA 2014

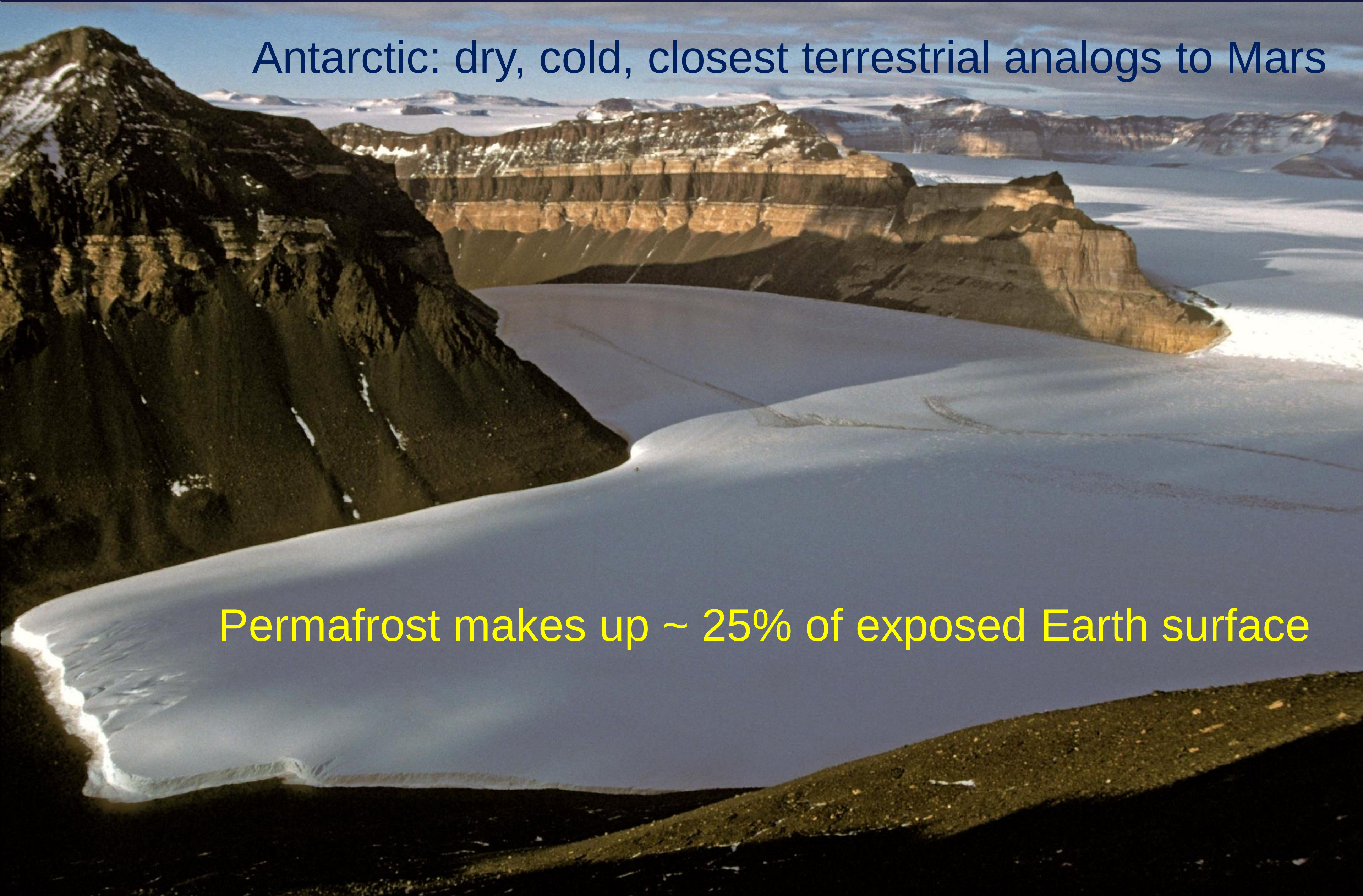
Mg isotope fractionation during chemical weathering

Weathered residuals are enriched in heavy Mg by 0.05 to 0.4‰



Liu et al. GCA 2014

Mg isotope fractionation in icy lands



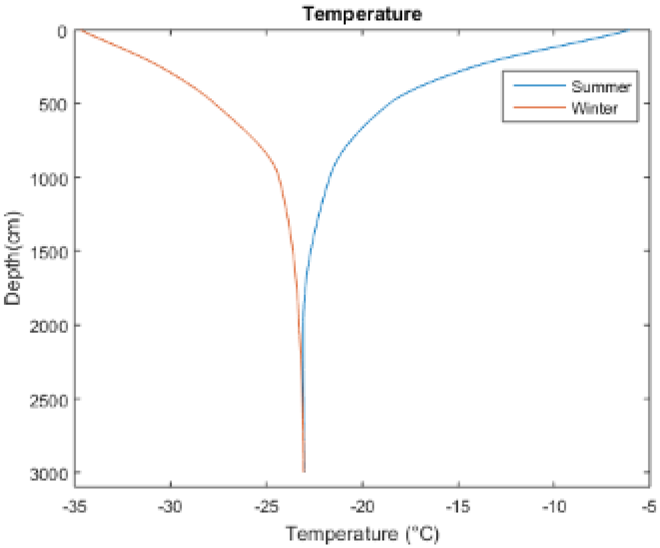
Antarctic: dry, cold, closest terrestrial analogs to Mars

Permafrost makes up ~ 25% of exposed Earth surface

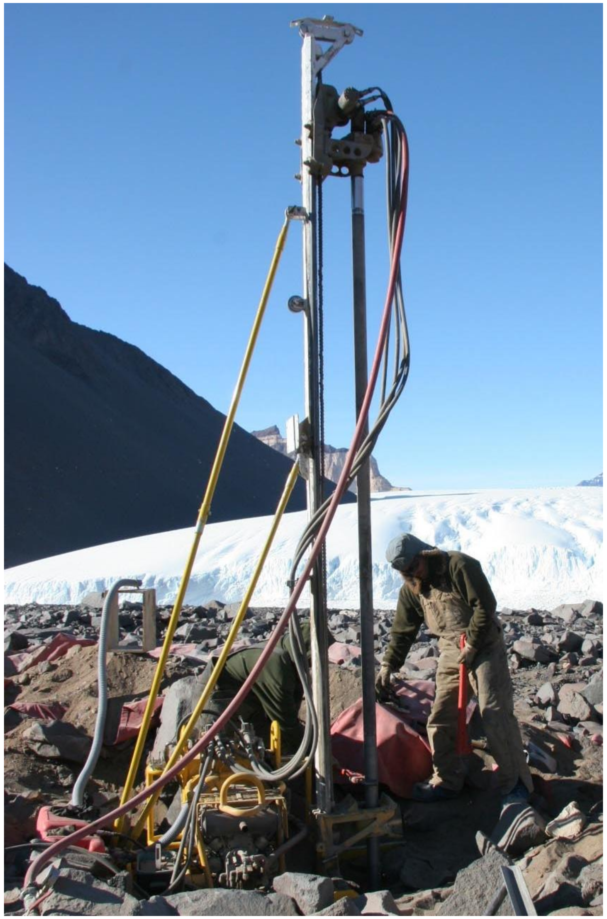
Mg isotope fractionation in icy lands

Permafrost is defined as ground that is continuously below 0 °C for 2 years

30-m core *ice-rich* permafrost core



Soils temperatures remain below freezing year round



Cuozzo et al. GCA 2020

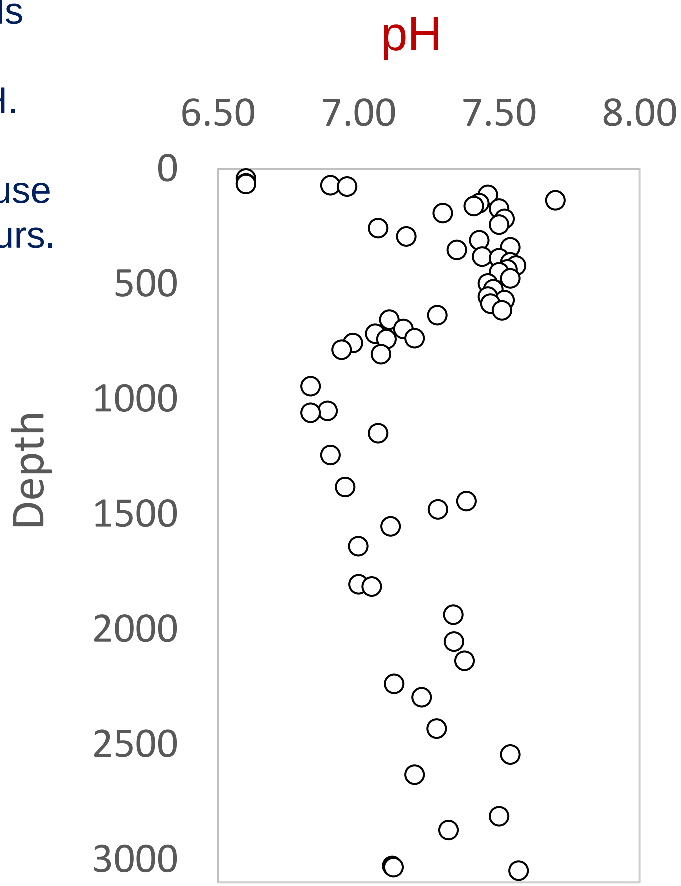
Evidence of chemical weathering

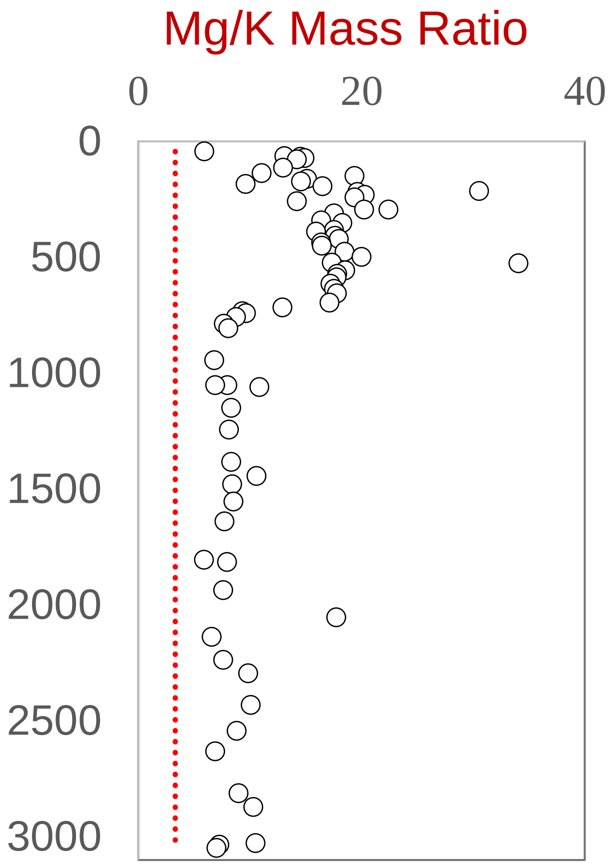
$$(Ca,Mg,Fe)SiO_{3(s)} + H_2O + 2H^+ \rightarrow \left(Ca^{2+}, Mg^{2+}, Fe^{2+}\right)_{(aq)} + H_4SiO_{4(aq)}$$

Elevated pH

Elevated Mg/K ratio

Weathering leads to increase in alkalinity and pH. This signal is preserved because no leaching occurs.



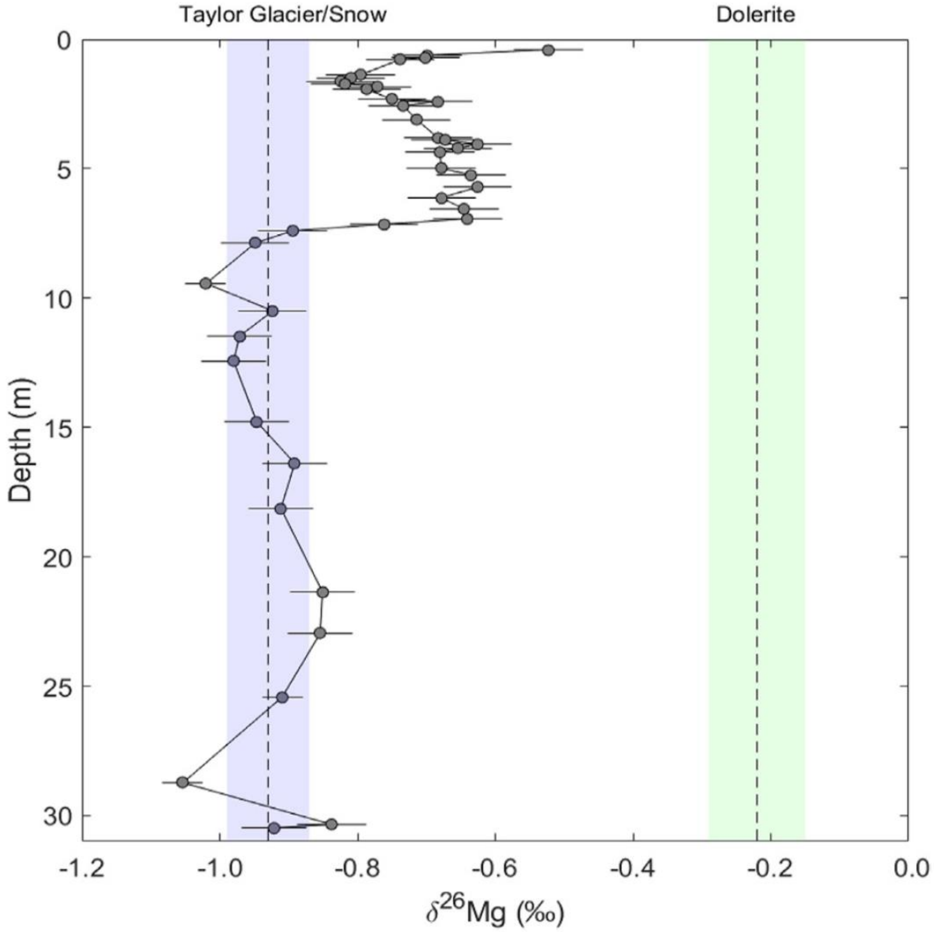


Cuozzo et al. GCA 2020

δ^{26}Mg evidence for chemical weathering

δ^{26}Mg in thawed permafrost ice suggest two Mg sources

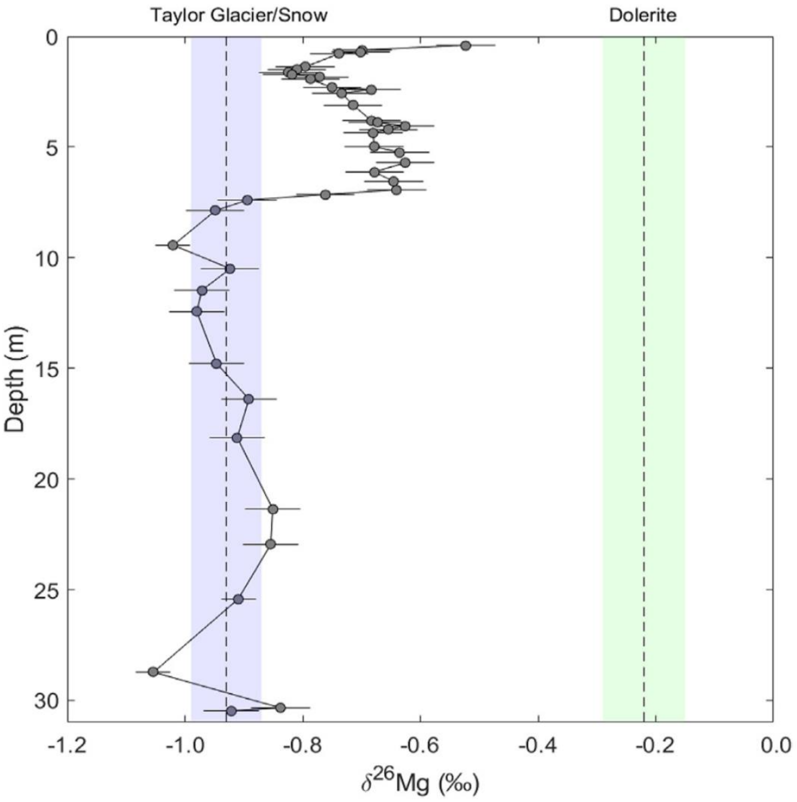
- local glacial ice (marine signature)
- dolerites clasts (silicate signature)

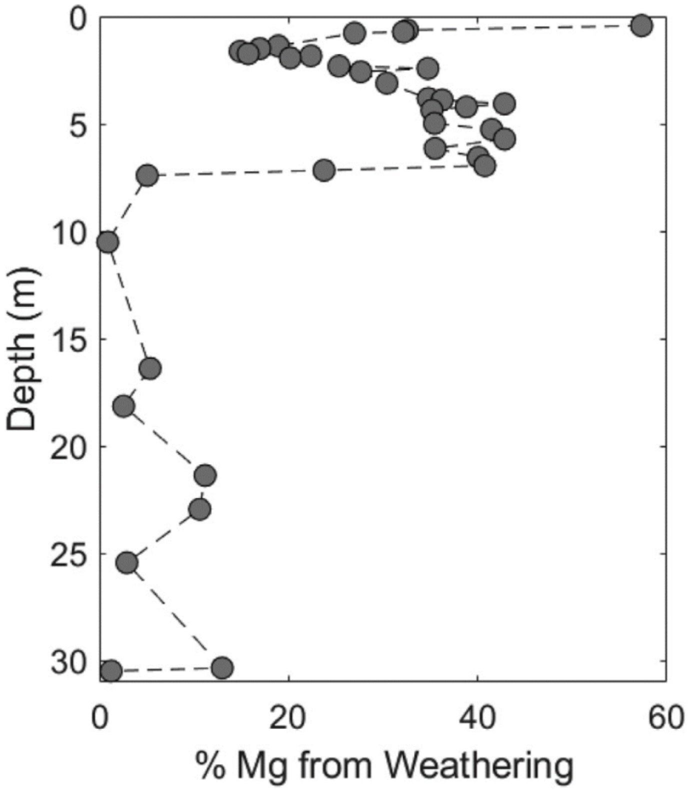


Cuozzo et al. GCA 2020

δ^{26}Mg evidence for chemical weathering

- Upper 7 m: average 40% of Mg is derived from dolerite weathering
- Lower 7-30 m: average 5% of Mg from dolerite weathering

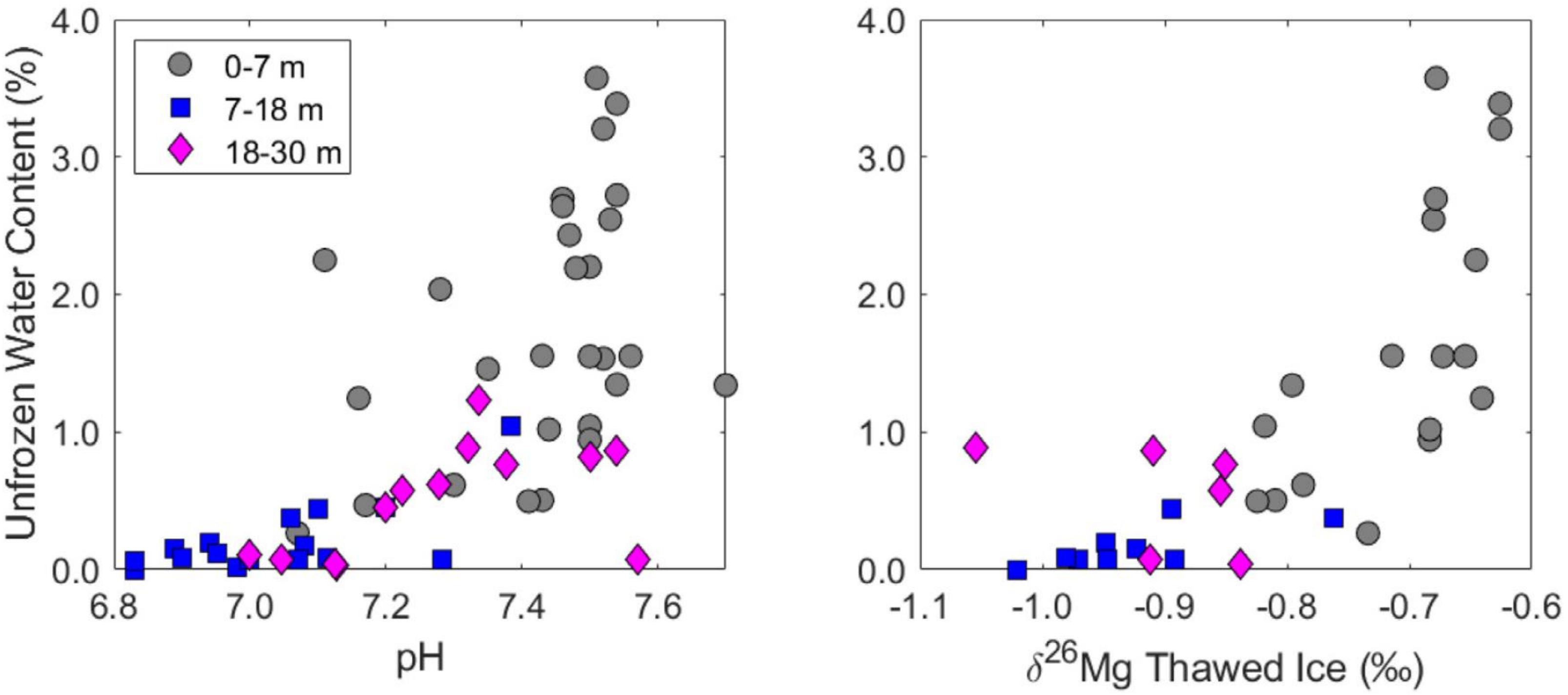




Cuozzo et al. GCA 2020

Controls on chemical weathering

- Unfrozen water is the major control on the degree of weathering
- Salts lower the freezing point of water, providing aqueous environment



Cuozzo et al. GCA 2020

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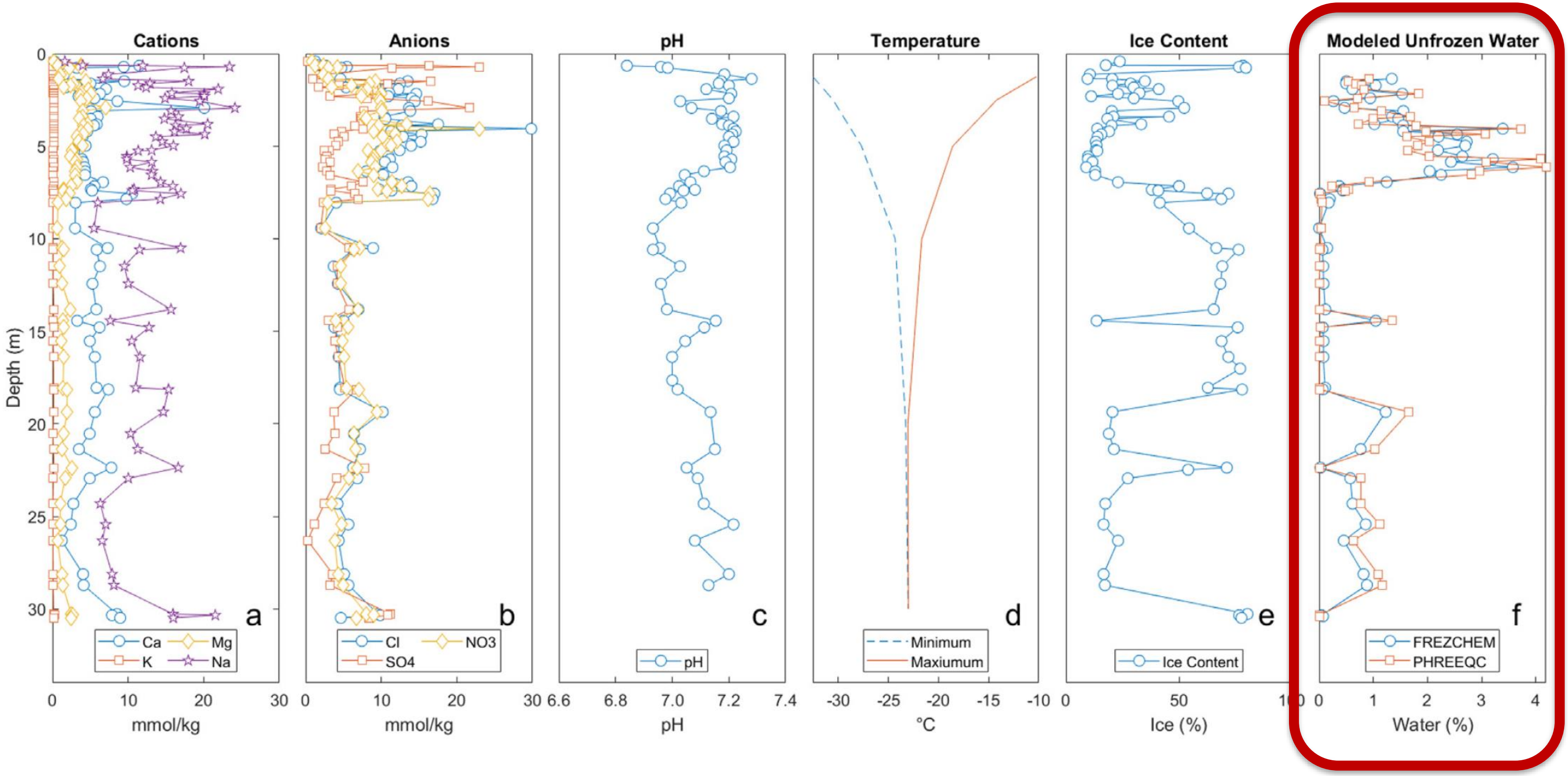


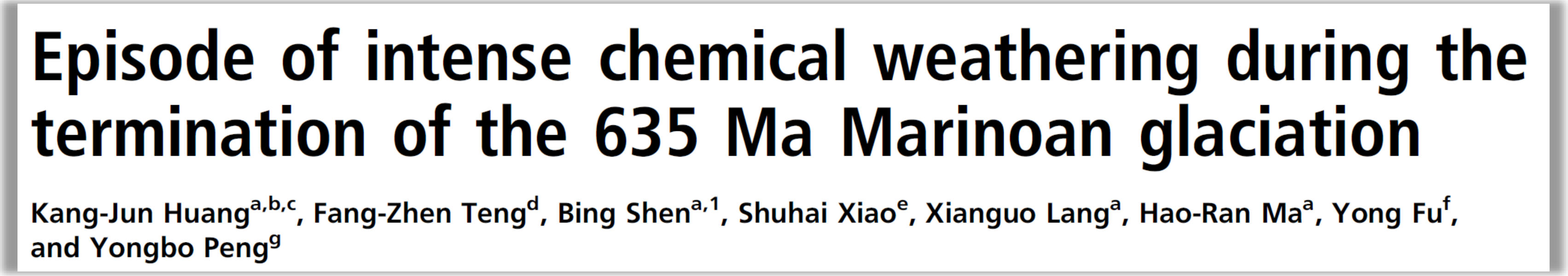
Cuozzo et al. GCA 2020

Summary

1. Significant chemical weathering occurs not only in wet and tropical regions but also in dry and cold regions
2. Chemical weathering produces large Mg isotope fractionation
3. Secondary minerals tend to retain heavy Mg in their structure
4. Exchangeable Mg affects δ^{26}Mg in secondary minerals
5. Light Mg is released to rivers that end up in the oceans
6. Other factors affecting Mg isotope fractionation during weathering:
    1) Primary mineral dissolution (e.g., Wimpenny et al. GCA 2010)
    2) Preferential dissolution of minerals with distinct δ^{26}Mg (Ryu et al. GCA 2011)
    3) Various Mg pools in soils and sources for exchangeable Mg (e.g, Opfergelt et al. EPSL 2012; Pogge von Strandmann et al. EPSL 2012)
    4) Biological factors (e.g., Brewer et al. Geobiology 2019)

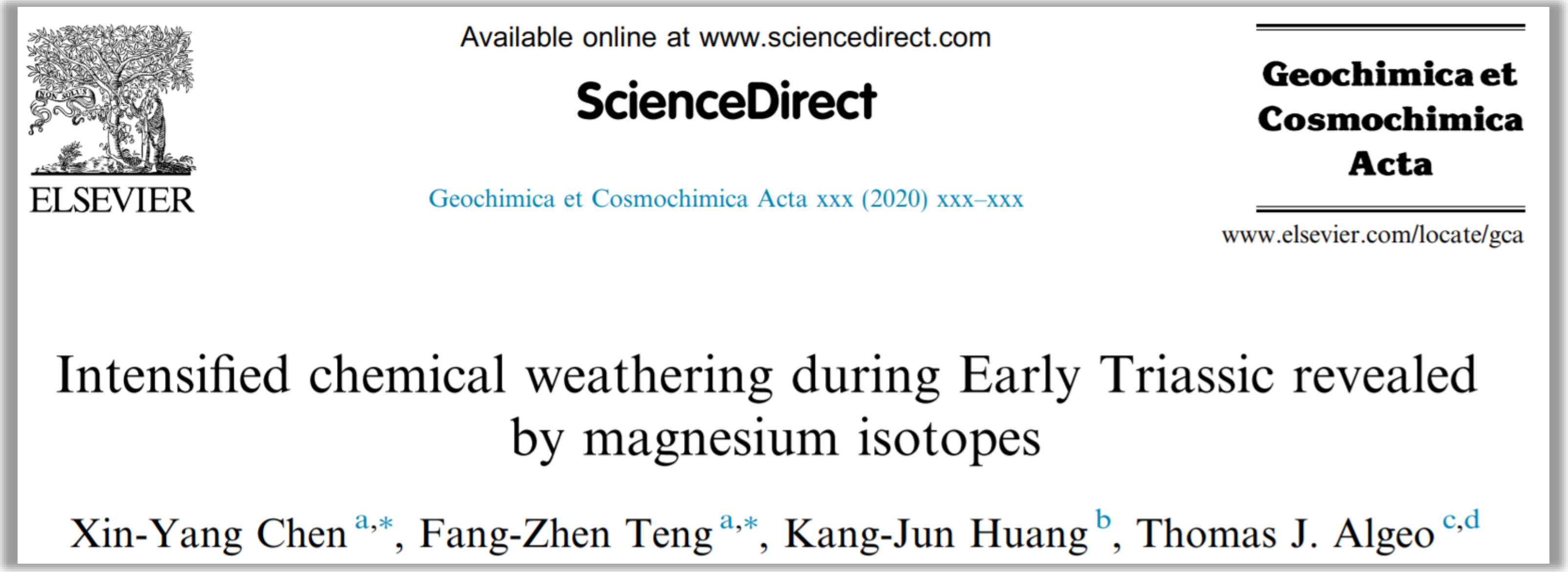
Applications

1. Mg isotopes can be used as a proxy for chemical weathering during geologic past



Episode of intense chemical weathering during the termination of the 635 Ma Marinoan glaciation

Kang-Jun Huang[a,b,c], Fang-Zhen Teng[d], Bing Shen[a,1], Shuhai Xiao[e], Xianguo Lang[a], Hao-Ran Ma[a], Yong Fu[f], and Yongbo Peng[g]



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Geochimica et Cosmochimica Acta xxx (2020) xxx–xxx

Geochimica et Cosmochimica Acta

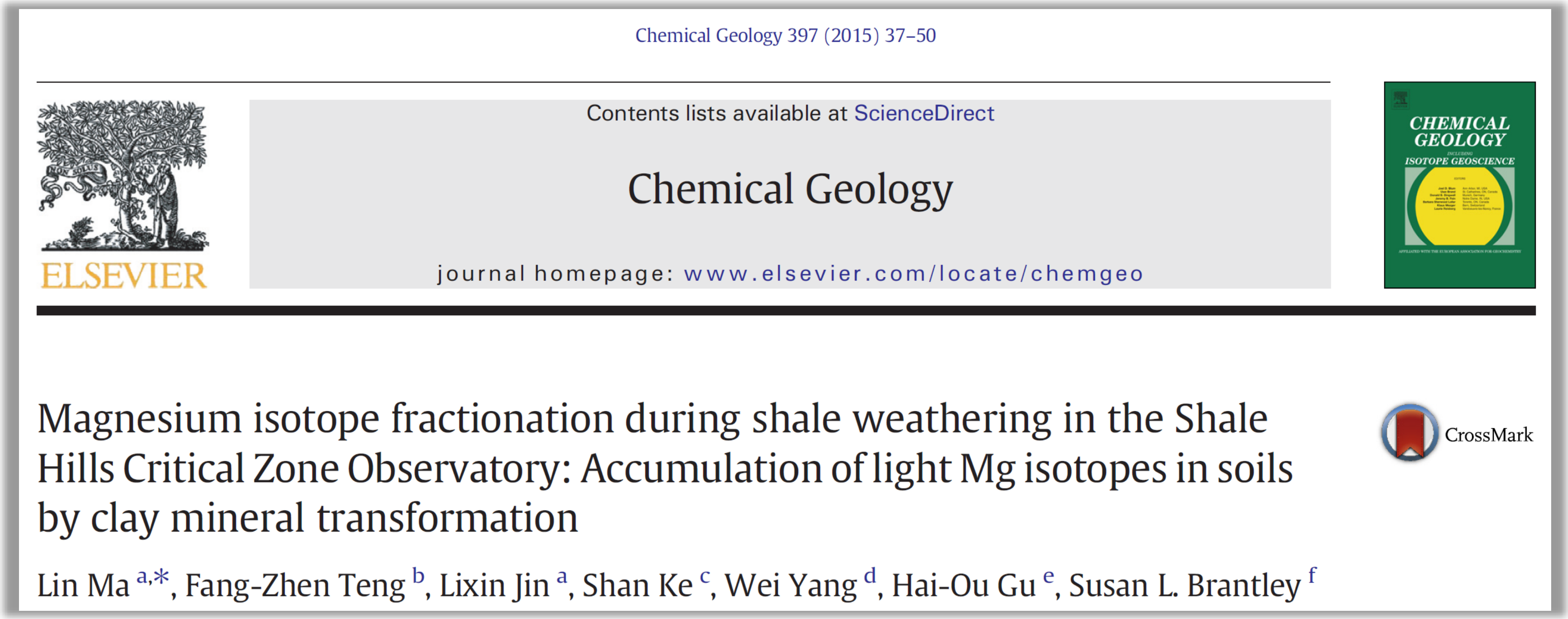
www.elsevier.com/locate/gca

Intensified chemical weathering during Early Triassic revealed by magnesium isotopes

Xin-Yang Chen[a,*], Fang-Zhen Teng[a,*], Kang-Jun Huang[b], Thomas J. Algeo[c,d]

Applications

2. Mg isotopes can be used to decipher soil processes



Chemical Geology 397 (2015) 37–50

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Chemical Geology

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

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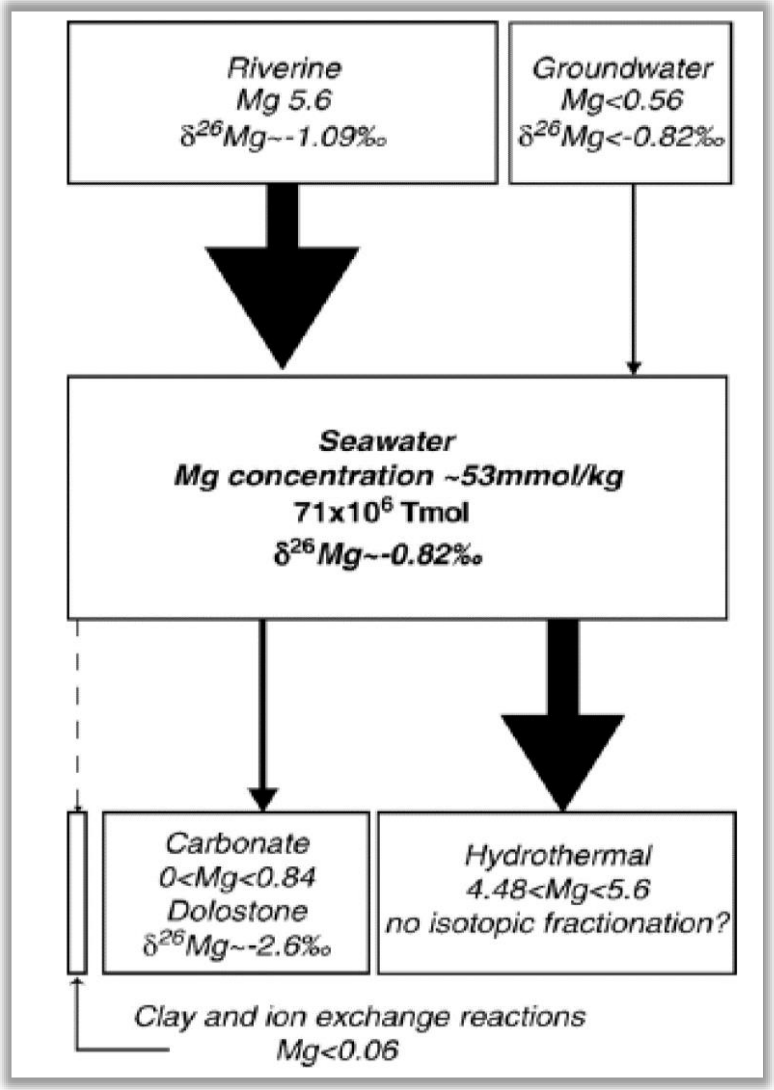
Magnesium isotope fractionation during shale weathering in the Shale Hills Critical Zone Observatory: Accumulation of light Mg isotopes in soils by clay mineral transformation

Lin Ma [a,*], Fang-Zhen Teng [b], Lixin Jin [a], Shan Ke [c], Wei Yang [d], Hai-Ou Gu [e], Susan L. Brantley [f]

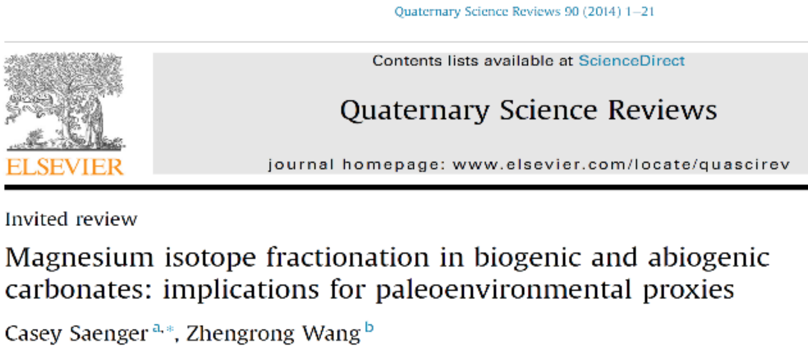
Applications

3. Quantifying long-term marine Mg cycling



Tipper et al. EPSL 2006

Applications in carbonate-related studies



Quaternary Science Reviews 90 (2014) 1–21

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Invited review

Magnesium isotope fractionation in biogenic and abiogenic carbonates: implications for paleoenvironmental proxies

Casey Saenger[a,*], Zhengrong Wang[b]

Earth and Planetary Science Letters 404 (2014) 22–32

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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Neoproterozoic cap-dolostone deposition in stratified glacial meltwater plume

CrossMark

Chao Liu[a,*], Zhengrong Wang[a,*], Timothy D. Raub[b], Francis A. Macdonald[c], David A.D. Evans[a]

Earth and Planetary Science Letters 545 (2020) 116403

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

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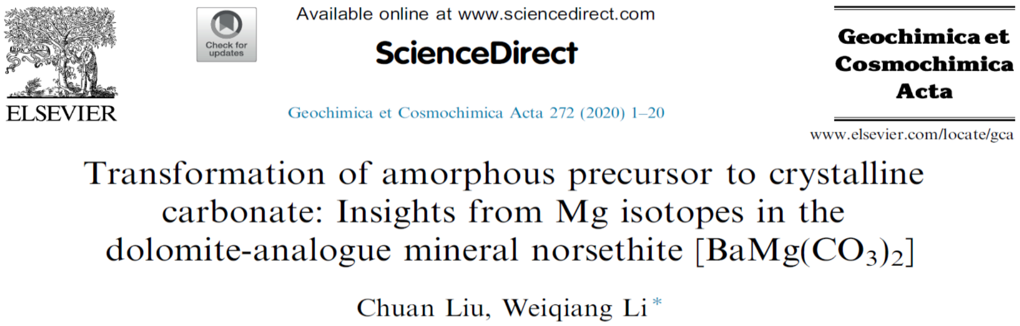
Towards understanding the origin of massive dolostones

Check for updates

Meng Ning[a], Xianguo Lang[b], Kangjun Huang[c], Chao Li[d], Tianzheng Huang[a], Honglin Yuan[c], Chaochao Xing[a], Runyu Yang[a], Bing Shen[a,*]



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Geochimica et Cosmochimica Acta 272 (2020) 1–20

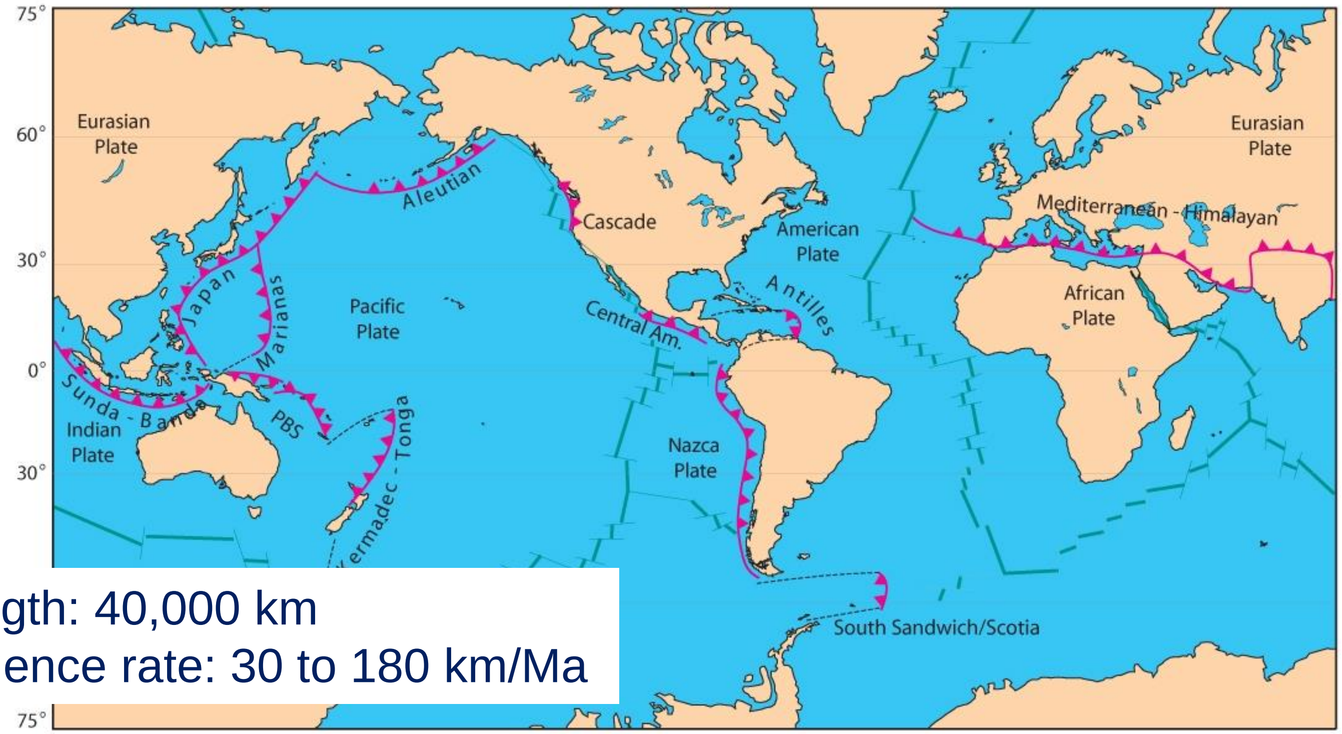
Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Transformation of amorphous precursor to crystalline carbonate: Insights from Mg isotopes in the dolomite-analogue mineral norsethite [$BaMg(CO_3)_2$]

Chuan Liu, Weiqiang Li[*]

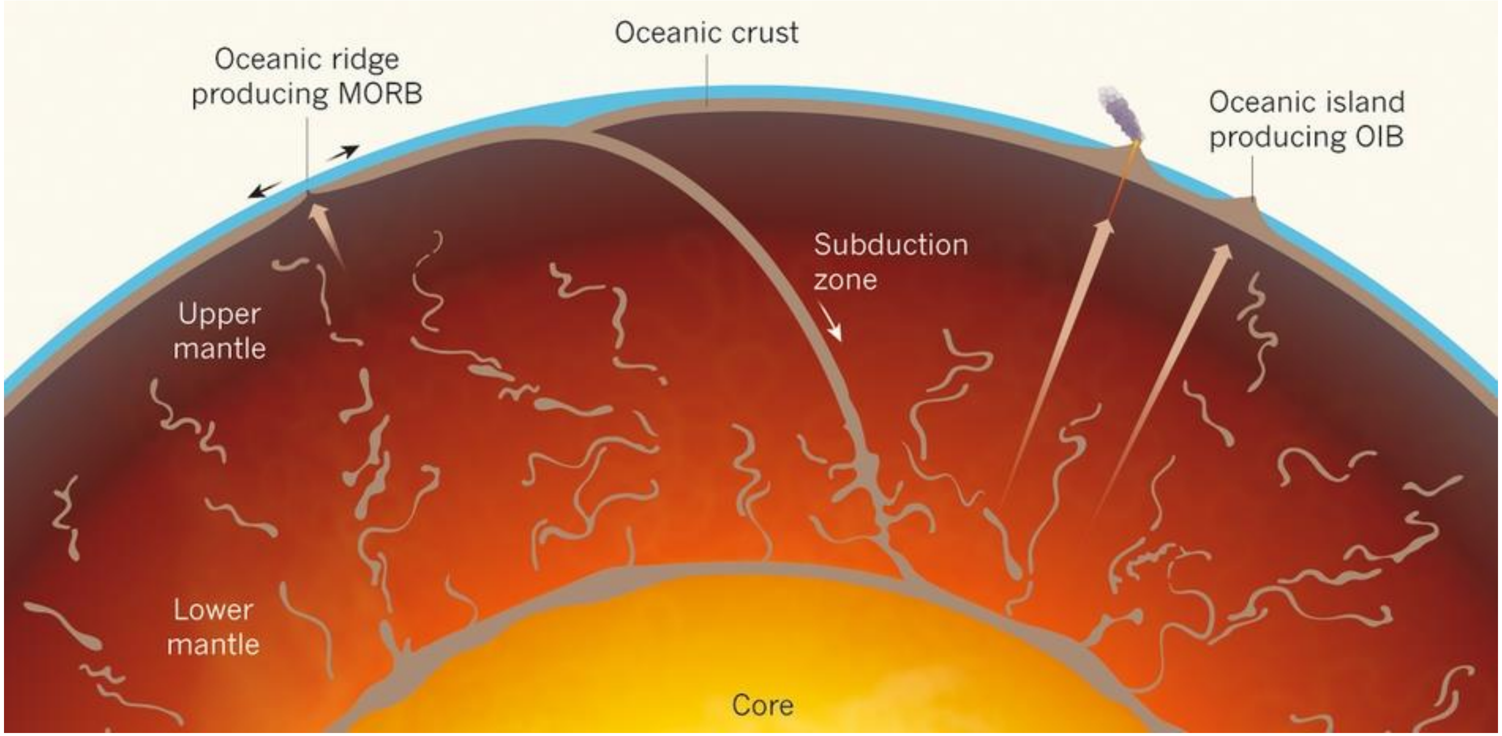
How does subduction recycling lead to Mg isotopic variation in the mantle?



Total length: 40,000 km
Convergence rate: 30 to 180 km/Ma

Winter, J. Introduction to Igneous & Metamorphic Petrology

How does subduction recycling lead to Mg isotopic variation in the mantle?

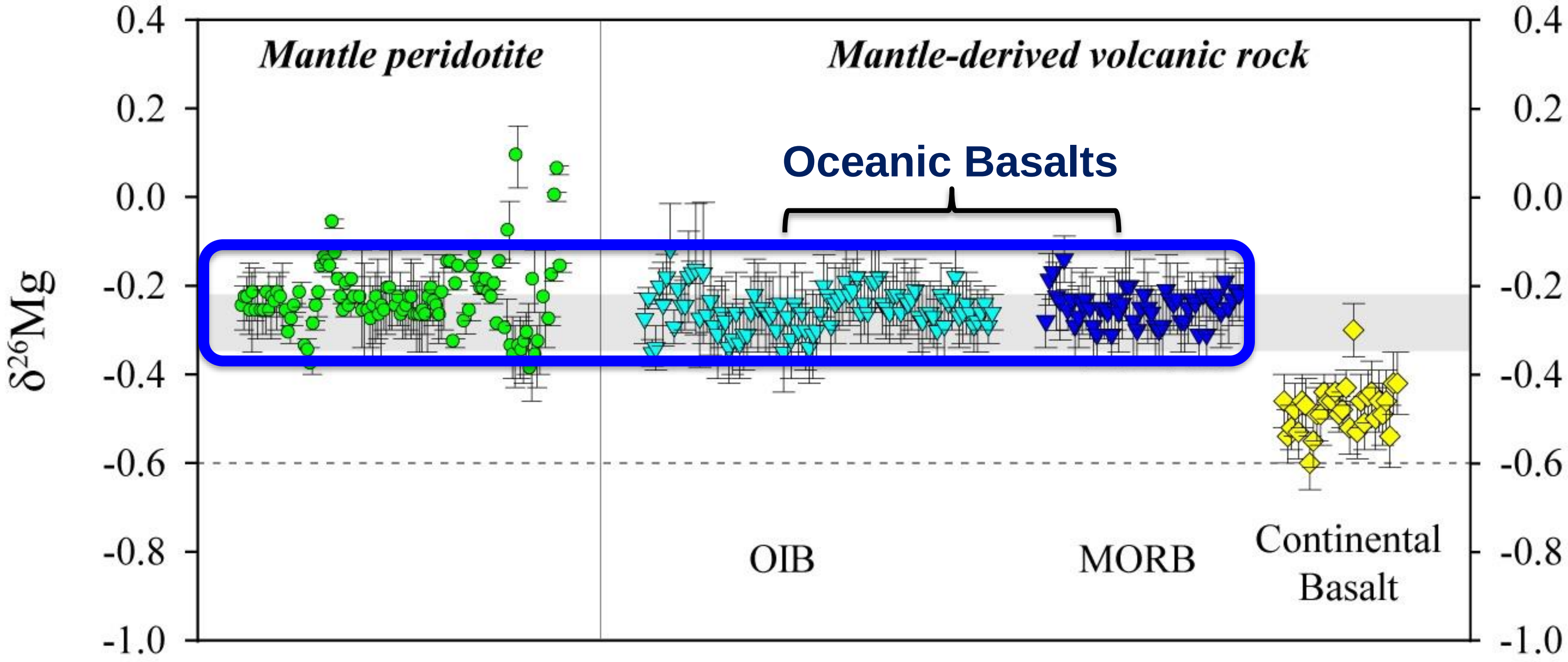


Woodhead Nature 2015

How does subduction recycling lead to Mg isotopic variation in the mantle?

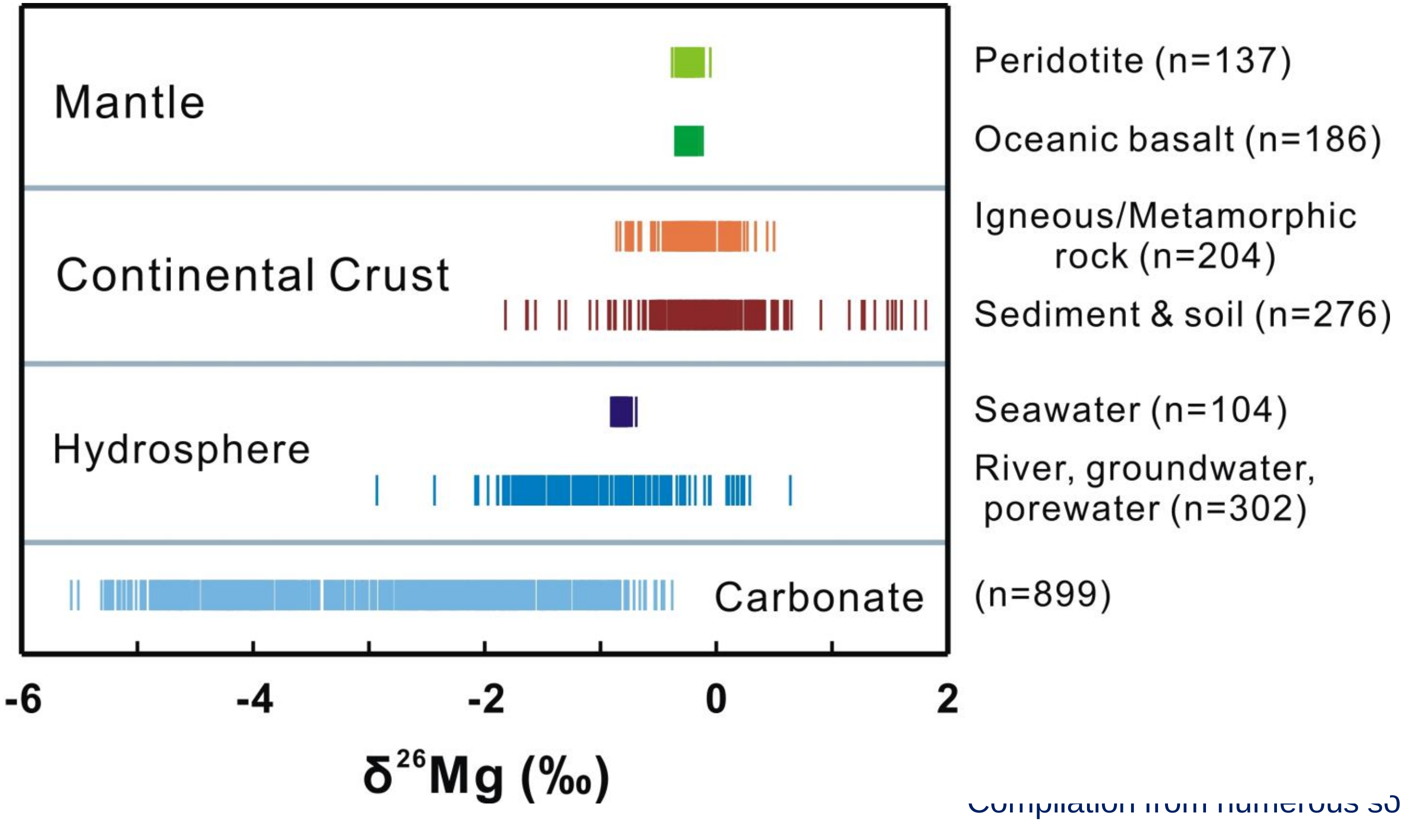
Direct mantle sample

Partial melting products of the mantle



Compilation from numerous sources

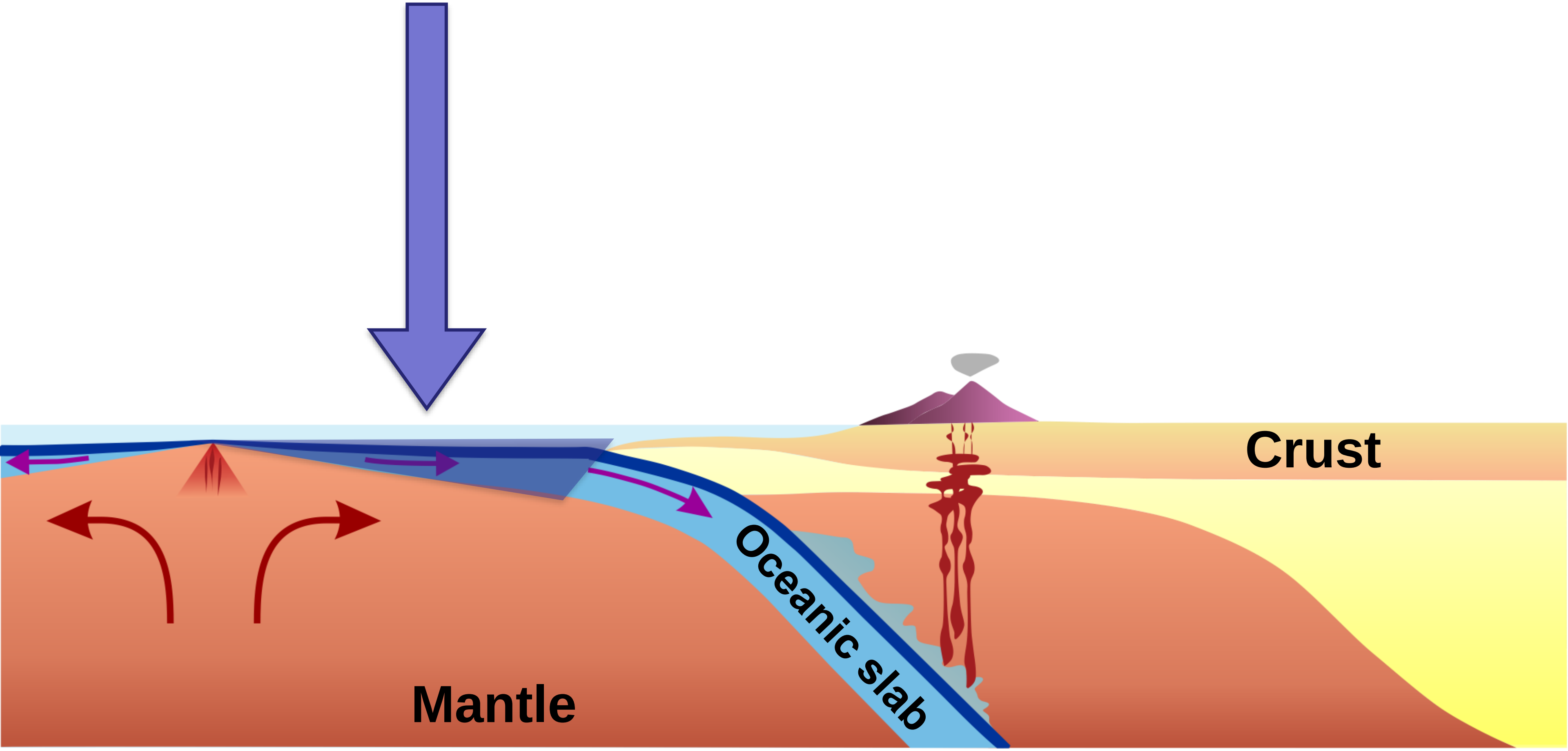
How does subduction recycling lead to Mg isotopic variation in the mantle?



Compilation from numerous sources

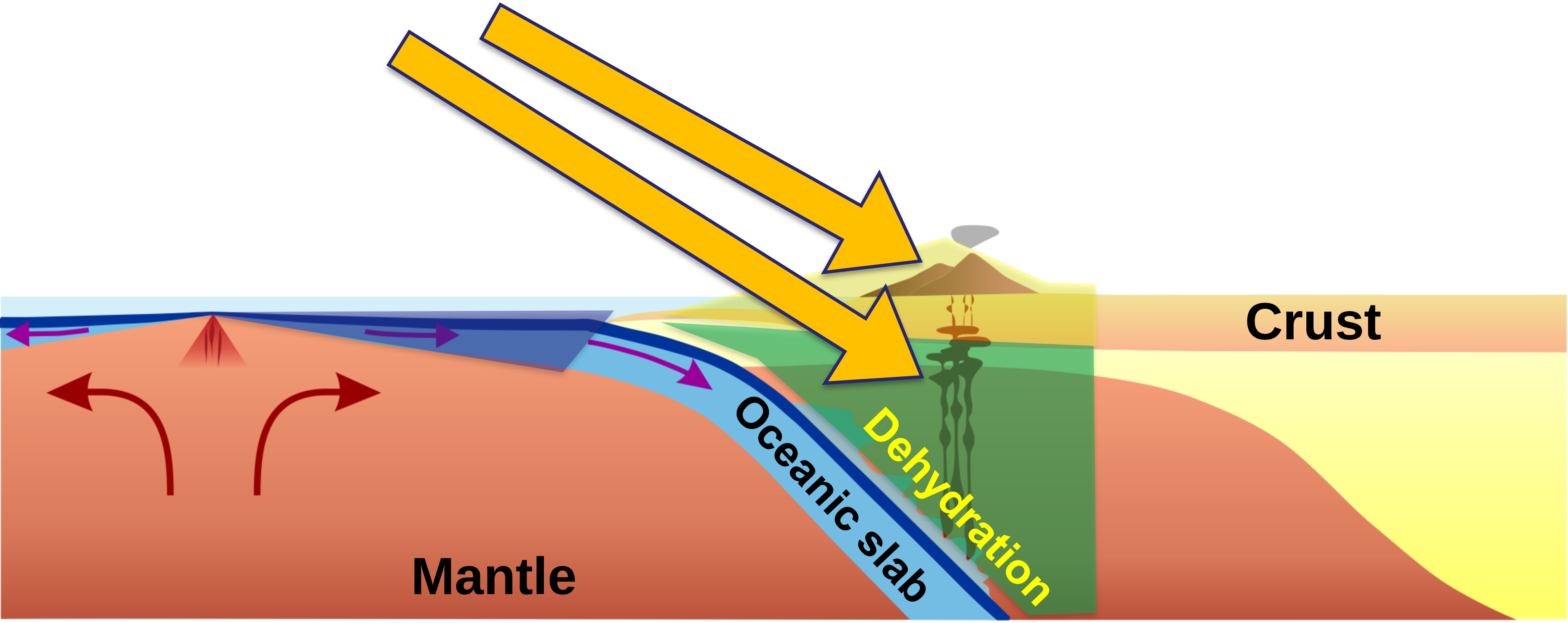
Tracing subduction recycling with Mg isotopes

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



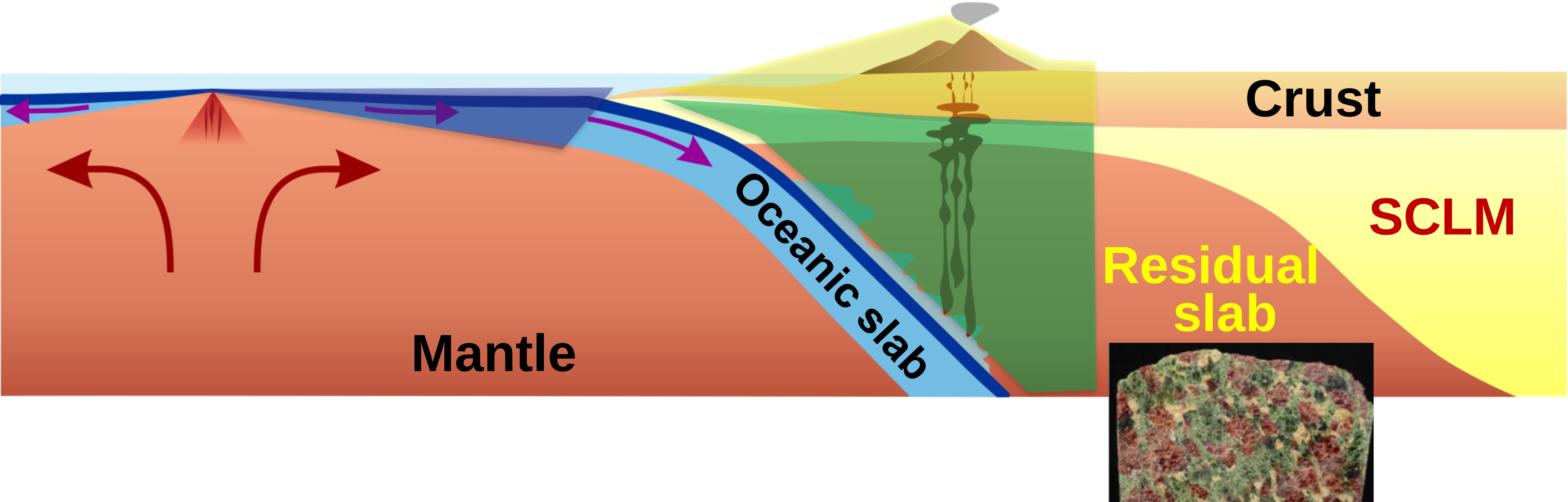
Tracing subduction recycling with Mg isotopes

1. What processes control the compositional variation in subducting slab?
2. How does slab signature transfer to mantle wedge and arc magmas?

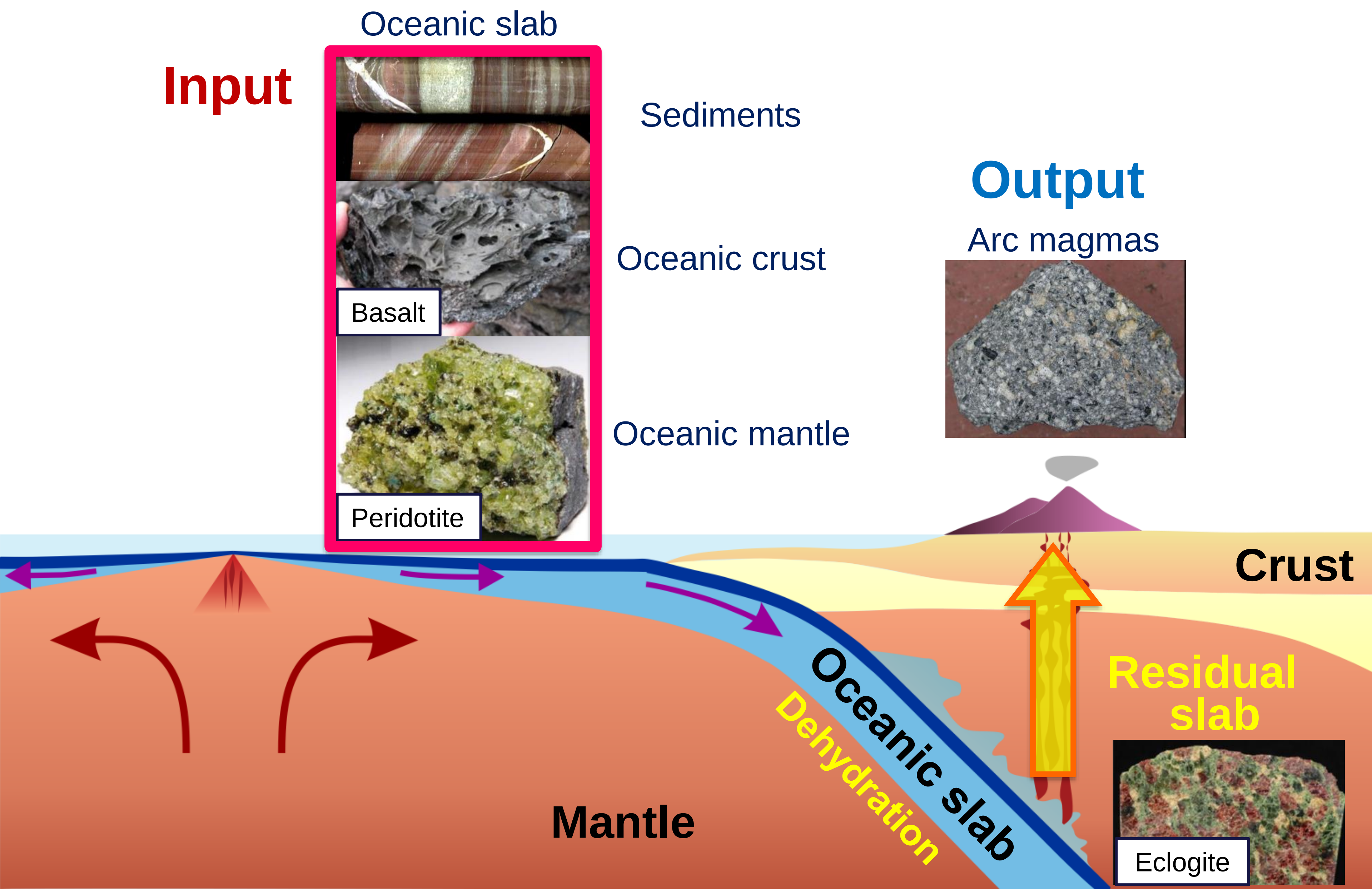


Tracing subduction recycling with Mg isotopes

1. What processes control the compositional variation in subducting slab?
2. How does slab signature transfer to mantle wedge and arc magmas?
3. How do subducted slabs contribute to mantle heterogeneity?



Subduction zone factory



Input

Oceanic slab

Sediments

Oceanic crust

Basalt

Oceanic mantle

Peridotite

Output

Arc magmas

Crust

Residual slab

Oceanic slab

Dehydration

Mantle

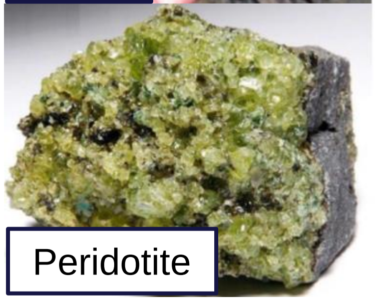
Eclogite

δ^{26}Mg variation in subducting slabs

Formation of oceanic slab

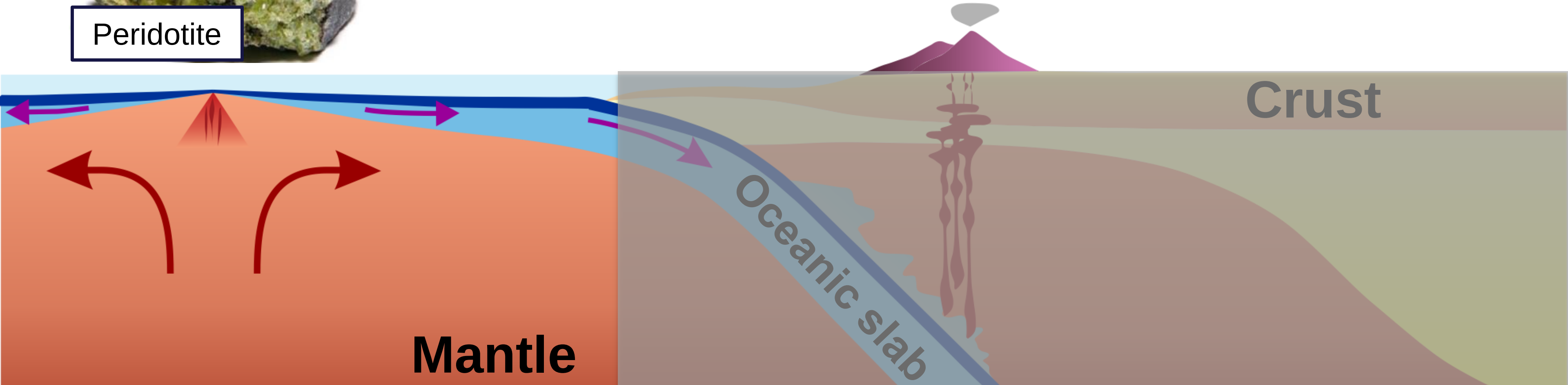
Oceanic crust

Melting product



Oceanic mantle

Melting residual

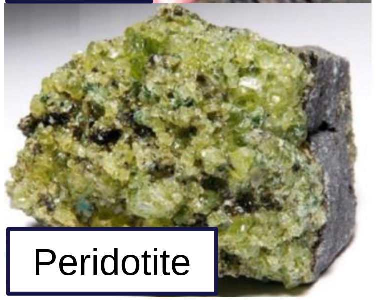


Fresh oceanic crust and oceanic mantle

Both fresh MORB and peridotite have homogeneous δ^{26}Mg

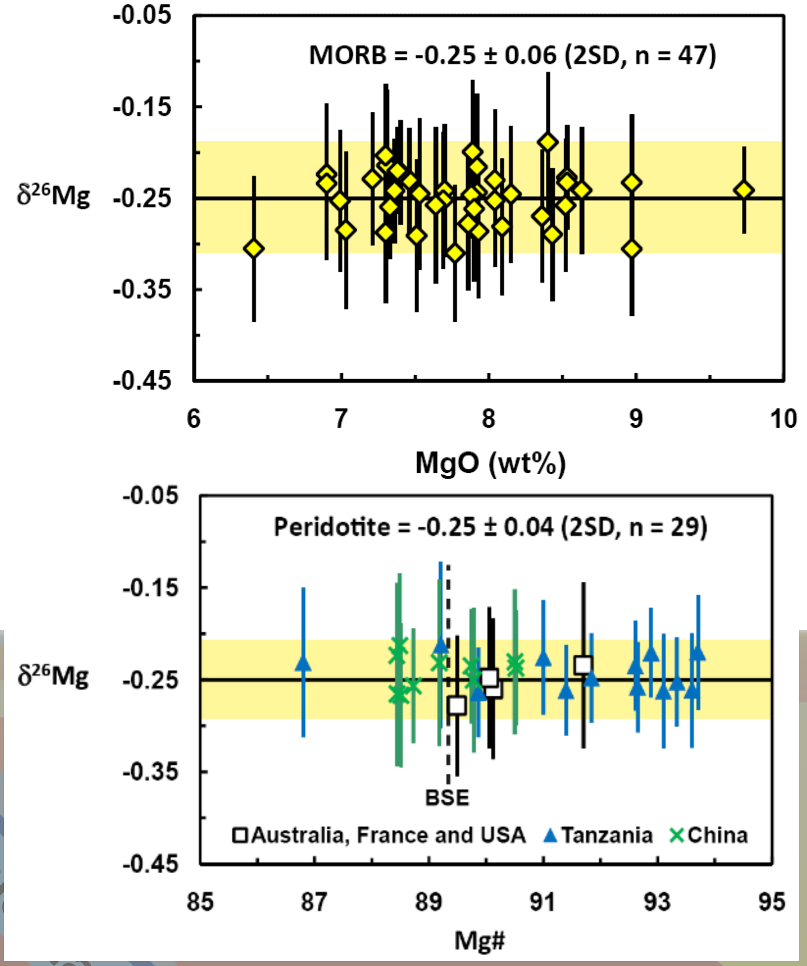
Oceanic crust

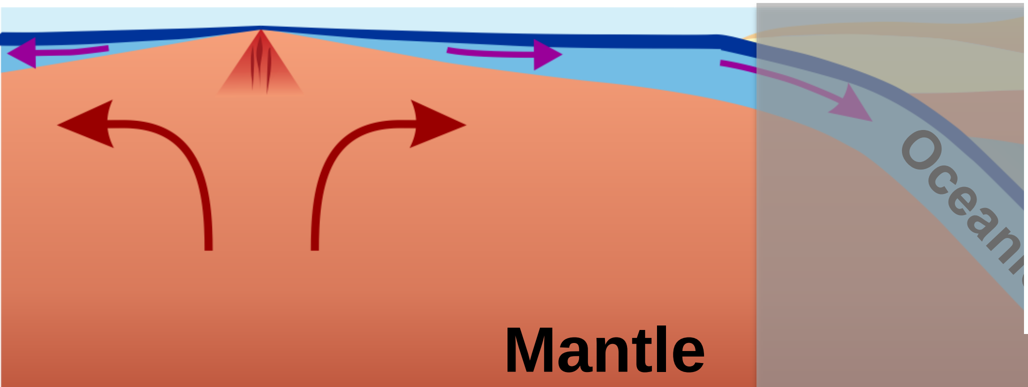
Melting product



Oceanic mantle

Melting residual



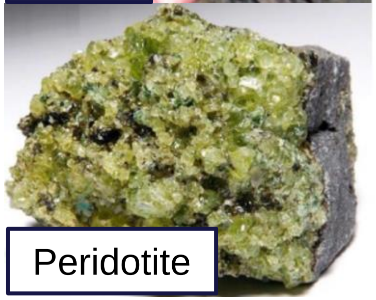


Teng et al. 2010 GCA

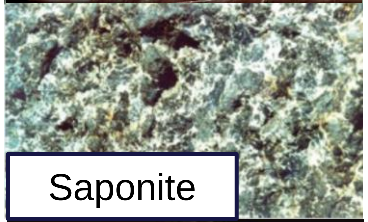
Alteration of oceanic slabs

Formation of oceanic slab


Basalt

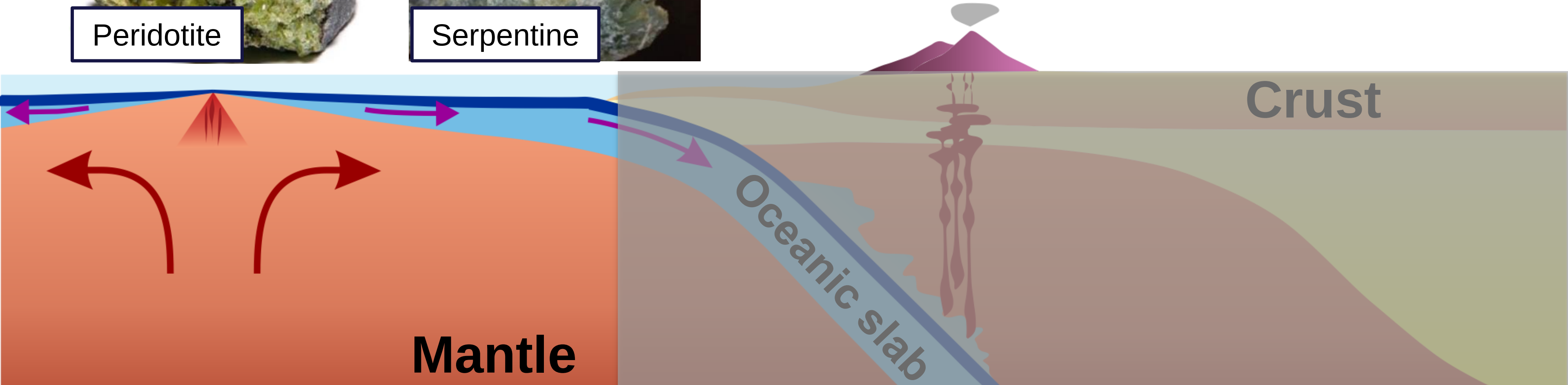

Peridotite


Sediments


Saponite


Serpentine

Alteration of oceanic slab

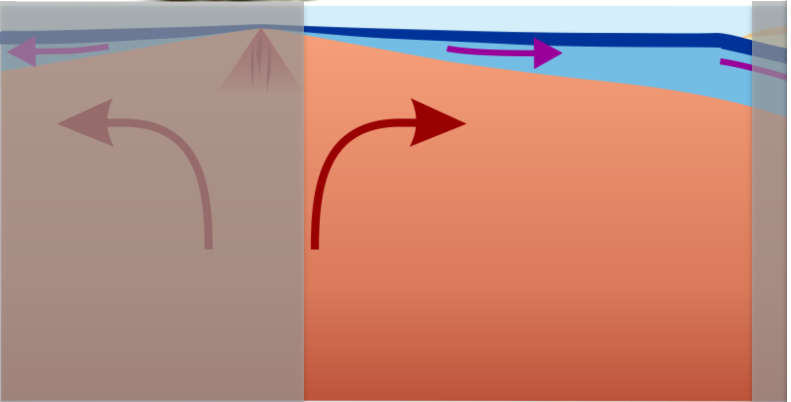


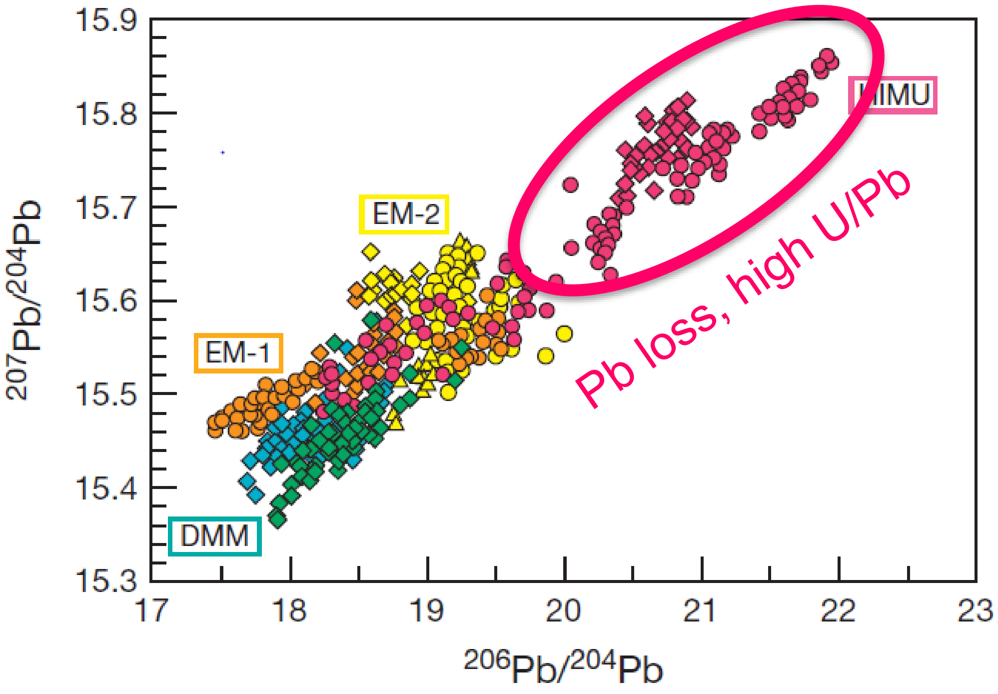
Alteration of oceanic crust

Primary mineral dissolution and secondary (hydrous) mineral formation

AOC is an important source for enriched Pb isotopes in mantle

Alteration of oceanic slab





Hofmann TOG 2014

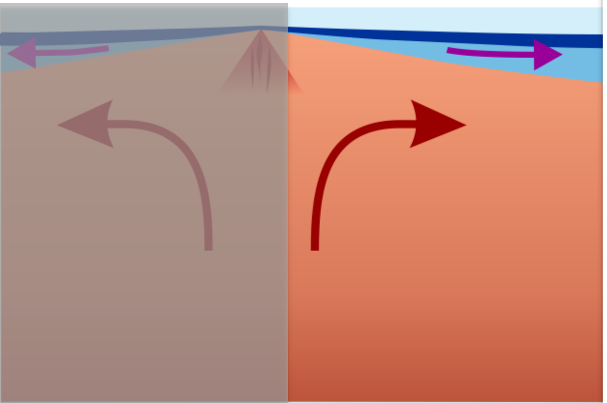
AOC from western Pacific

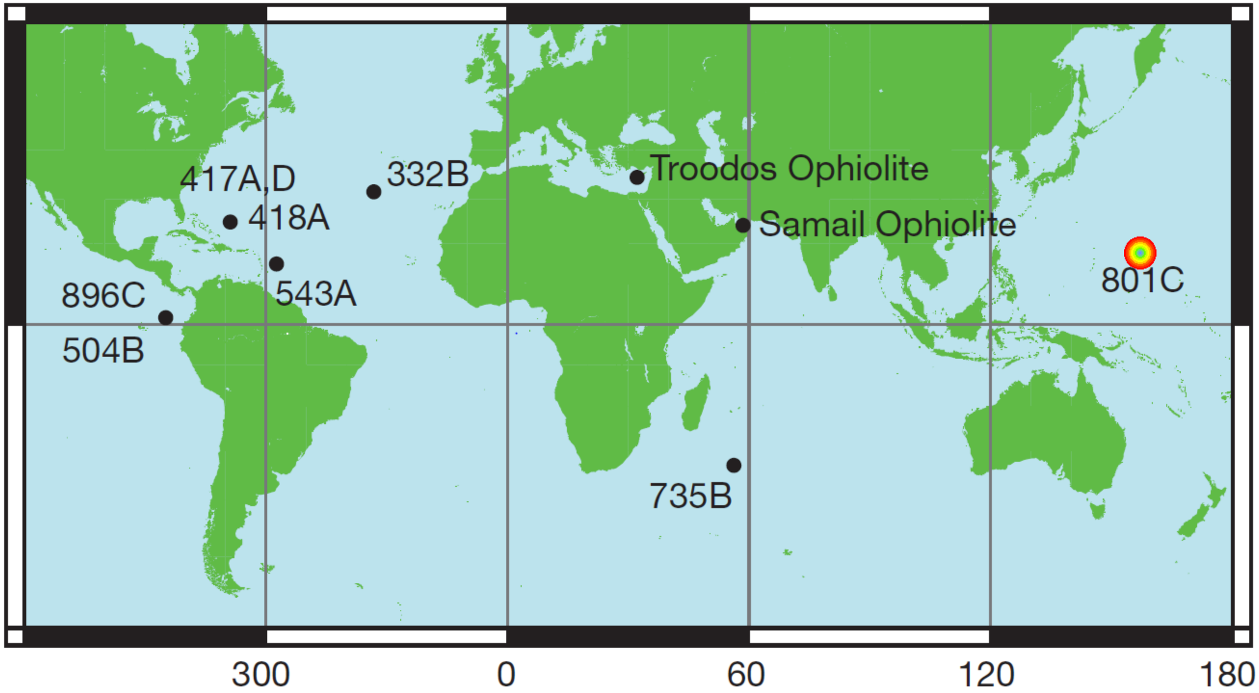
AOC in front of Mariana trench (ODP 801C Hole)

The oldest drilled AOC (~170 Ma)

→ Extensive secondary mineral formation

Saponite





Staudigel TOG 2014; Koppers et al. G3 2003

AOC from western Pacific

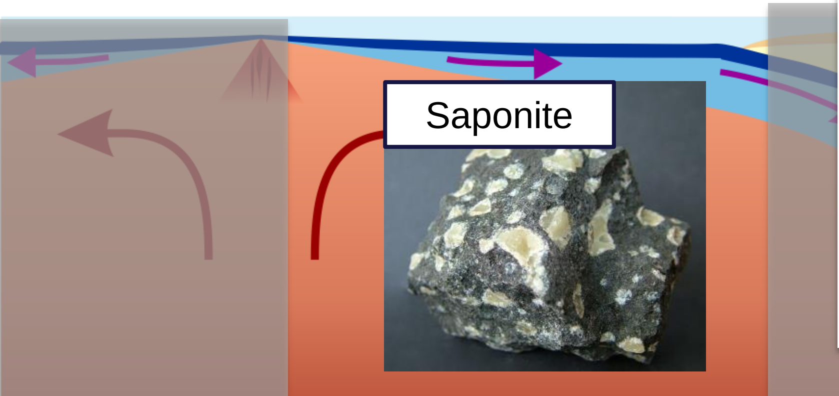
AOC is heterogeneous, on average heavier than mantle

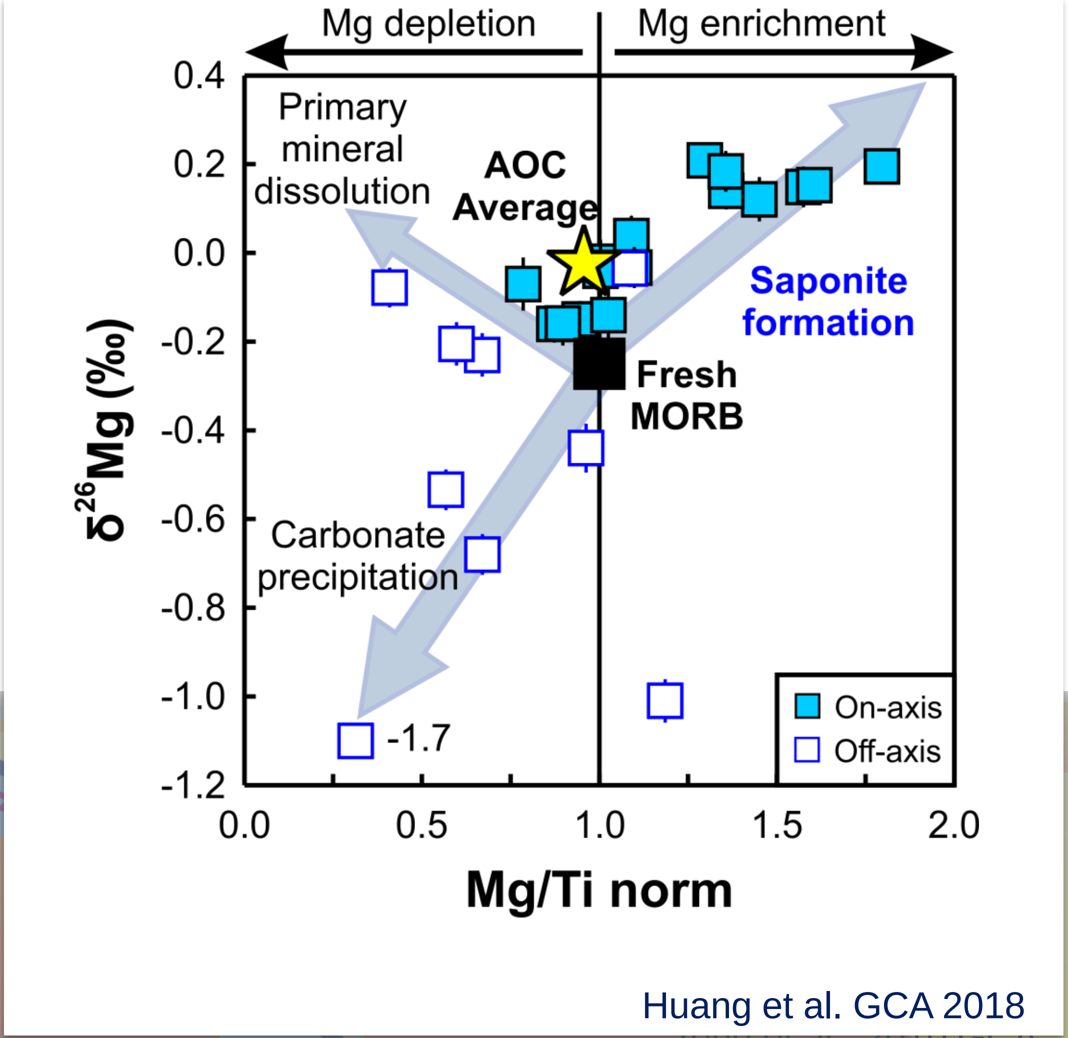
On-axis crust (lower 315 m)

Formed at mid-ocean ridge

Off-axis crust (upper 175 m)

Formed at ridge flanks



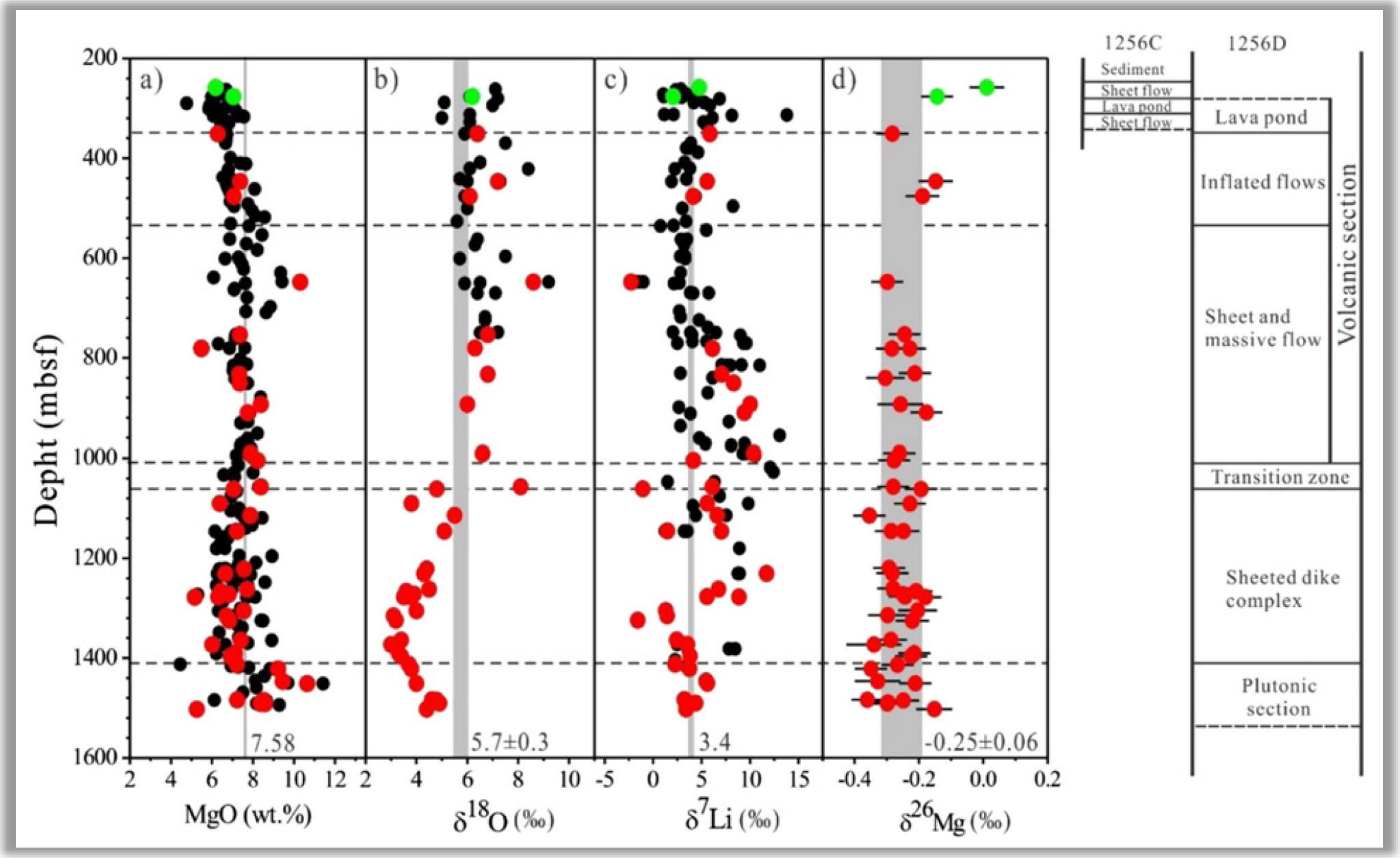


Huang et al. GCA 2018

AOC from East Pacific Rise

IODP site 1265 (15 Ma)

δ^{26}Mg = -0.25 ± 0.11 ‰ (2SD, n = 43)

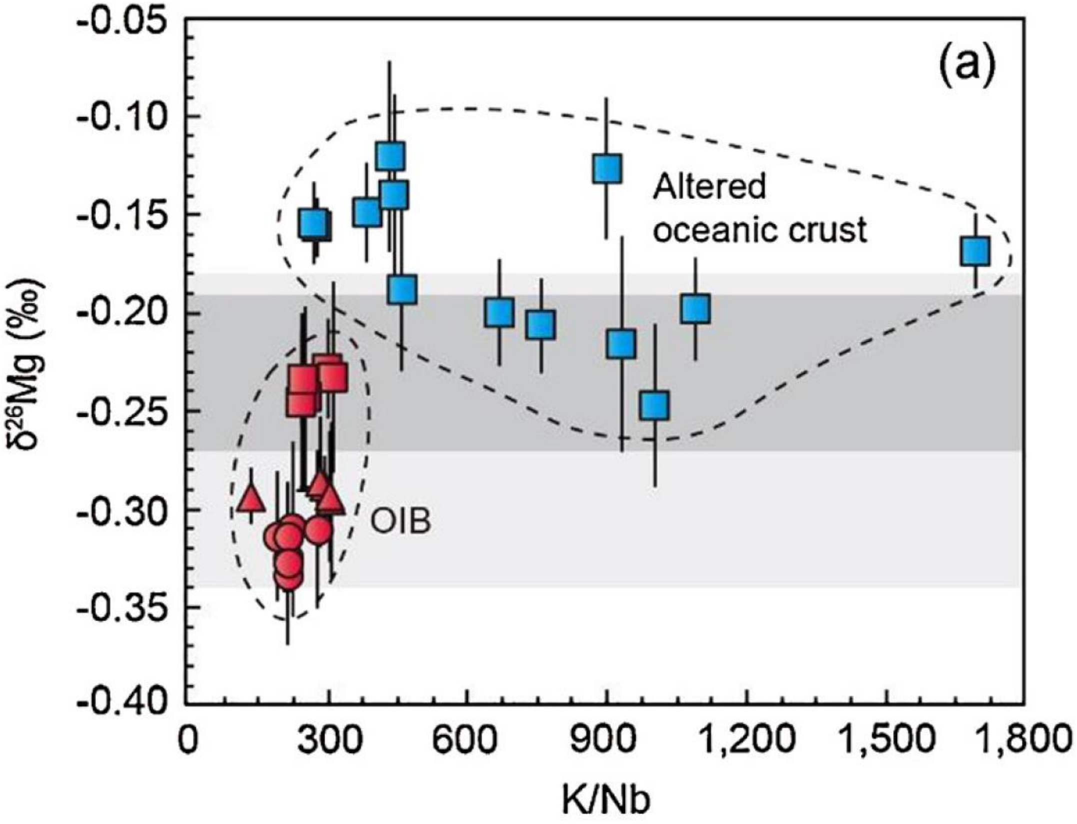


Huang et al. Lithos 2015

AOC from southern Pacific

IODP sites U1365, U1367, and U1368

δ^{26}Mg = -0.18 ± 0.08‰ (2SD, n = 13)

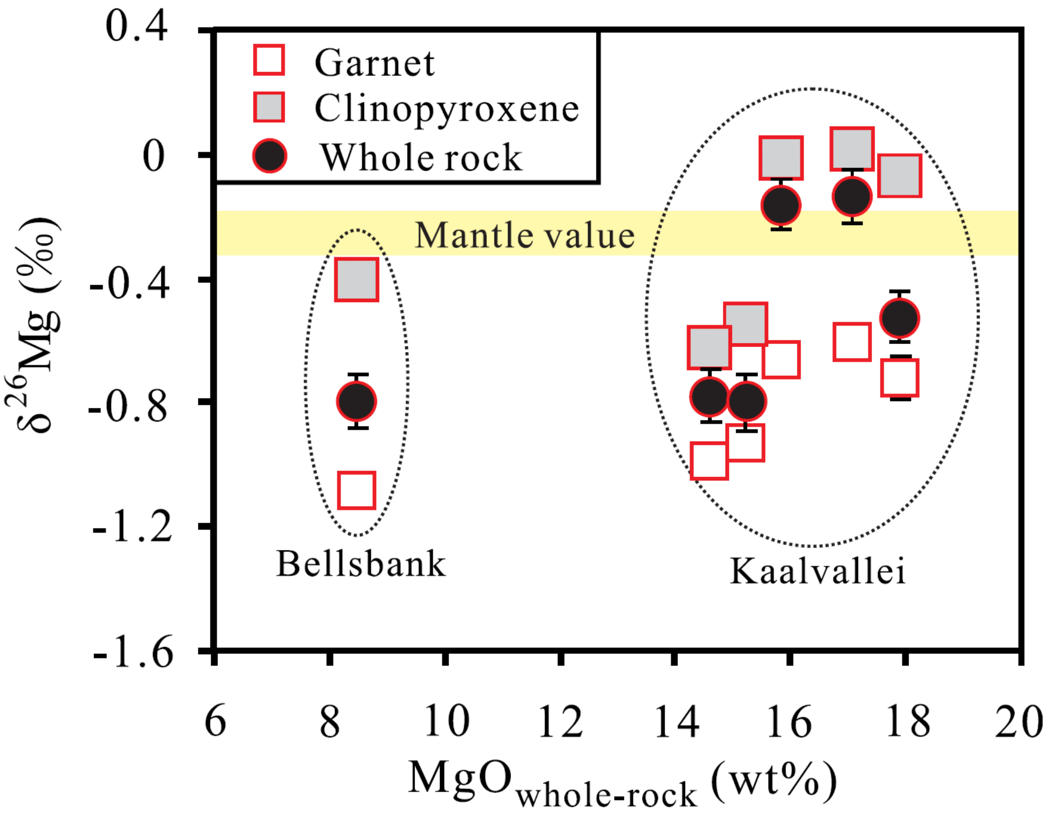


Zhong et al. EPSL 2017

Cratonic eclogites

Kaapvaal craton, South Africa

δ^{26}Mg = -0.78 to -0.14‰



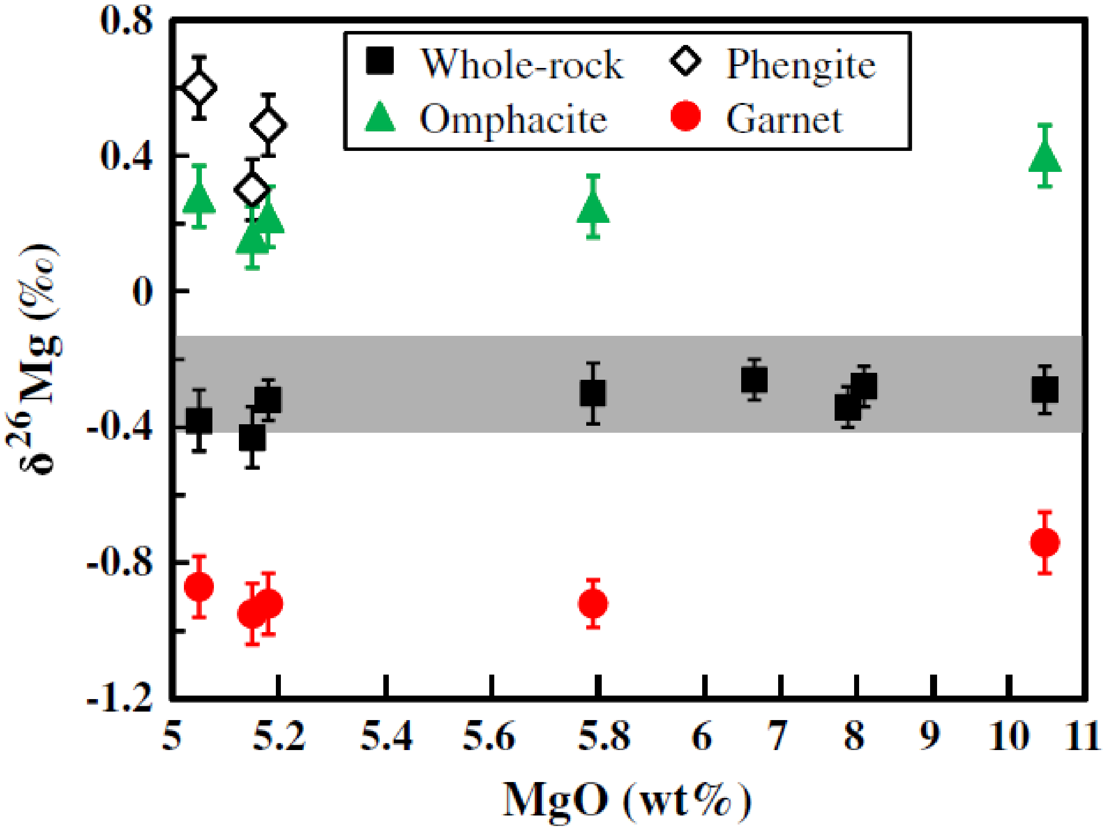
Wang et al. EPSL 2012

Orogenic eclogites

Dabie Orogen, Bixiling, δ^{26}Mg = -0.44 to -0.26‰

Eclogite-facies metamorphism does not fractionate Mg isotopes

δ^{26}Mg in eclogites reflects protolith compositions

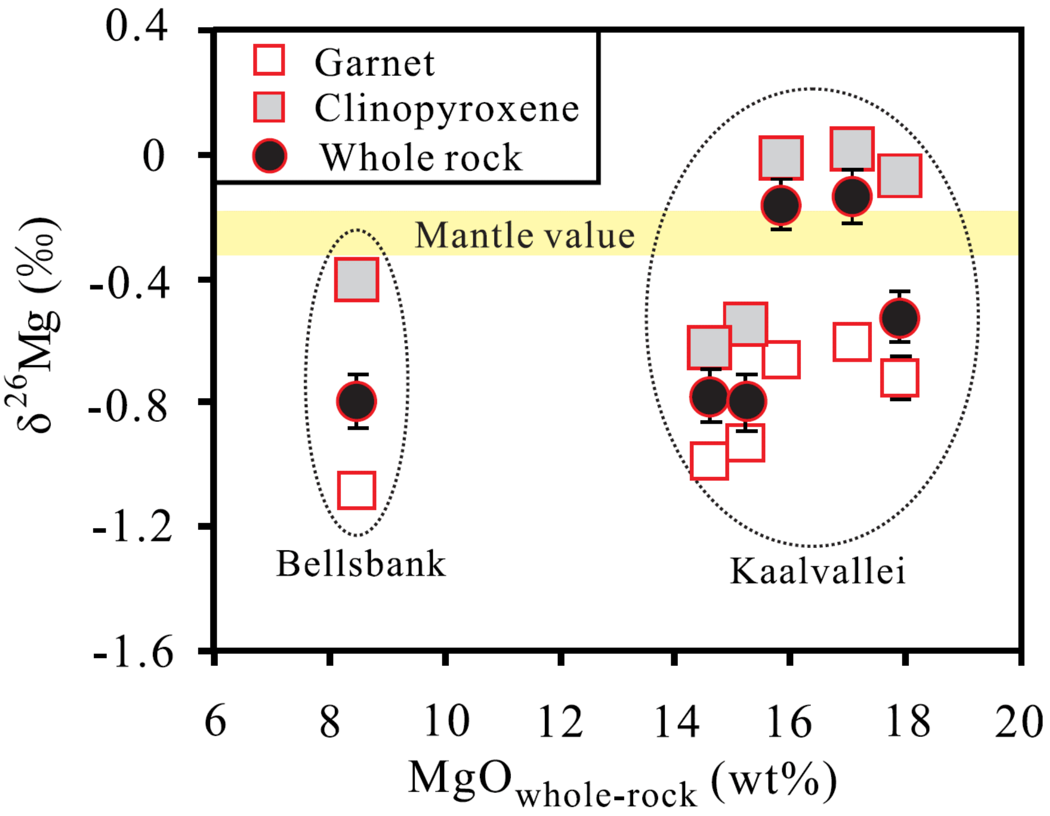


Li et al. EPSL 2011

Cratonic eclogites

Kaapvaal craton, South Africa, δ^{26}Mg = -0.78 to -0.14‰

Originated from AOC rather than mantle basaltic cumulates

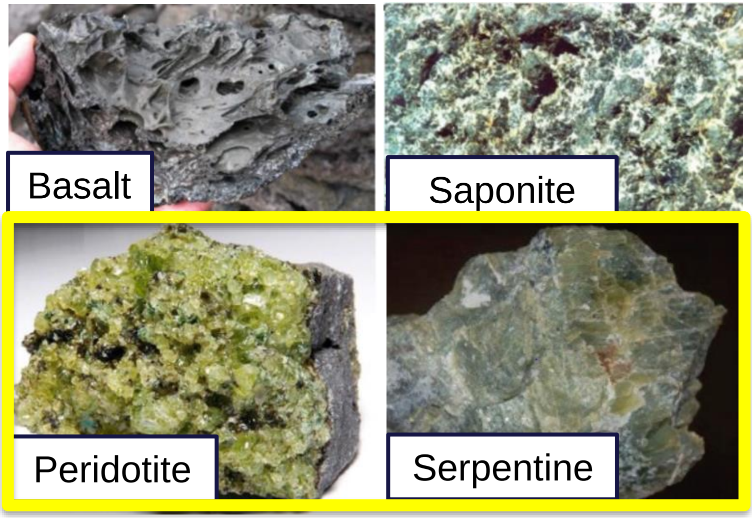


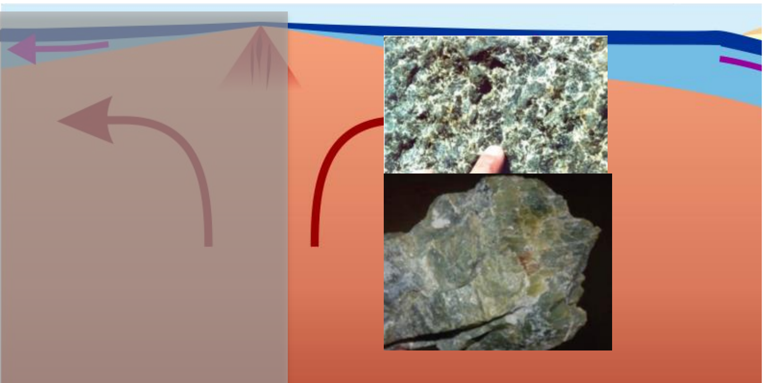
Wang et al. EPSL 2012

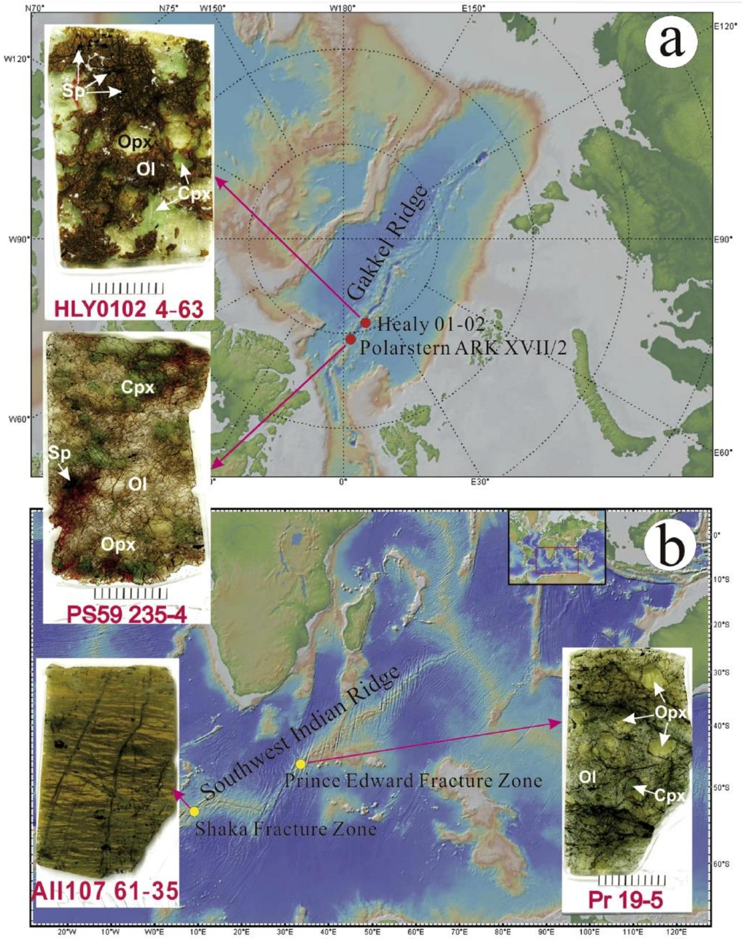
Altered oceanic mantle (AOM)

Abyssal peridotites from Gakkel and SW Indian ridges

Alteration of oceanic slab





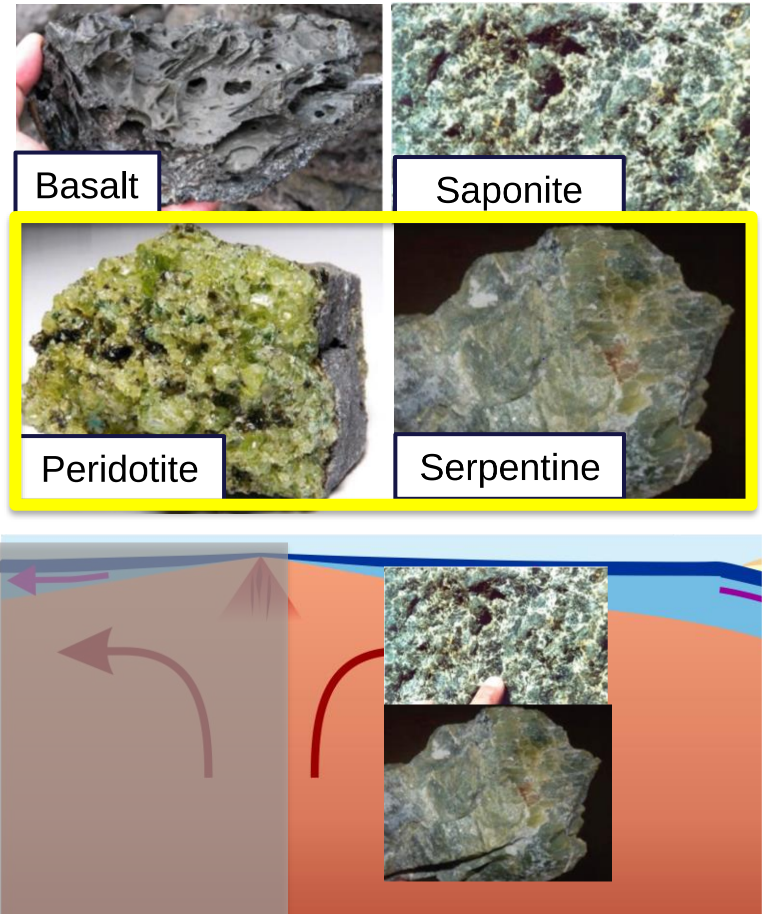


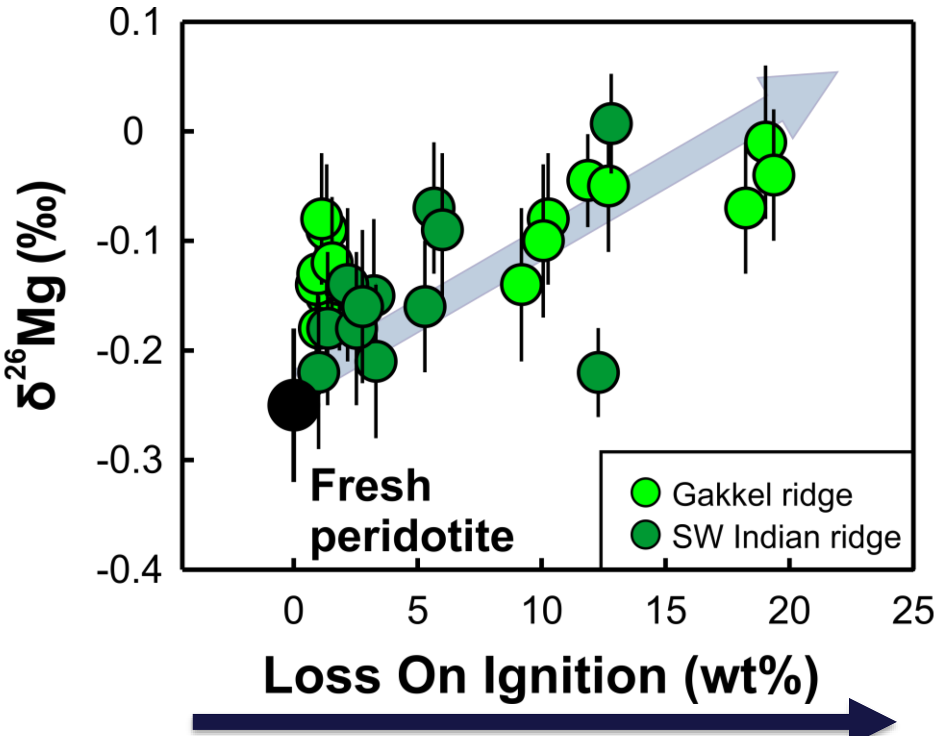
Liu et al. GCA 2017

Altered oceanic mantle (AOM)

AOM is heterogeneous, typically heavier than mantle

Alteration of oceanic slab





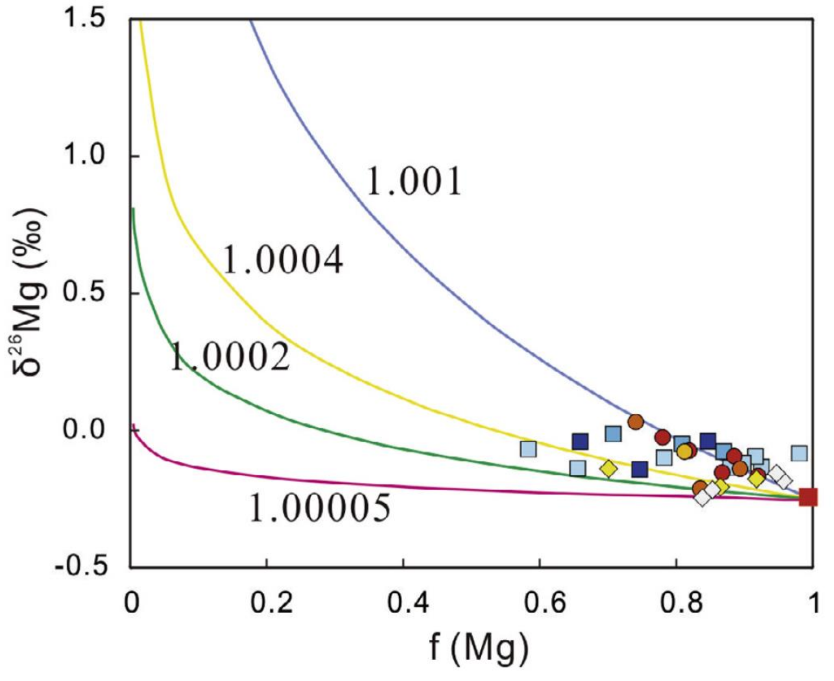
Seafloor weathering

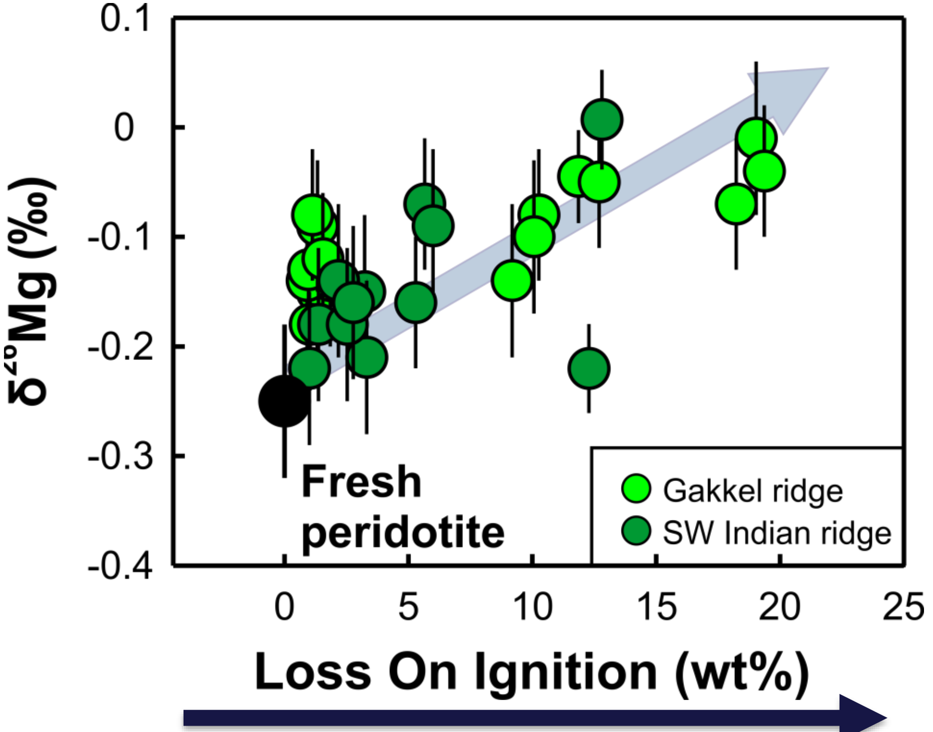
Liu et al. GCA 2017

Altered oceanic mantle (AOM)

AOM is heterogeneous, typically heavier than mantle

0.2 to 1.0‰ fractionation

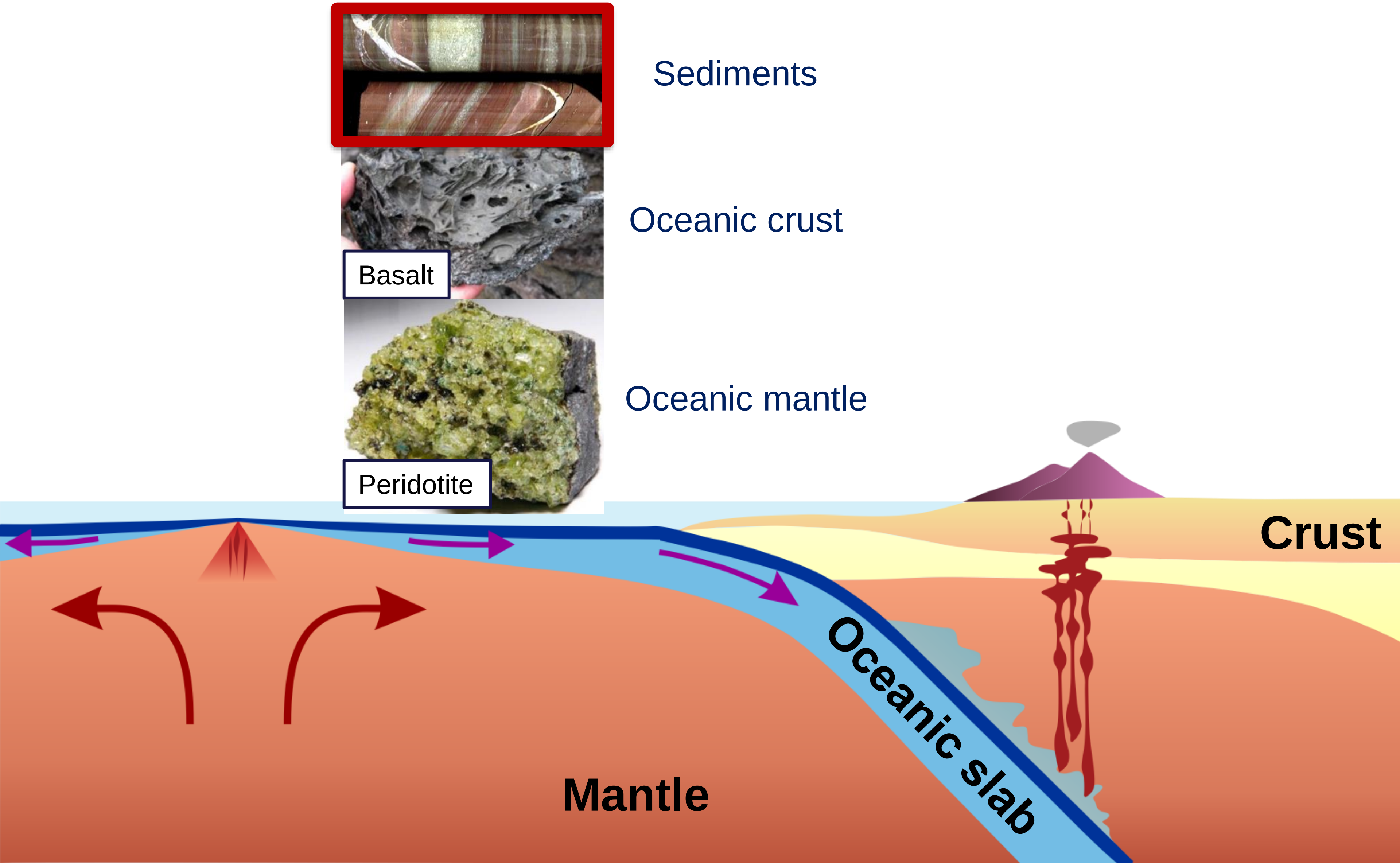




Seafloor weathering

Liu et al. GCA 2017

Subduction zone input



Oceanic slab

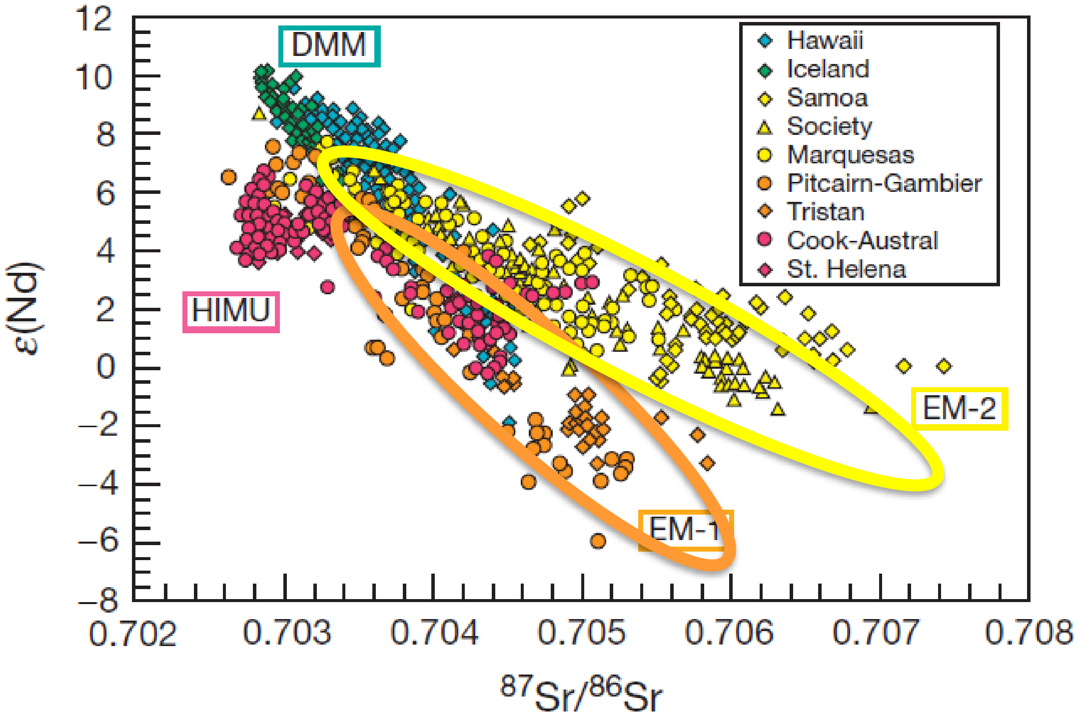
Sediments

Oceanic crust

Oceanic mantle

Sediments overlying oceanic crust

Sediments are the geochemically most heterogeneous component in the slab

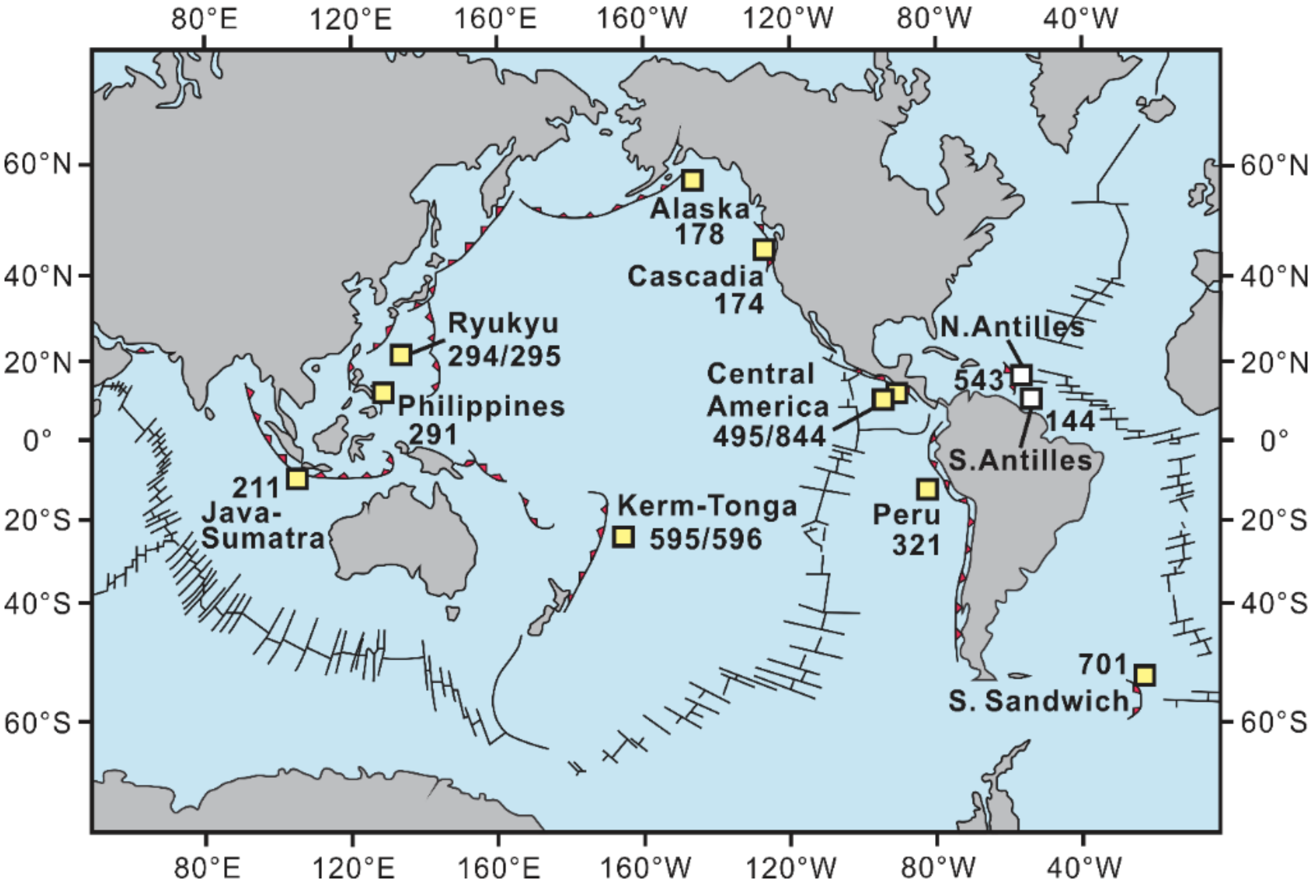


Hofmann 2014 TOG

Sediments overlying oceanic crust

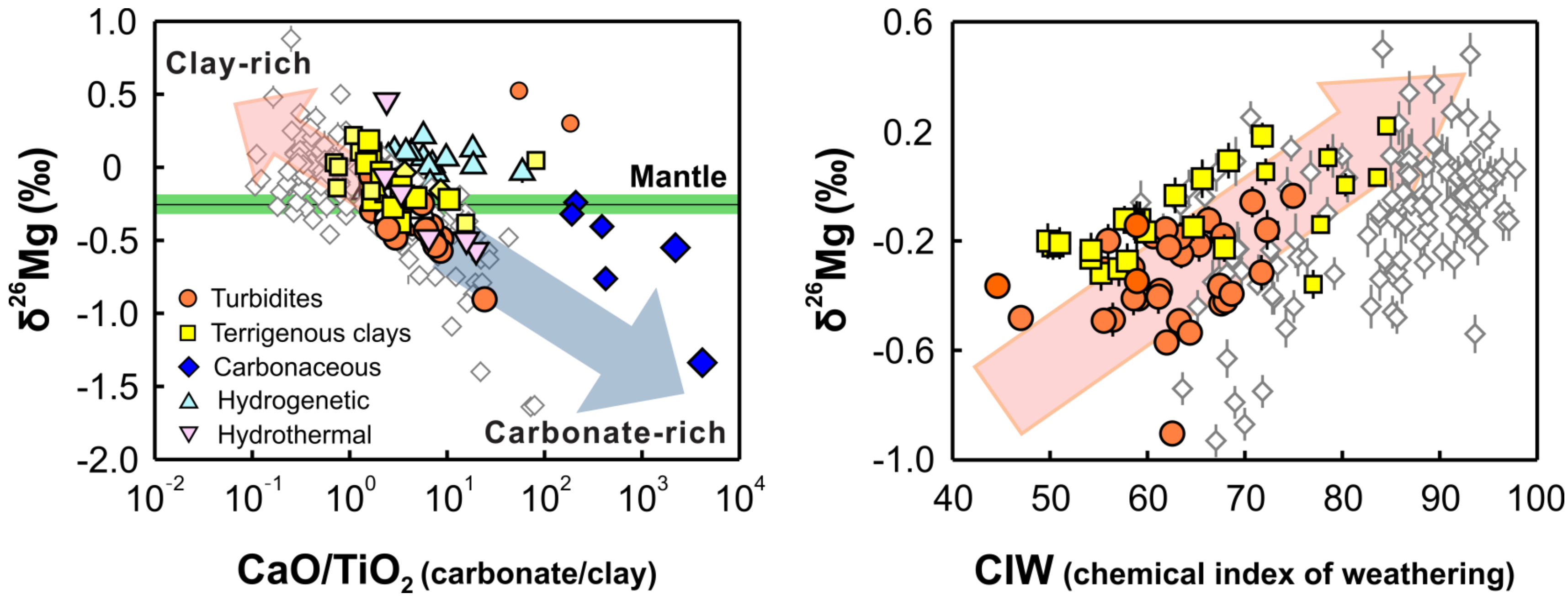
92 bulk sediments from drill cores in front of 12 major subducting zones

Used for establishing GLOSS-II (Global Subducting Sediment, Plank, 2014)



Modified from Plank TOG 2014

$\delta^{26}Mg$ of subducting sediments

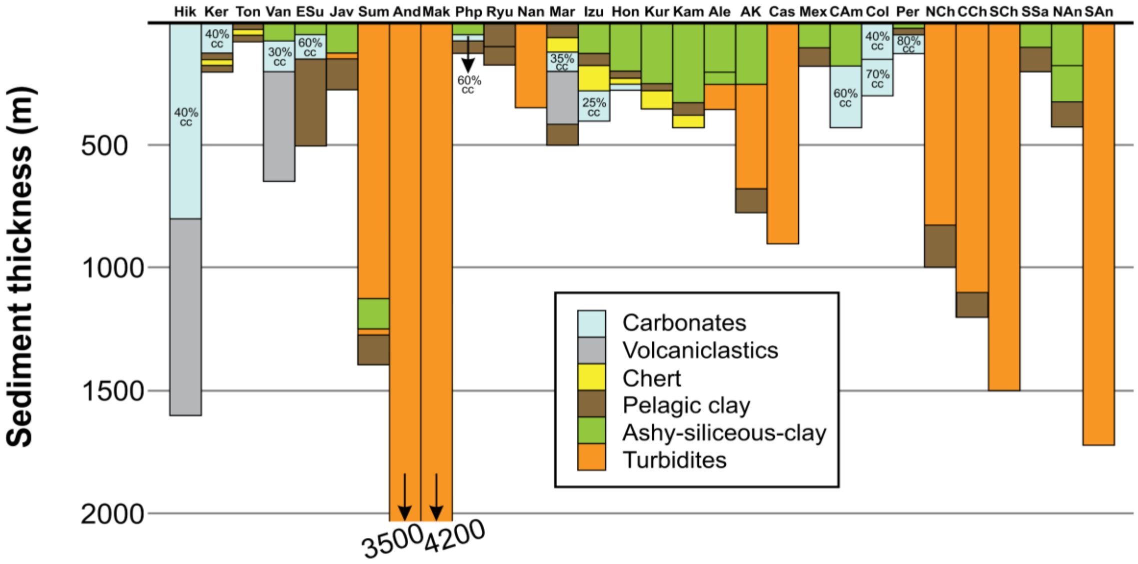


- Carbonate-rich sediments are isotopically light.
- Clay-rich sediments are variably heavier due to weathering.

Hu et al. CG 2017; Teng et al. PNAS 2016

Sedimentary Mg input to global subduction zones

Significant inter-arc variations in sediment thickness and lithology.

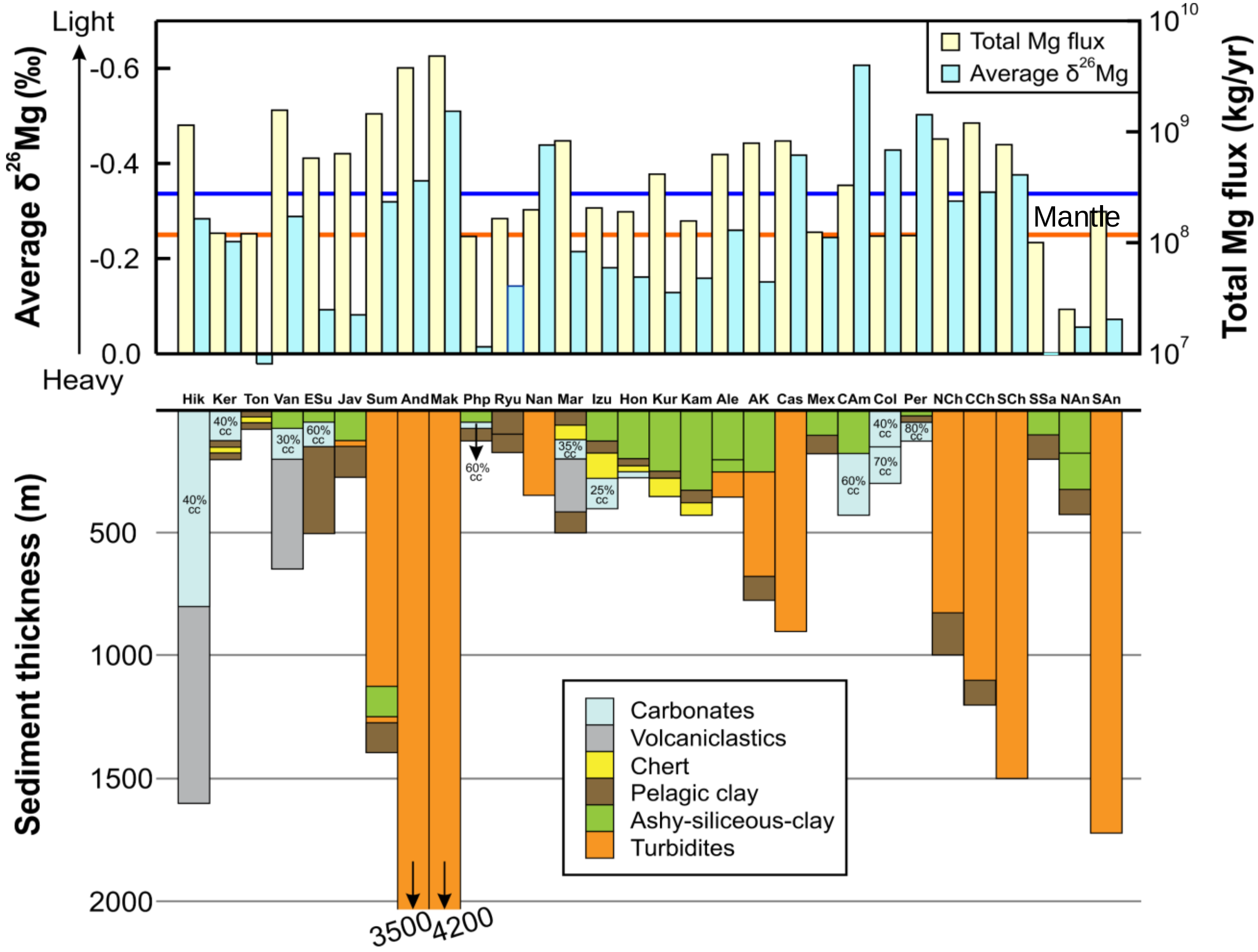


Hu et al. 2017 CG

Sedimentary Mg input to global subduction zones

Significant inter-arc variations in Mg flux and average δ^{26}Mg

Subducting sediments are a source of heterogeneous Mg to the mantle



Hu et al. CG 2017; Teng et al. PNAS 2016

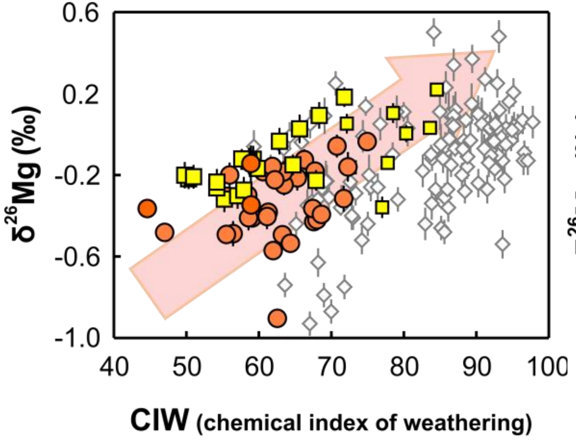
Summary

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

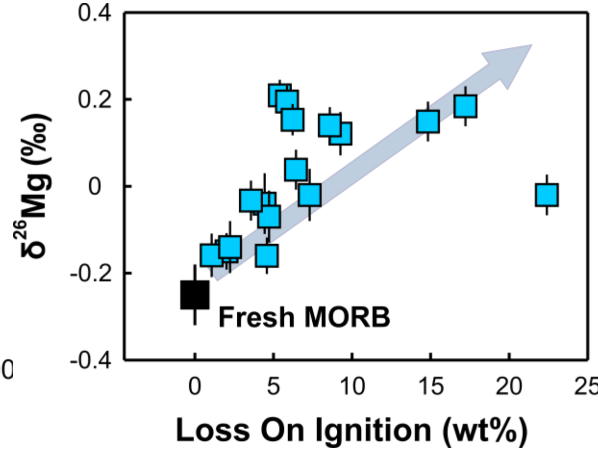
Seafloor weathering and continental weathering (for sediments)

- Weathering forms clay, preferentially retaining heavy Mg isotopes.
- Carbonate preferentially incorporate light Mg isotopes.

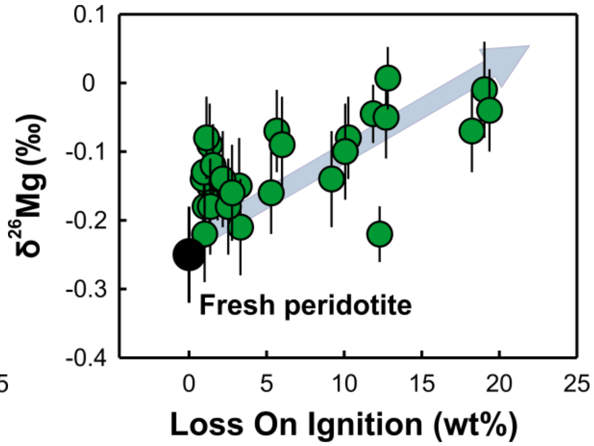
δ^{26}Mg of subducting components depends on mineralogy.



Subducting sediments



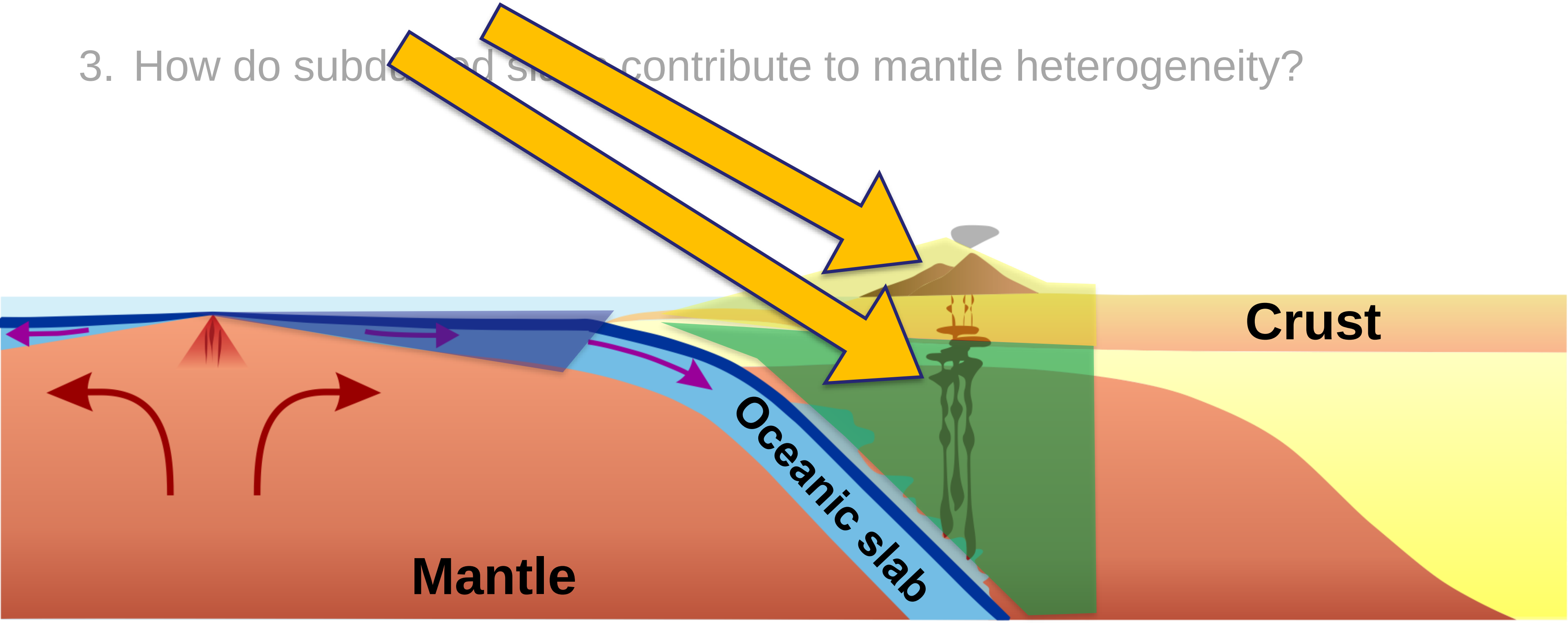
Altered oceanic crust



Altered oceanic mantle

Tracing subducting recycling with Mg isotopes

1. What processes control the compositional variation in subducting slab?
2. How does slab signature transfer to mantle wedge and arc magmas?
3. How do subducted slabs contribute to mantle heterogeneity?



Tracing subducting recycling with Mg isotopes

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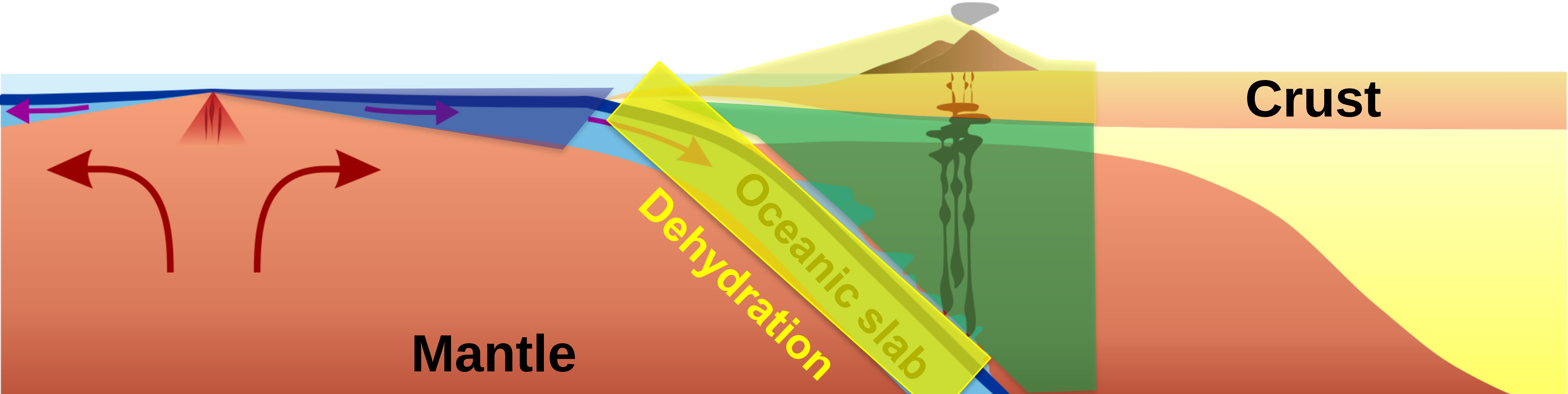
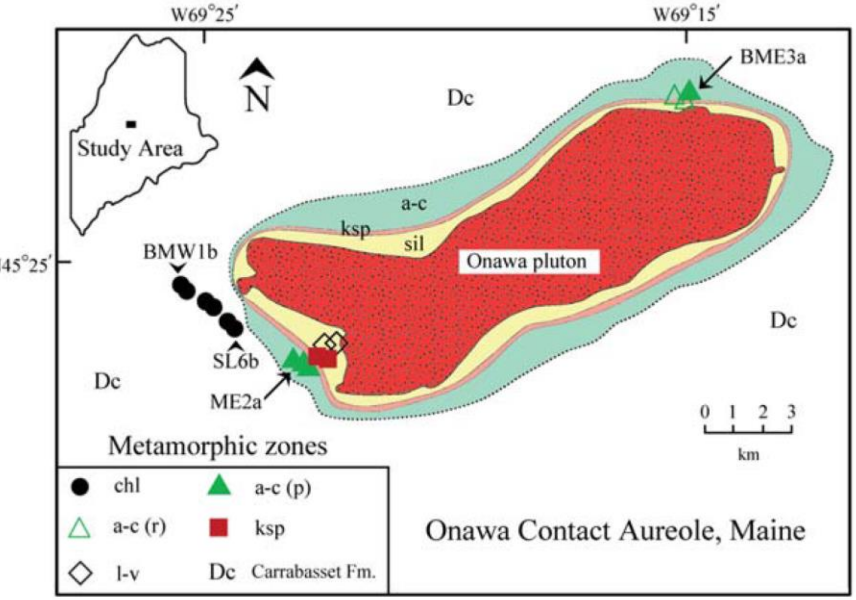
   1) *Does subduction dehydration fractionate Mg isotopes?*

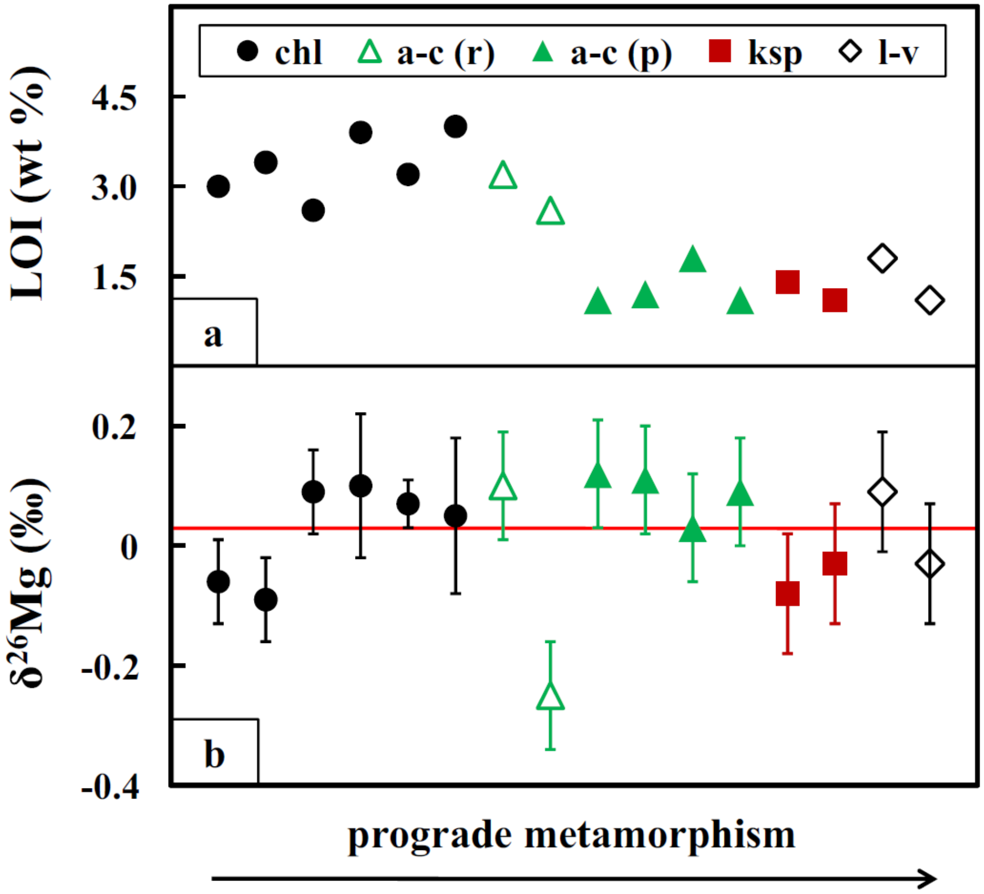


Mg isotope fractionation during dehydration

Metapelites from Onawa contact aureole, Maine, USA

δ^{26}Mg = -0.09 to +0.12‰



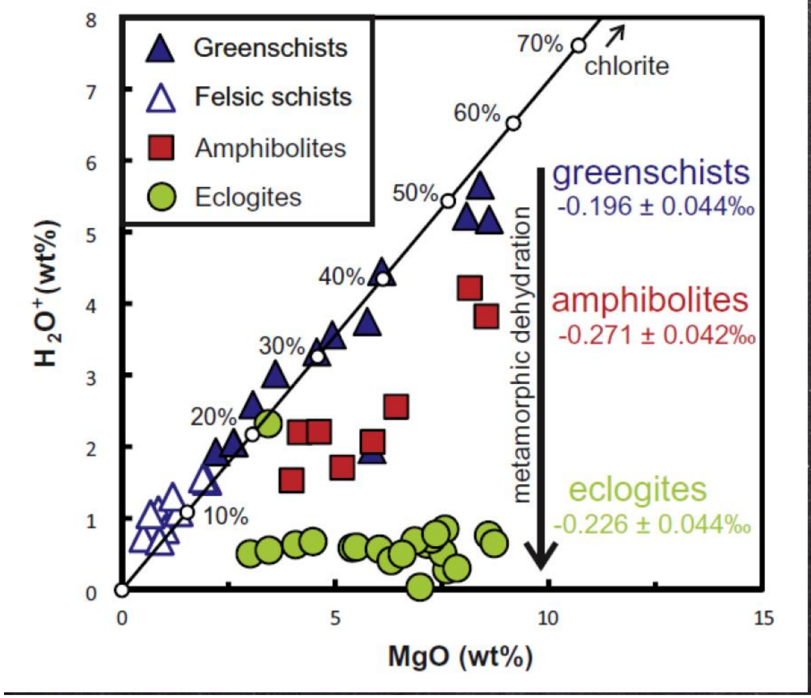


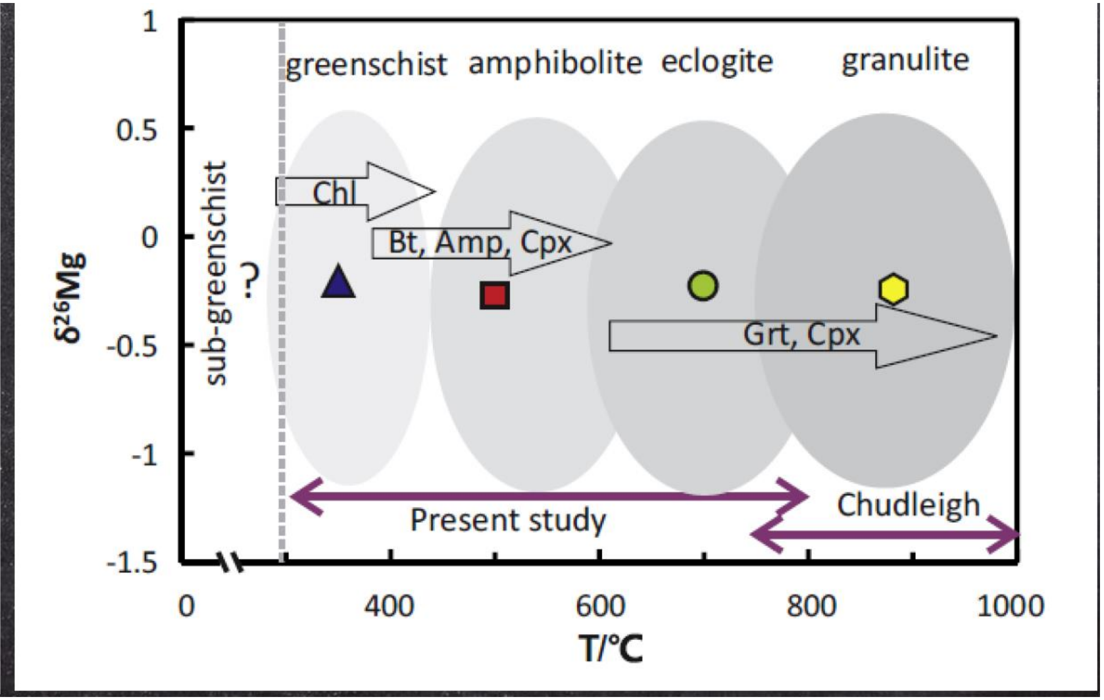
Li et al. G3 2014

Mg isotope fractionation during dehydration

Greenschists = Amphibolites = Eclogites

(-0.2 ± 0.44‰) (-0.27 ± 0.042‰) (-0.23 ± 0.044‰)





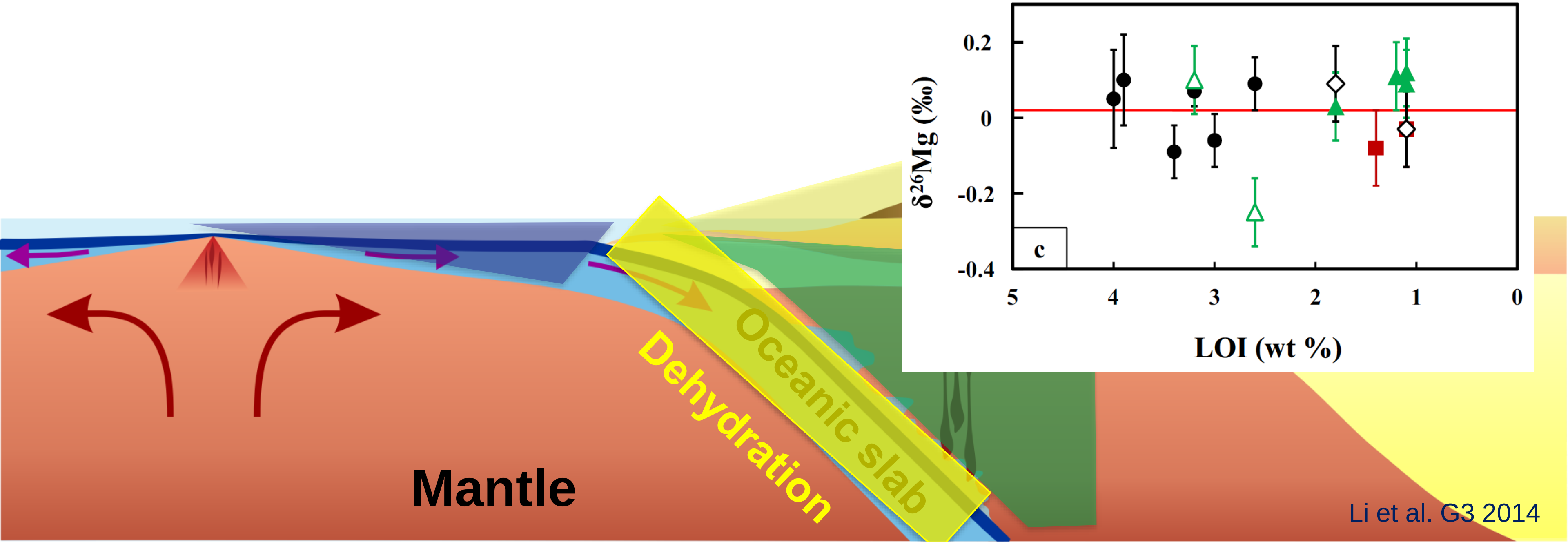
Wang et al. GCA 2014

Tracing subducting recycling with Mg isotopes

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

2. How does slab signature transfer to mantle wedge and arc magmas?
   1) *Does subduction dehydration fractionate Mg isotopes?*

      Limited fractionation during metamorphic dehydration, because Mg tends to stay in rocks than entering fluids



Li et al. G3 2014

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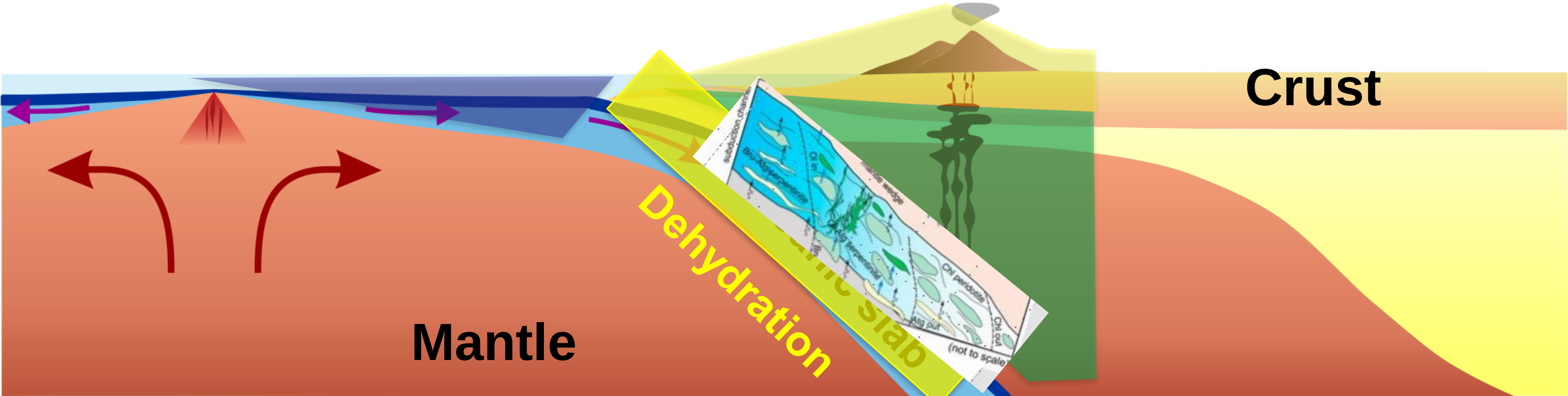
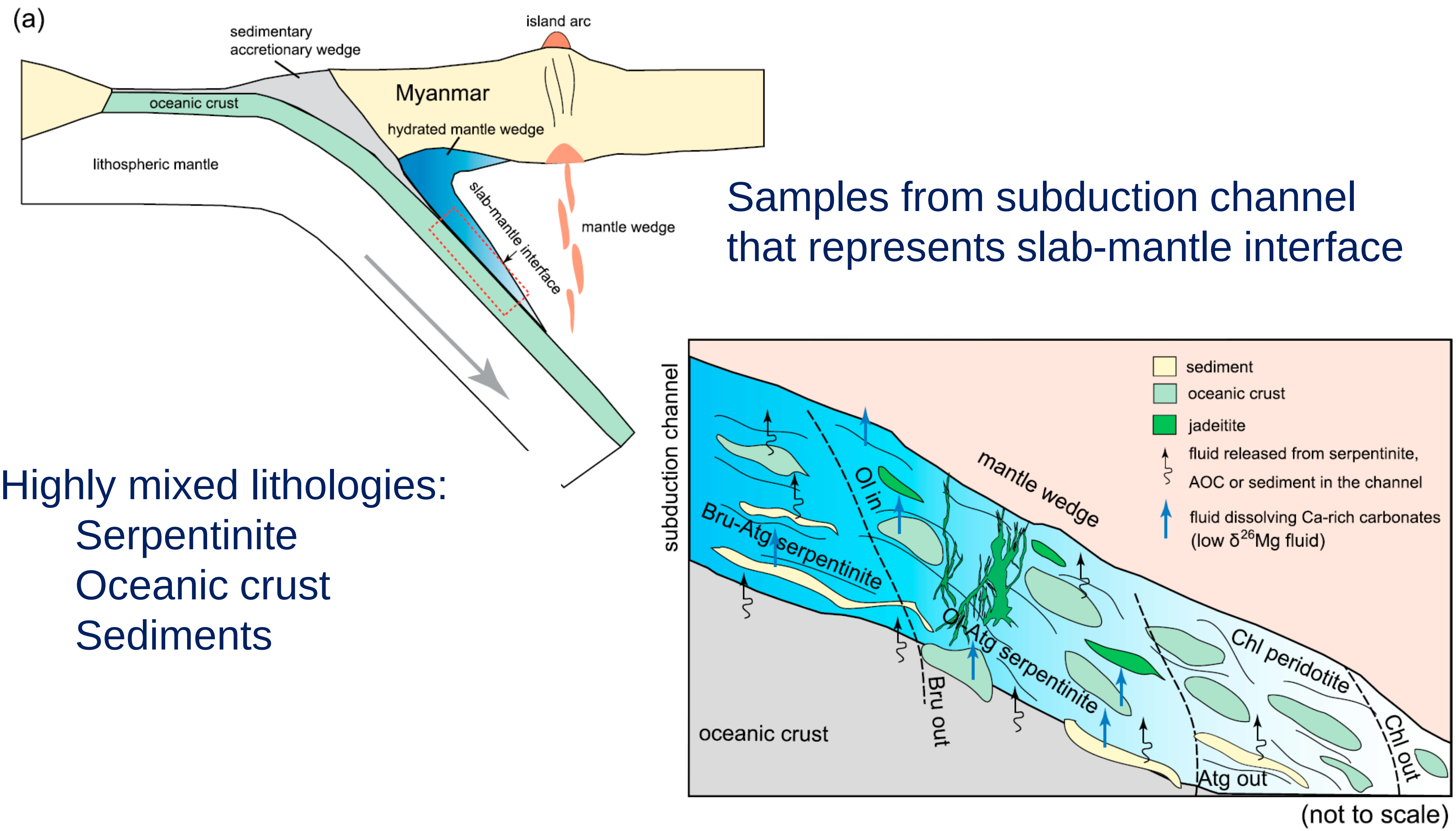


δ^{26}Mg of dehydration fluids



Samples from subduction channel that represents slab-mantle interface

Highly mixed lithologies:

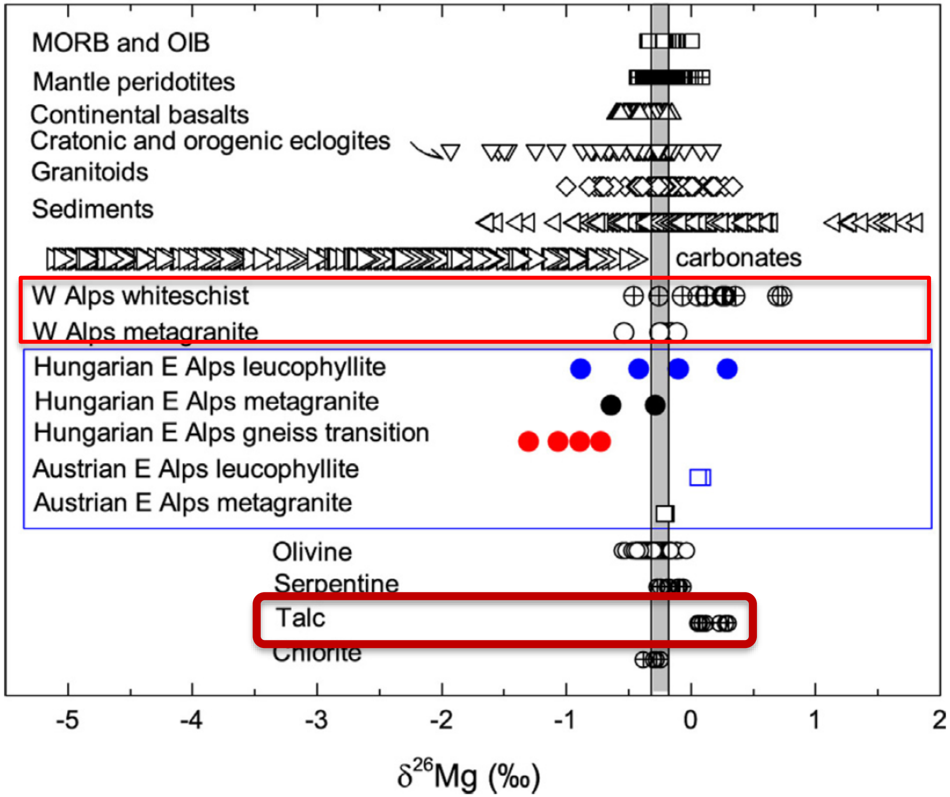
- Serpentinite
- Oceanic crust
- Sediments

Chen et al. JGR 2018

δ^{26}Mg of dehydration fluids

Subduction fluids have heterogeneous δ^{26}Mg values

- High δ^{26}Mg (> 0.3‰) fluids from talc-rich serpentinites
- Low δ^{26}Mg fluids (< -1.3‰) from carbonate dissolution



Chen et al. EPSL 2016; GCA 2020

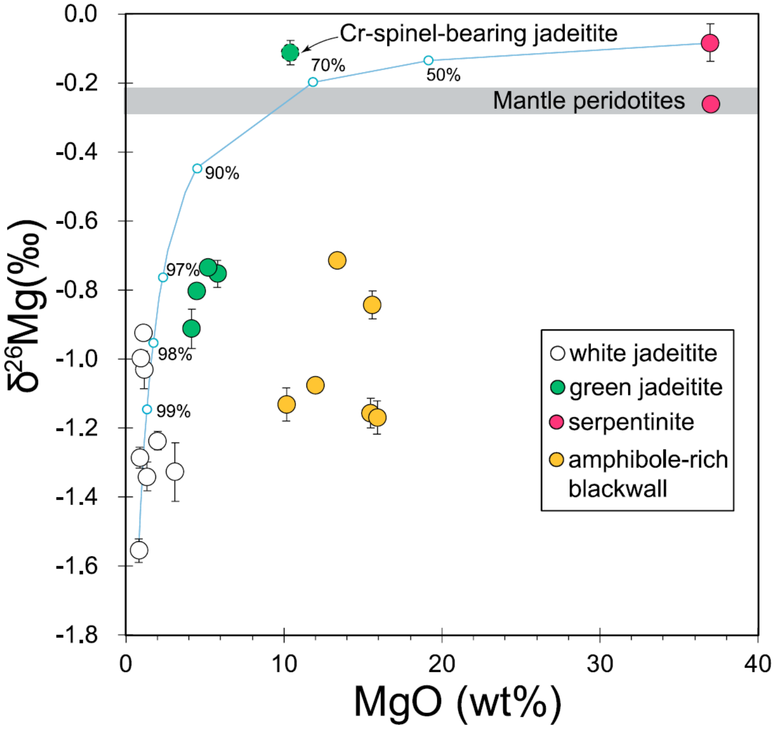
δ^{26}Mg of dehydration fluids

Myanmar jadeitites recorded carbonate dissolution at forearc

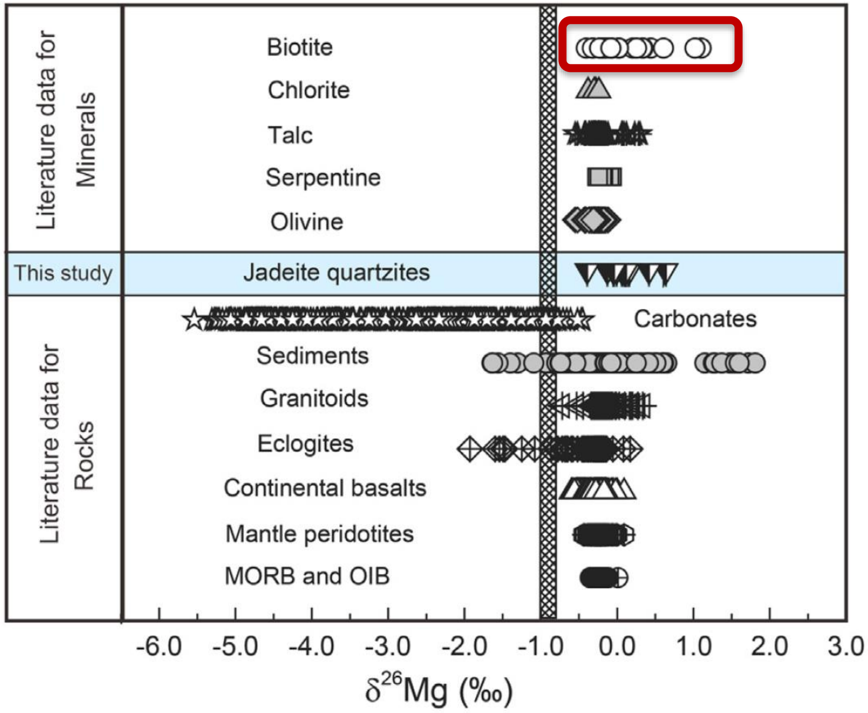
δ^{26}Mg = -1.55 to -0.74‰

Jadeite quartzites from Dabie Orogen

δ^{26}Mg = -0.16 to 0.61‰



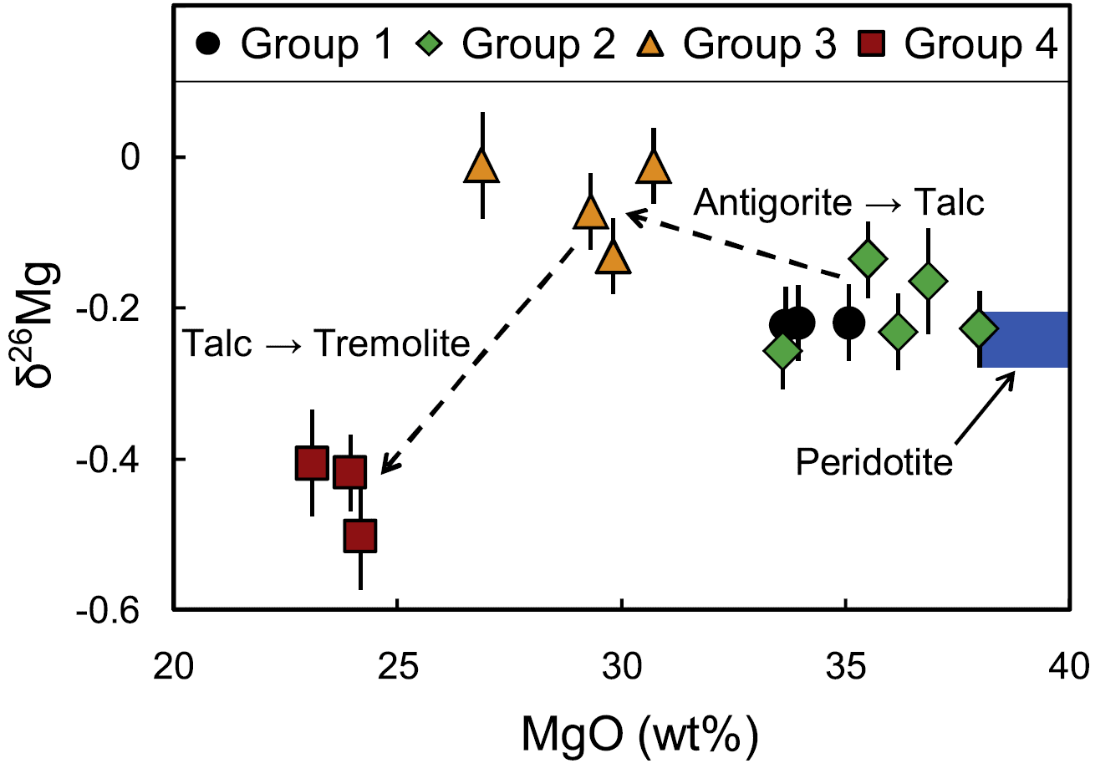
Chen et al. JGR 2018



Gao et al. GCA 2019

δ^{26}Mg of dehydration fluids

- Limited fractionation during serpentinization (δ^{26}Mg = -0.26 to -0.14‰)
- Preferential loss of light Mg during replacement of antigorite by talc
- Carbonate fluids result in light Mg in tremolite



Li et al. GCA 2018

Tracing subduction recycling with Mg isotopes

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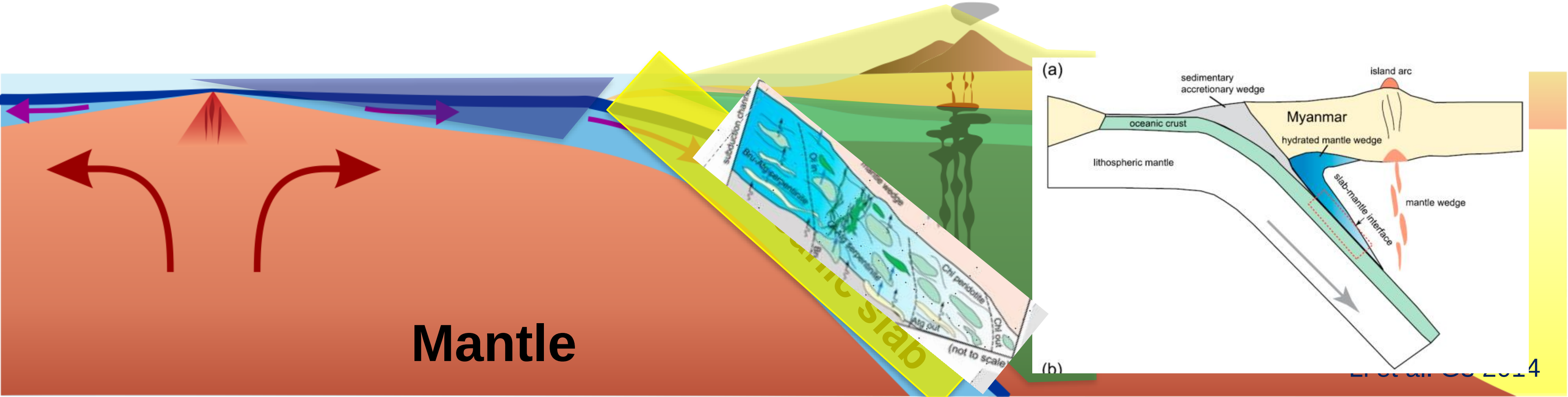
      Dehydration fluids have heterogeneous δ^{26}Mg



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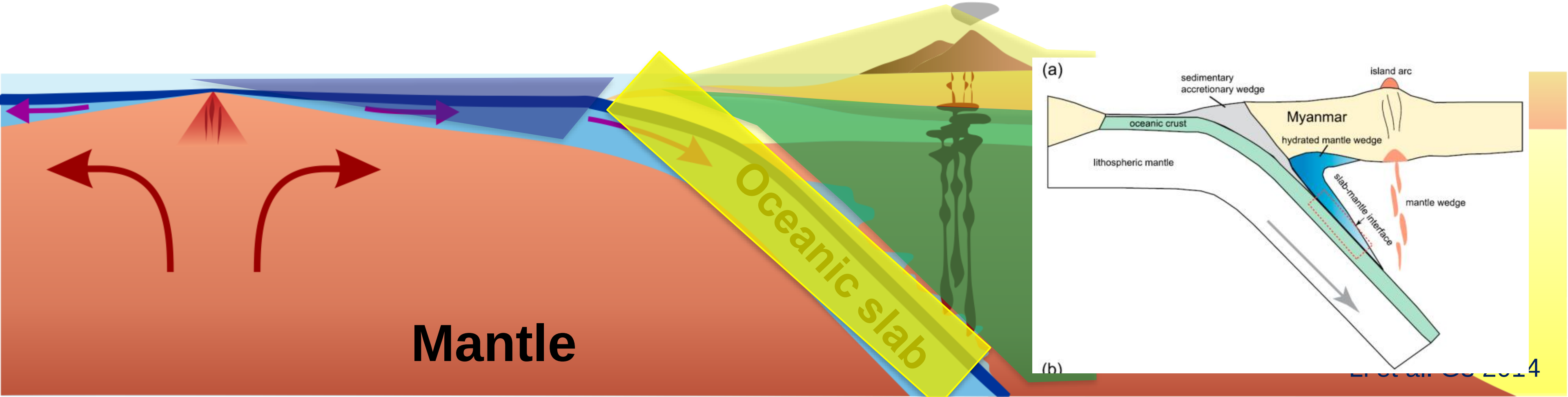
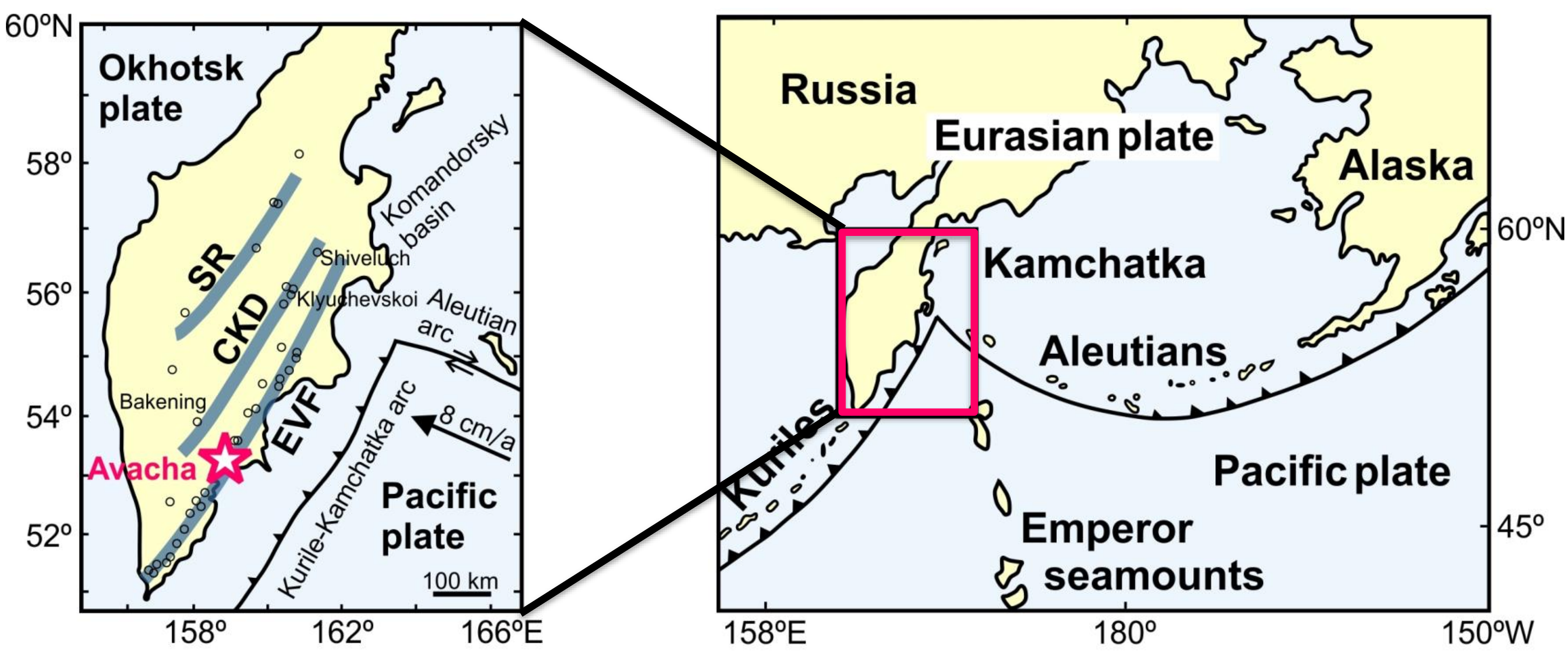
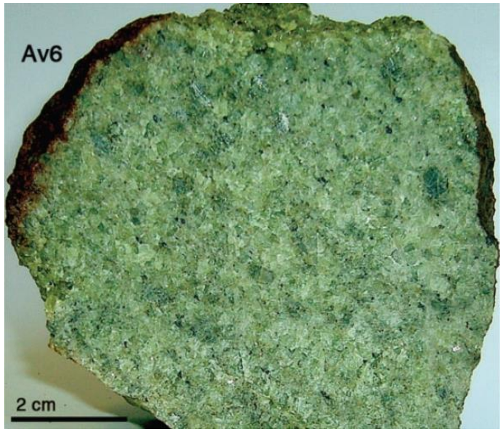
   3) *Are slab δ^{26}Mg signatures detected in mantle wedge & arc magma?*



Mantle wedge: source of arc lavas





The active Avacha volcano is one of the few volcanoes around the world that has abundant mantle wedge peridotites.

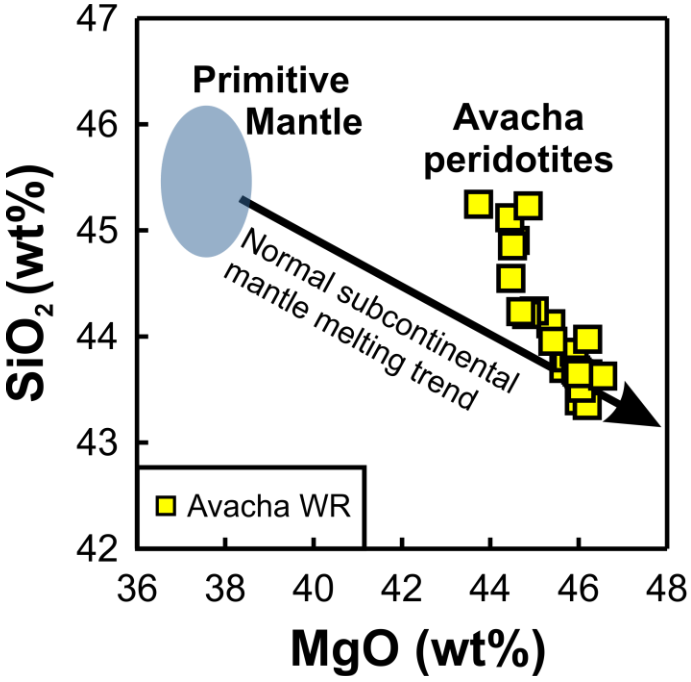
Evidence for slab-derived modification

Avacha peridotites underwent two stages of slab-fluid modification

Prior to melting

Asthenosphere

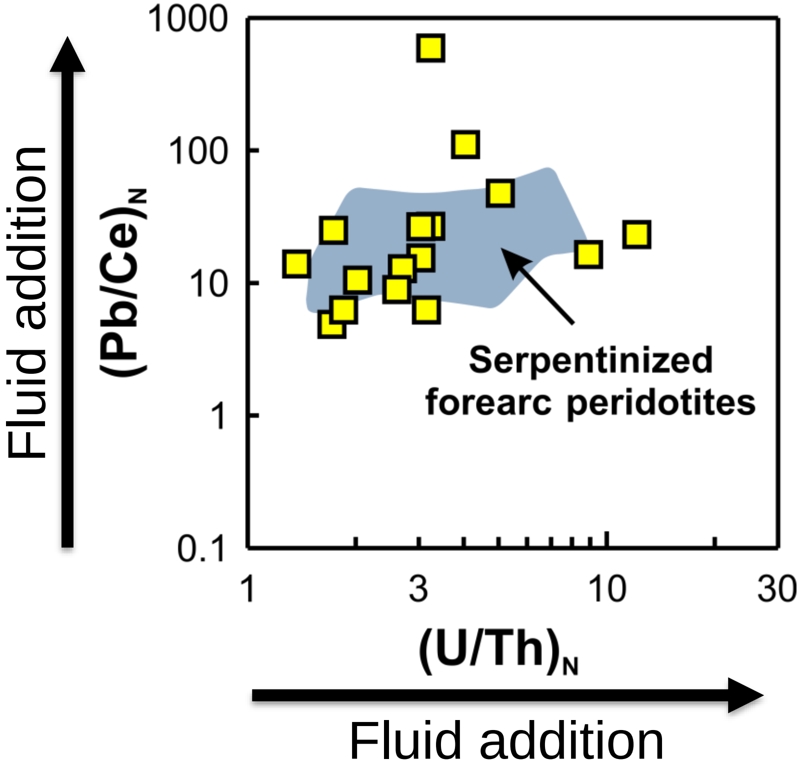
Protolith rich in SiO_2



Post-melting

Lithospheric mantle

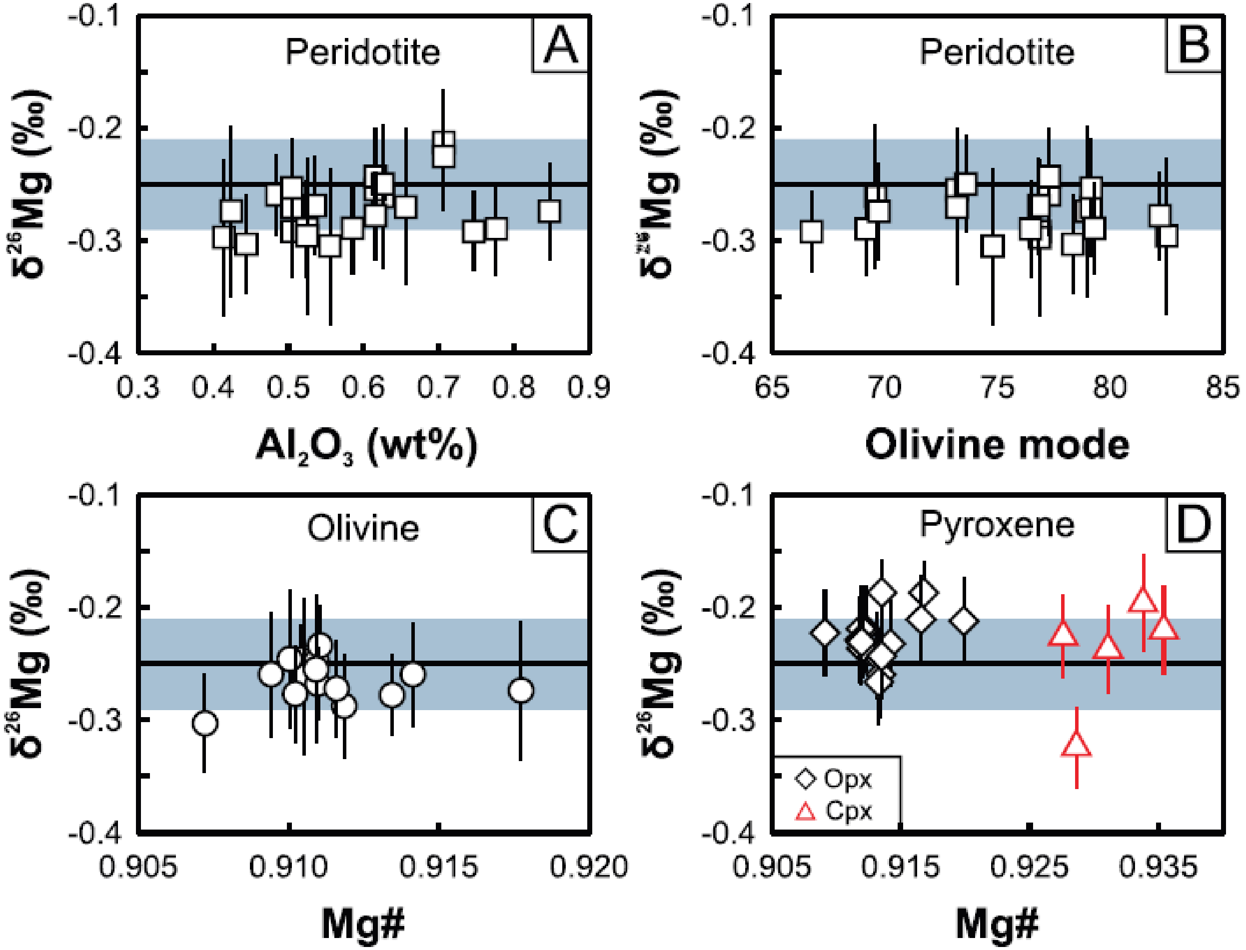
Residual peridotite rich in fluid-mobile elements



Ionov JP 2010

δ^{26}Mg of mantle wedge

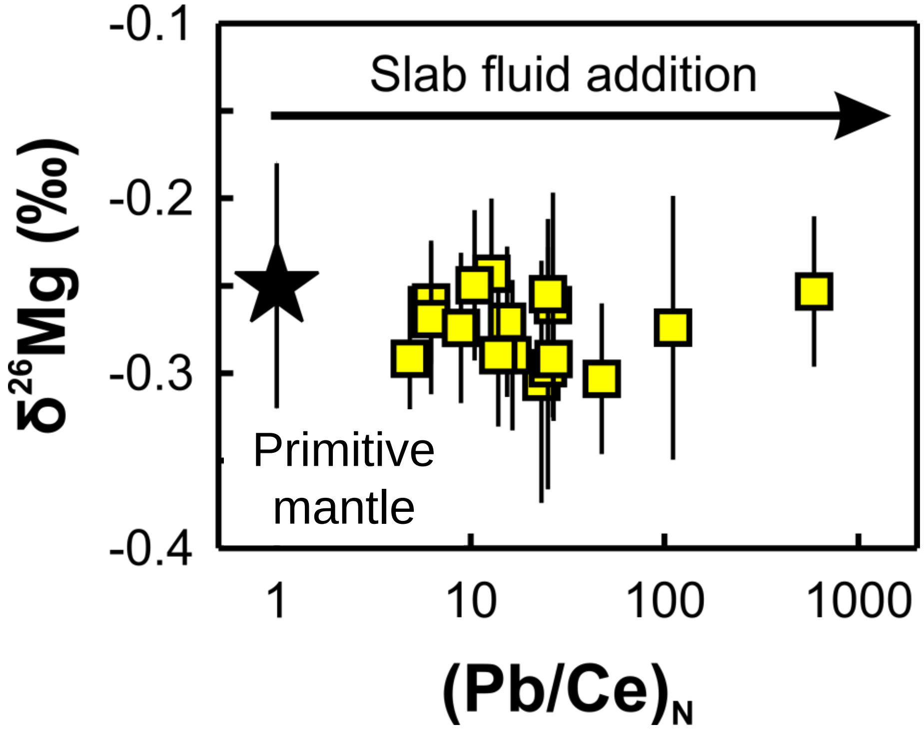
Both peridotites and their minerals have δ^{26}Mg similar to the mantle



Hu et al. GCA 2020

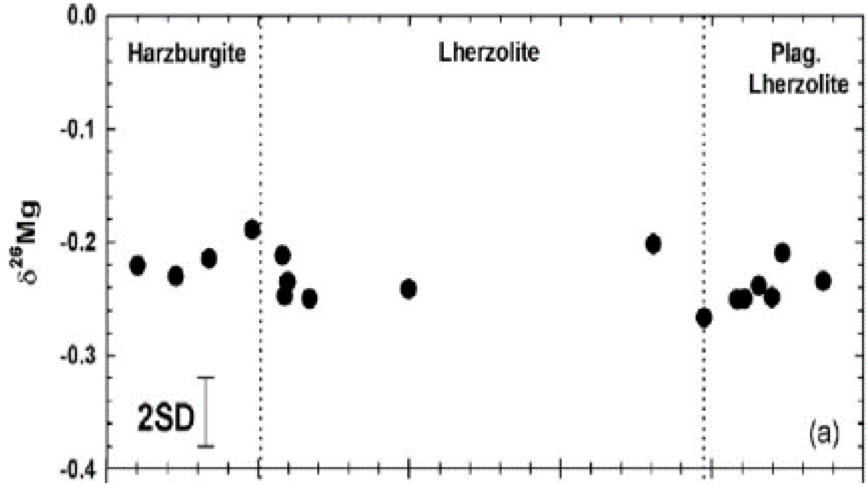
Comparison with massif peridotites

Both peridotites and their minerals have δ^{26}Mg similar to the mantle



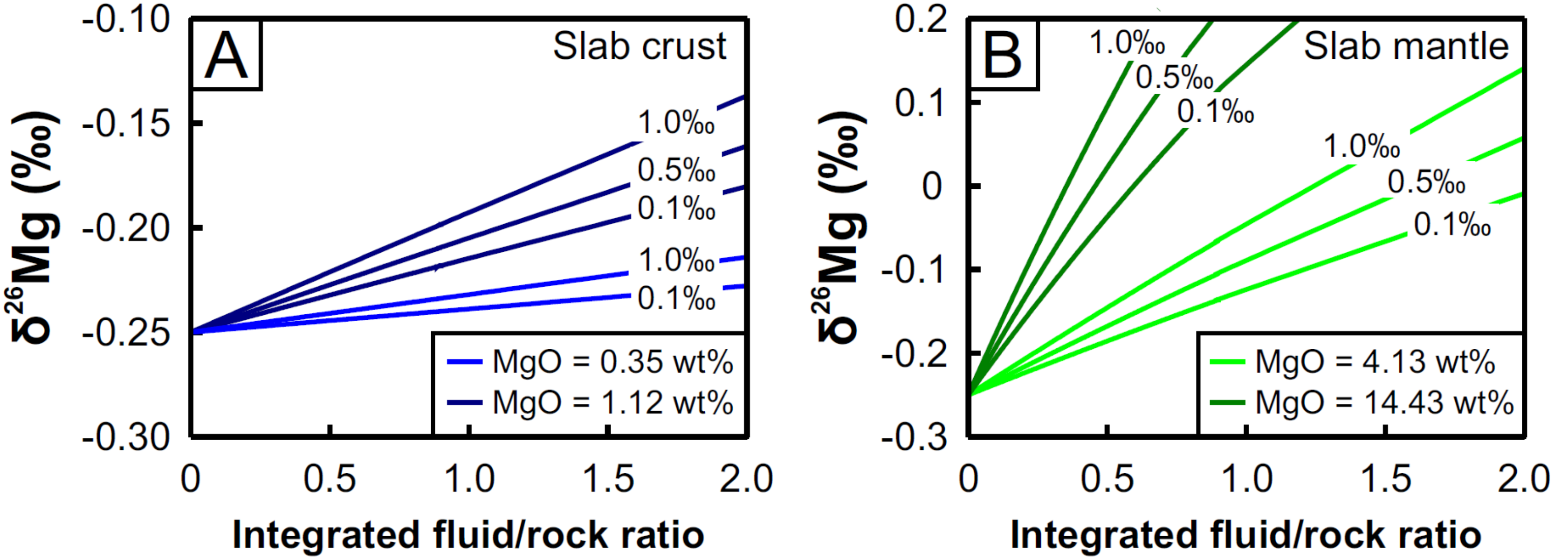
Hu et al. GCA 2020

Fluid-metasomatism:
Phl, LREE enrichment



Lai et al. GCA 2015

δ^{26}Mg of mantle wedge

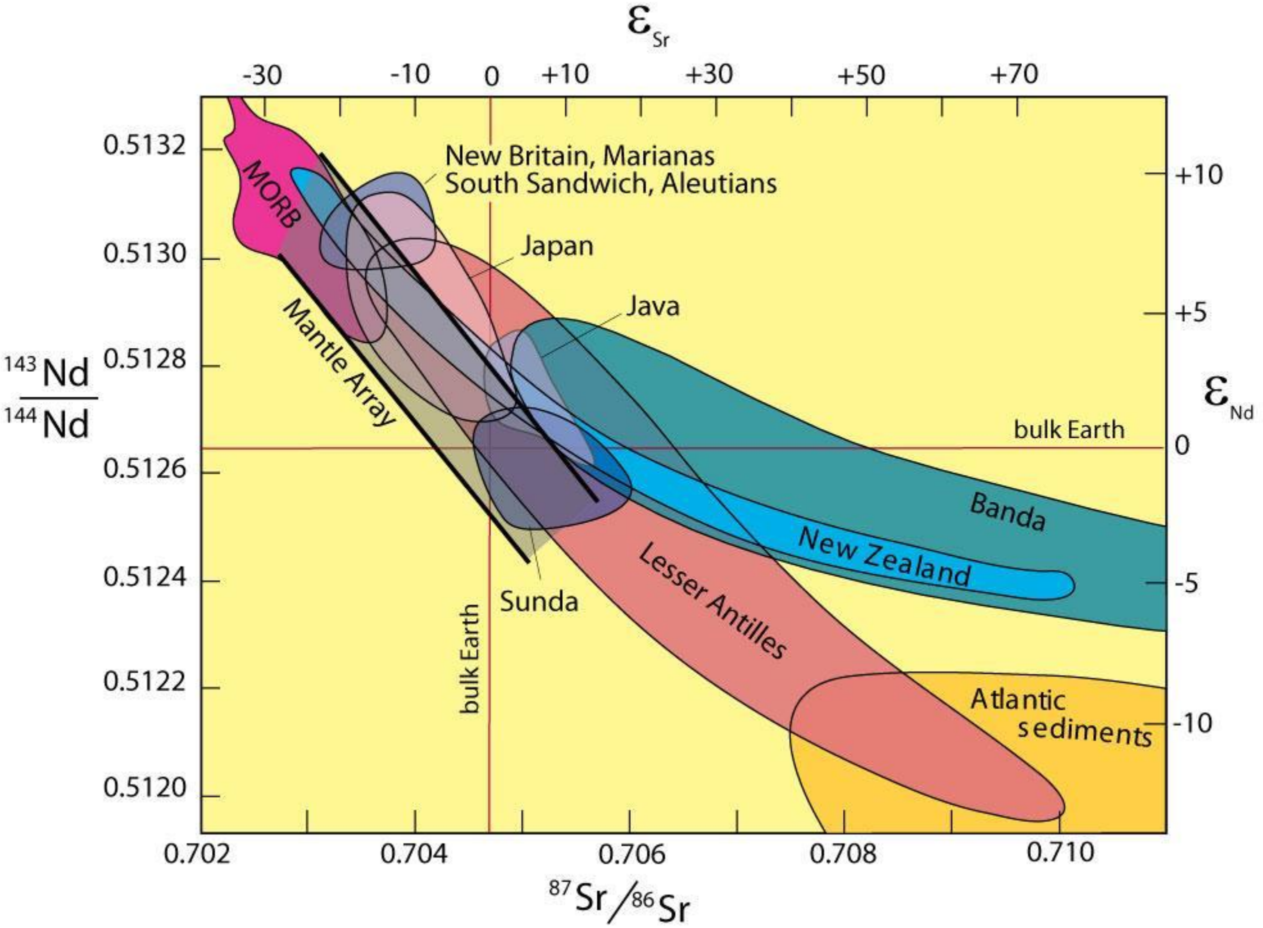


- Fluids from shallow dehydration of oceanic crust is too dilute in Mg to affect the mantle wedge.
- Serpentinized peridotites are more effective metasomatic agents.

Hu et al. GCA 2020

Do arc lavas show slab signatures?

Lesser Antilles arc lavas have highly enriched isotopic signatures (Sr, Nd, Pb), similar to sediments



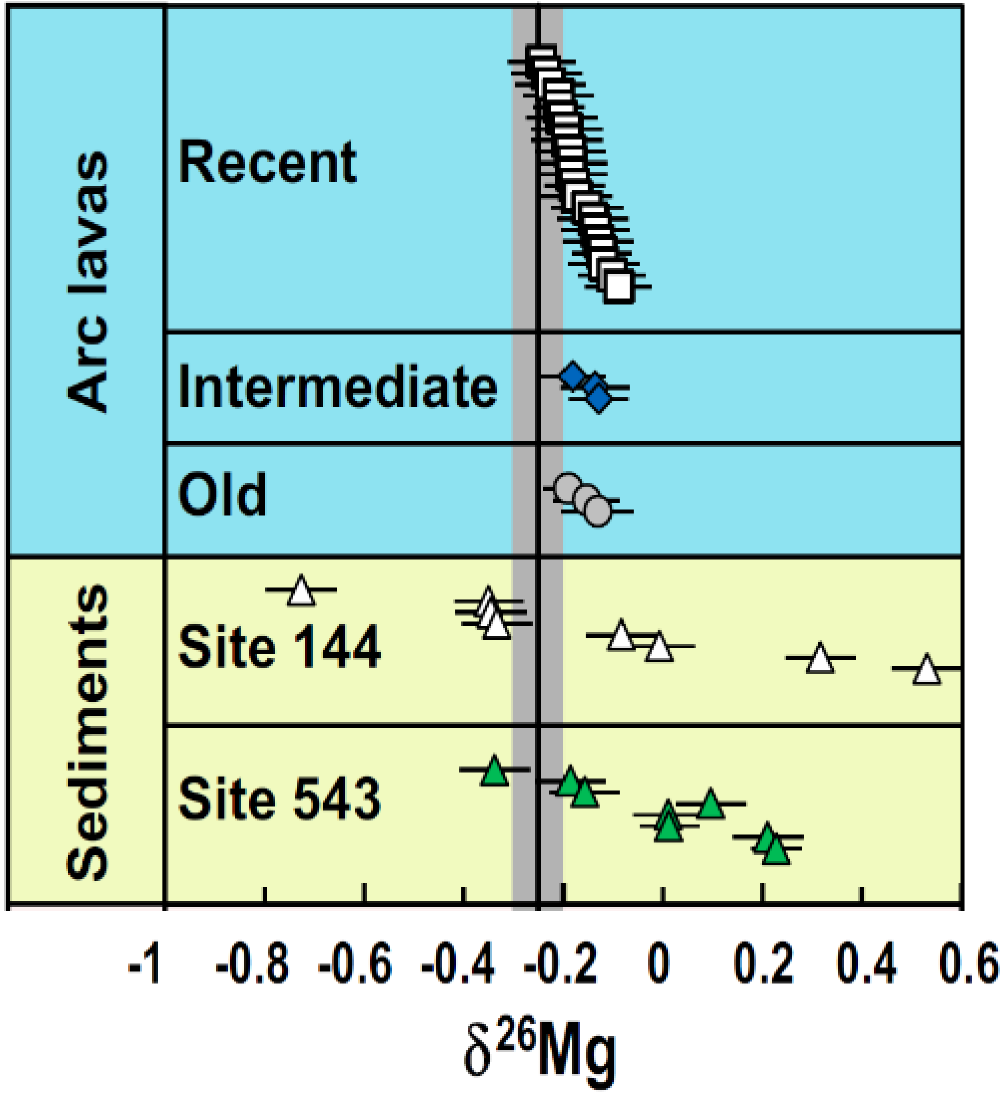
Winter, J. Introduction to Igneous & Metamorphic Petrology

δ^{26}Mg of Lesser Antilles arc lavas

Subducting sediments:
-0.76‰ to 0.52‰,

Arc lavas:
-0.25‰ to -0.10‰,
Mean = -0.18‰

Mantle: -0.25 ± 0.04‰

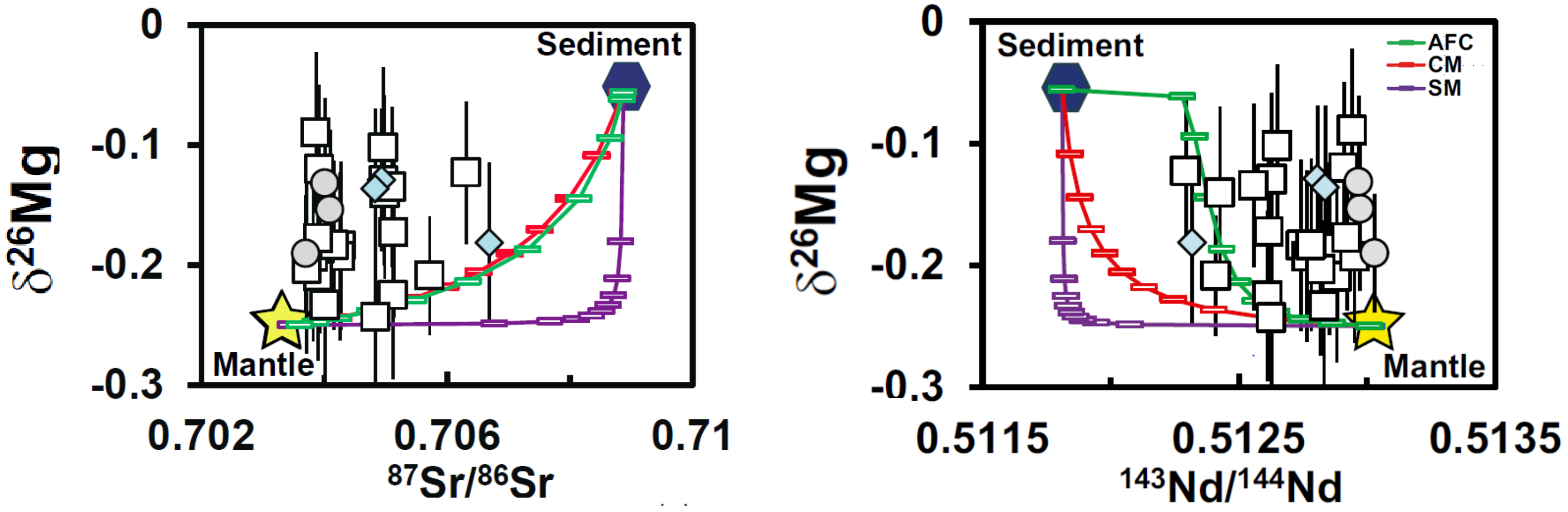


Teng et al. PNAS 2016

Origins of elevated δ^{26}Mg in arc lavas

Sediment addition caused elevated δ^{26}Mg?

- **SM**: adding sediments to mantle source
- **CM**: adding sediments to arc magma in arc crust
- **AFC**: assimilation and fractional crystallization of arc magma



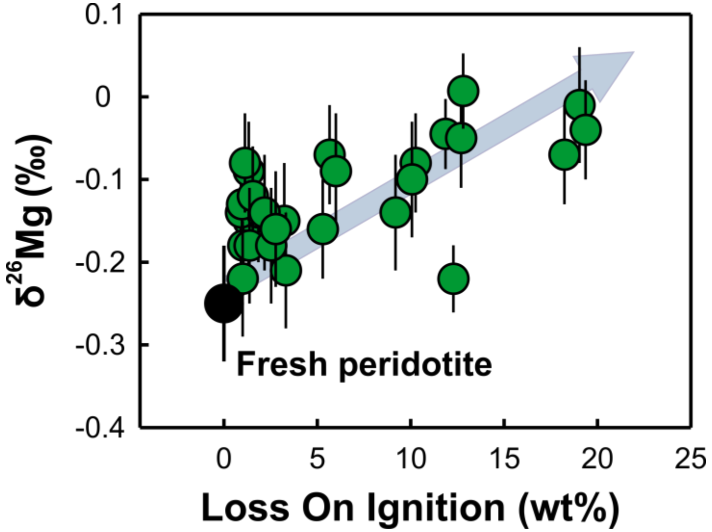
Sediment addition alone cannot explain their δ^{26}Mg variations.

Teng et al. PNAS 2016

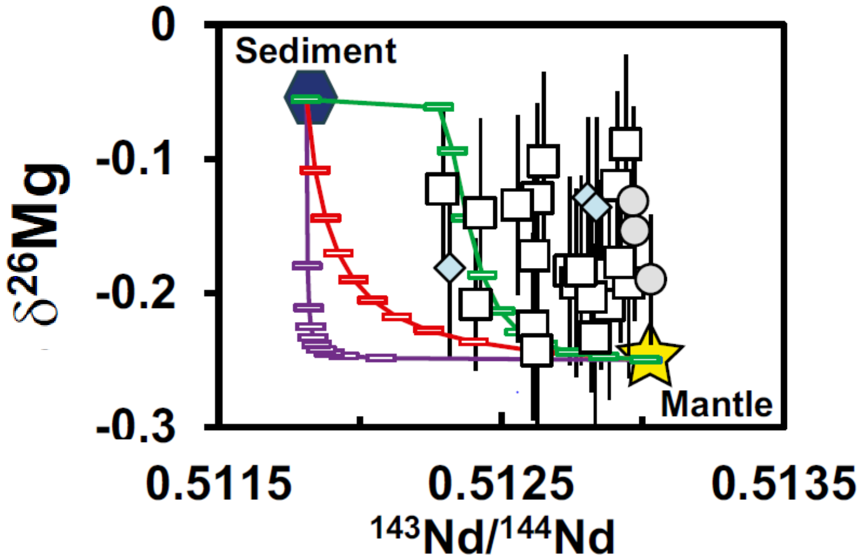
Sources for elevated δ^{26}Mg in arc lavas

Mg-rich, high-δ^{26}Mg fluids are required

→ Dehydration of altered oceanic mantle


Altered oceanic mantle

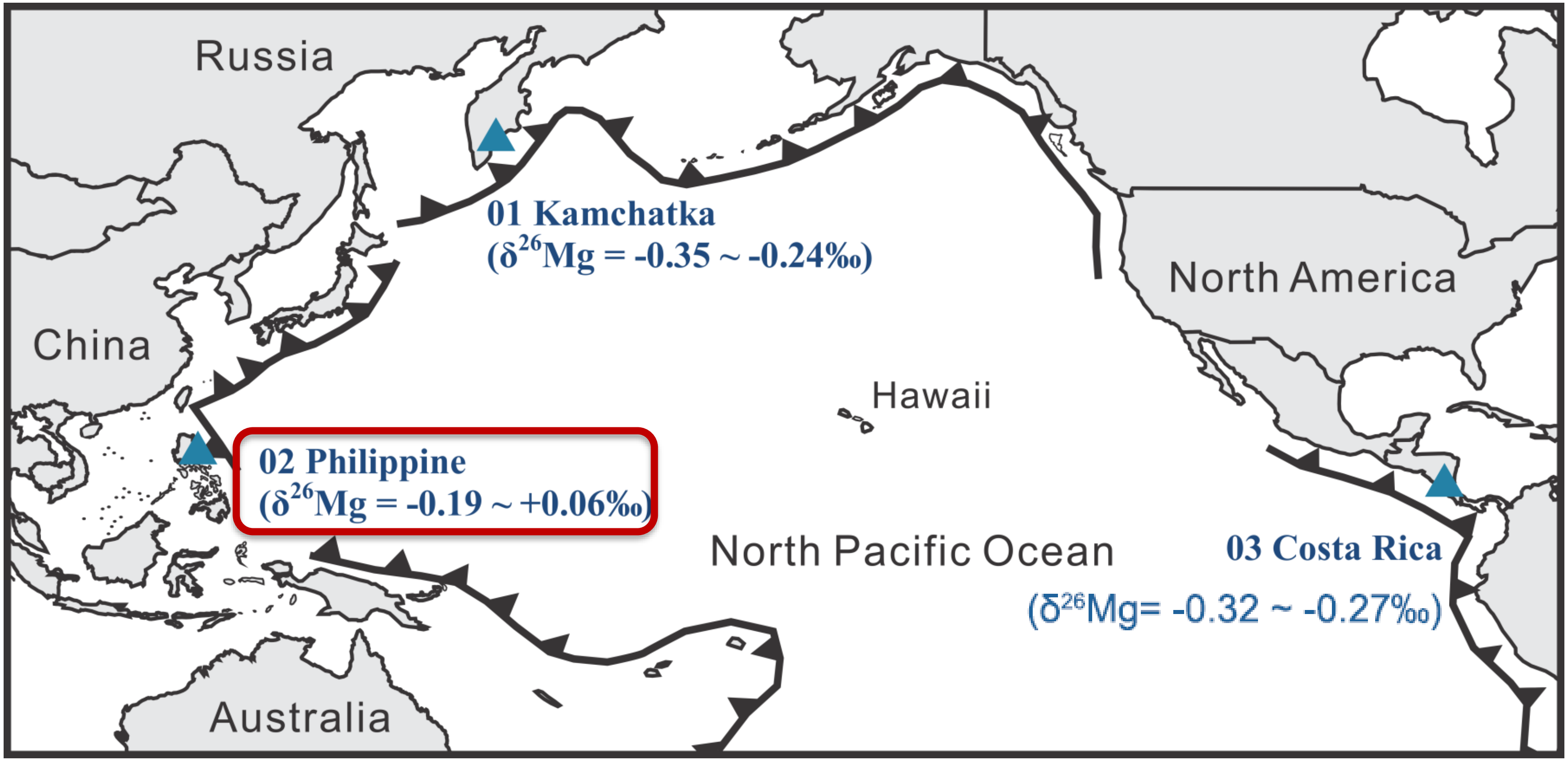
Liu et al. 2017 GCA



Teng et al. PNAS 2016

Comparison with other arcs

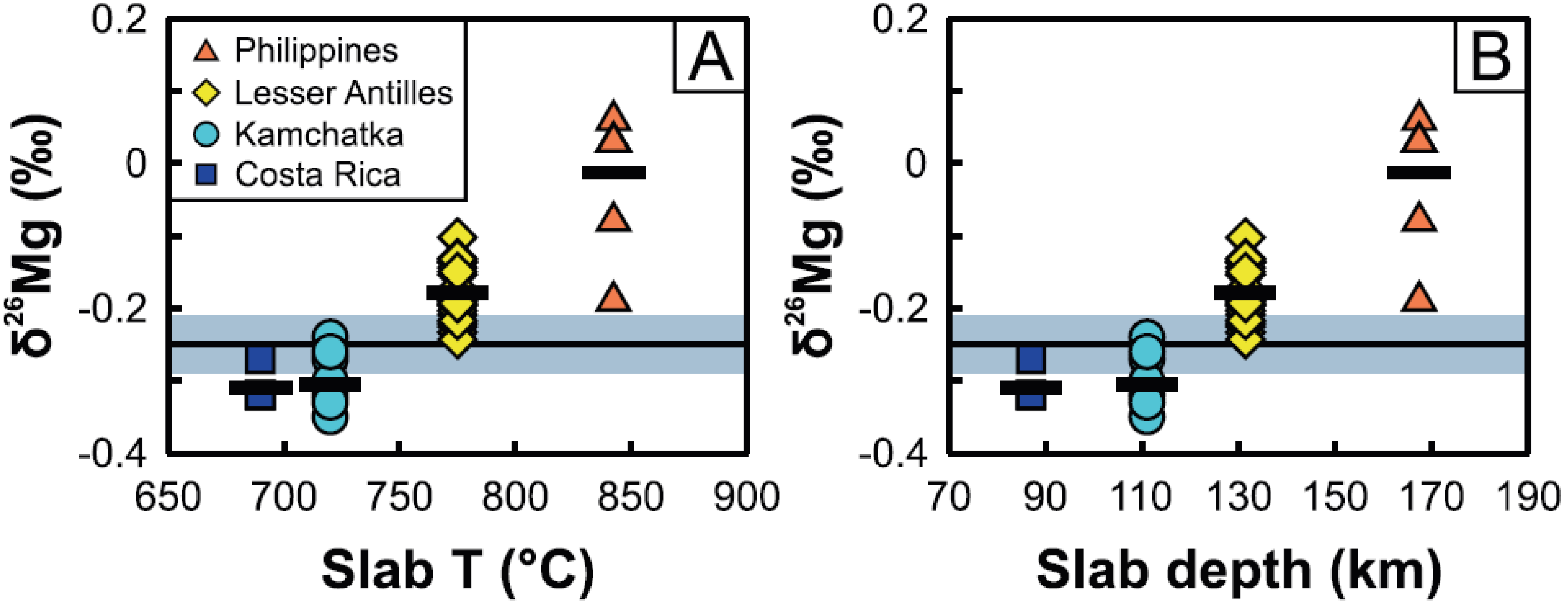
Is high-δ^{26}Mg a common feature for arc lavas?



Li et al. NSR 2017

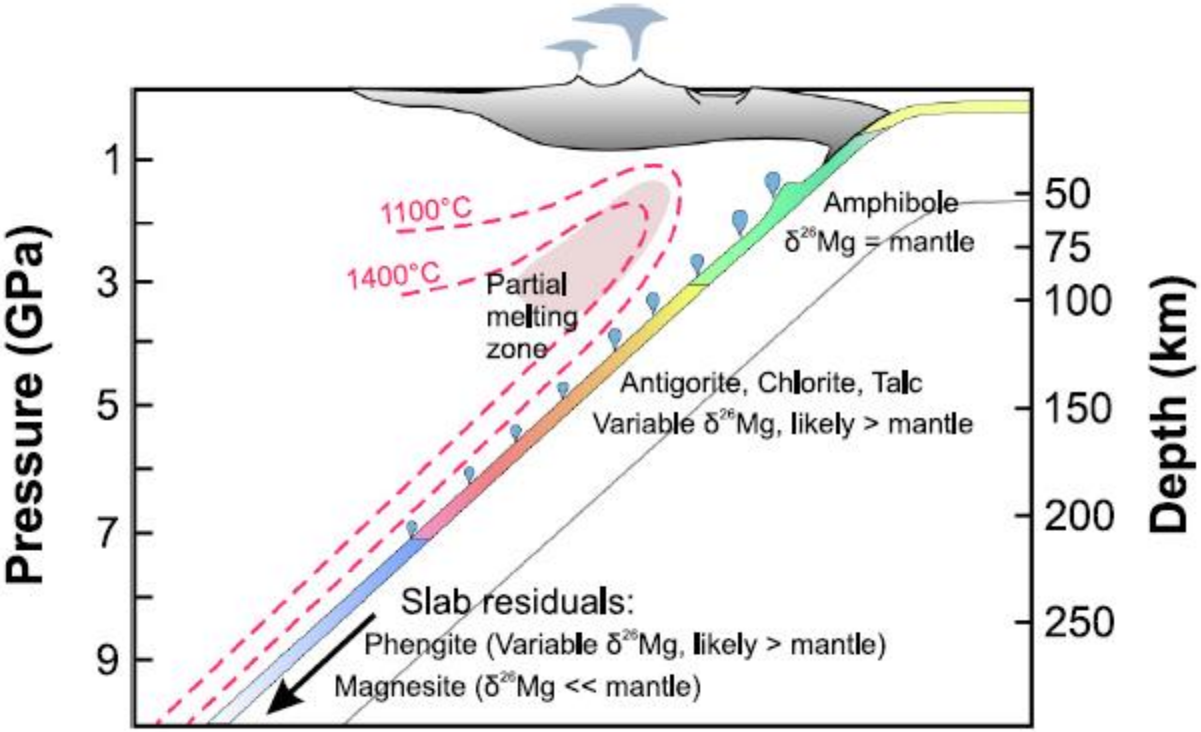
Thermal structure control on arc lava δ^{26}Mg

Altered oceanic mantle (serpentinite) dehydrates at deeper depth than hydrous minerals in oceanic crust.



Hu et al. GCA 2020

Implications for Mg cycling in subduction zones and beyond



Shallow oceanic crust dehydration: amphibole, chlorite → δ^{26}Mg = mantle

Deep oceanic mantle dehydration: serpentine, talc → δ^{26}Mg >> mantle

Beyond volcanic front:

K-rich phengite, phlgopite → δ^{26}Mg likely different from the mantle

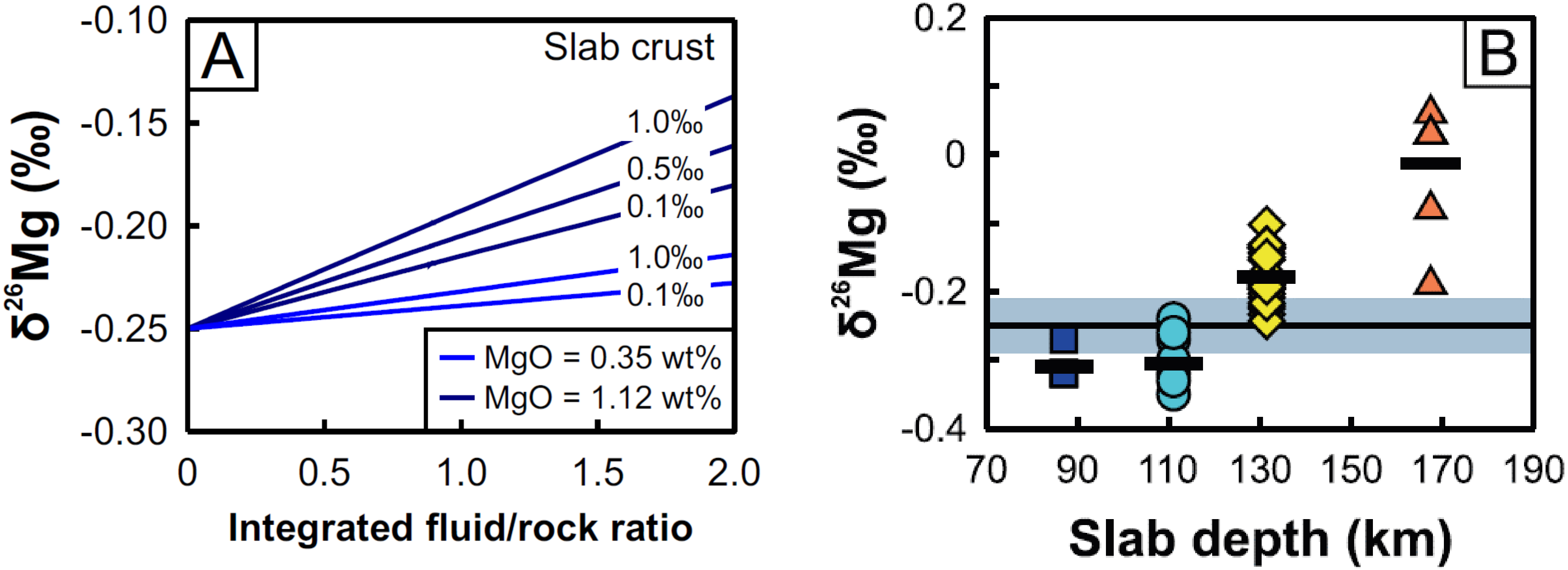
Magnesite → δ^{26}Mg << mantle

Summary

2. How does slab signature transfer to mantle wedge and arc magmas?

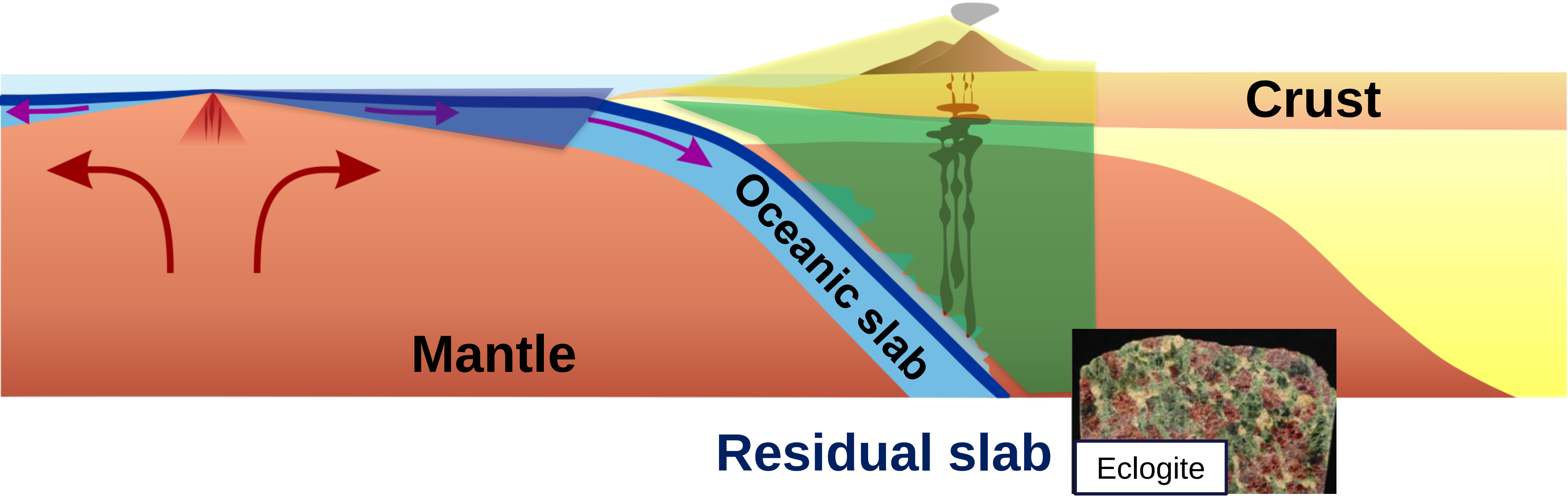
   Thermal structure of subduction zone affects arc magma composition.

   - Dehydration of oceanic crust does not supply enough Mg to alter the mantle wedge.
   - Dehydration of oceanic mantle is more likely the mechanism.



Tracing subduction recycling with Mg isotopes

1. What processes control the compositional variation in subducting slab?
2. How does slab signature transfer to mantle wedge and arc magmas?
3. How do subducted slabs contribute to mantle heterogeneity?
   eclogites, pyroxenites, and basalts



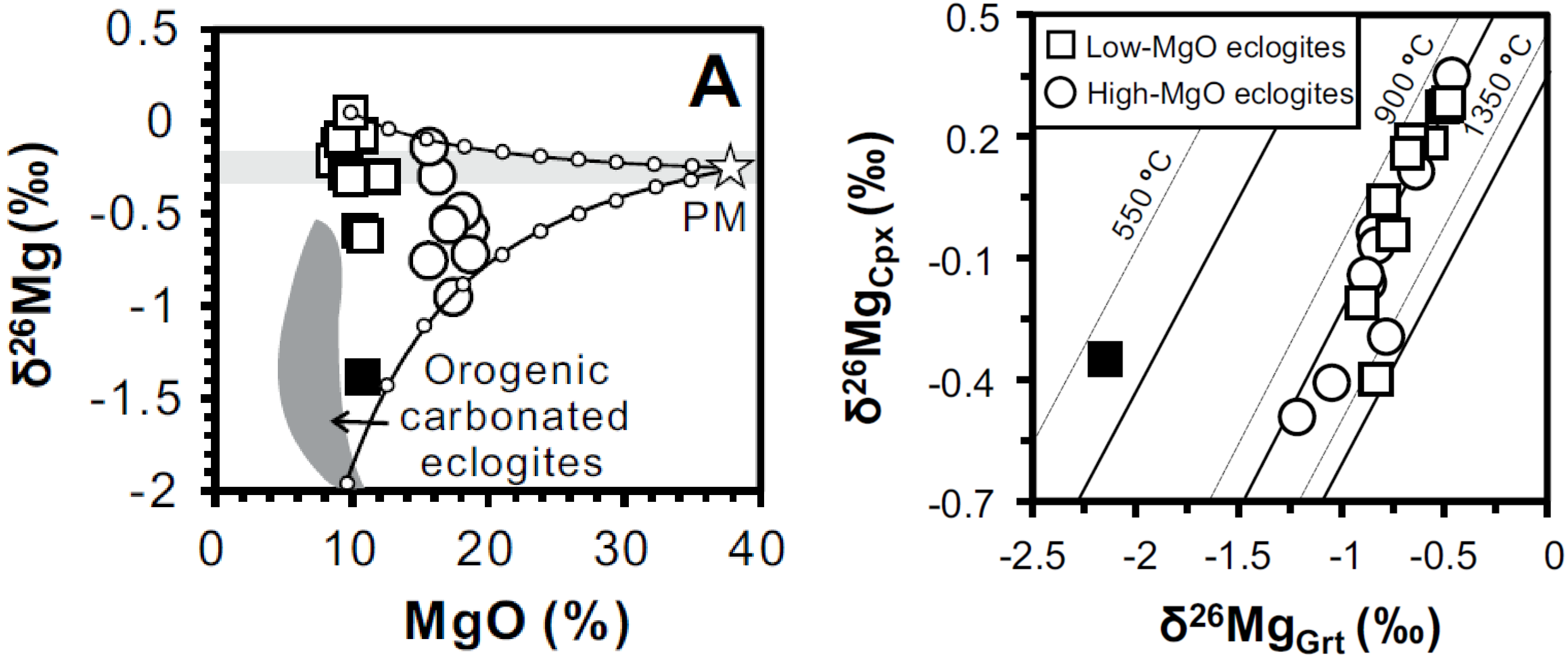
Cratonic eclogite δ^{26}Mg vary with origins

- **Low-MgO eclogites (MgO < 15 wt%)**

  δ^{26}Mg = -1.38 to 0.05‰; originated as recycled AOC

- **High-MgO eclogites (MgO>15 wt%)**

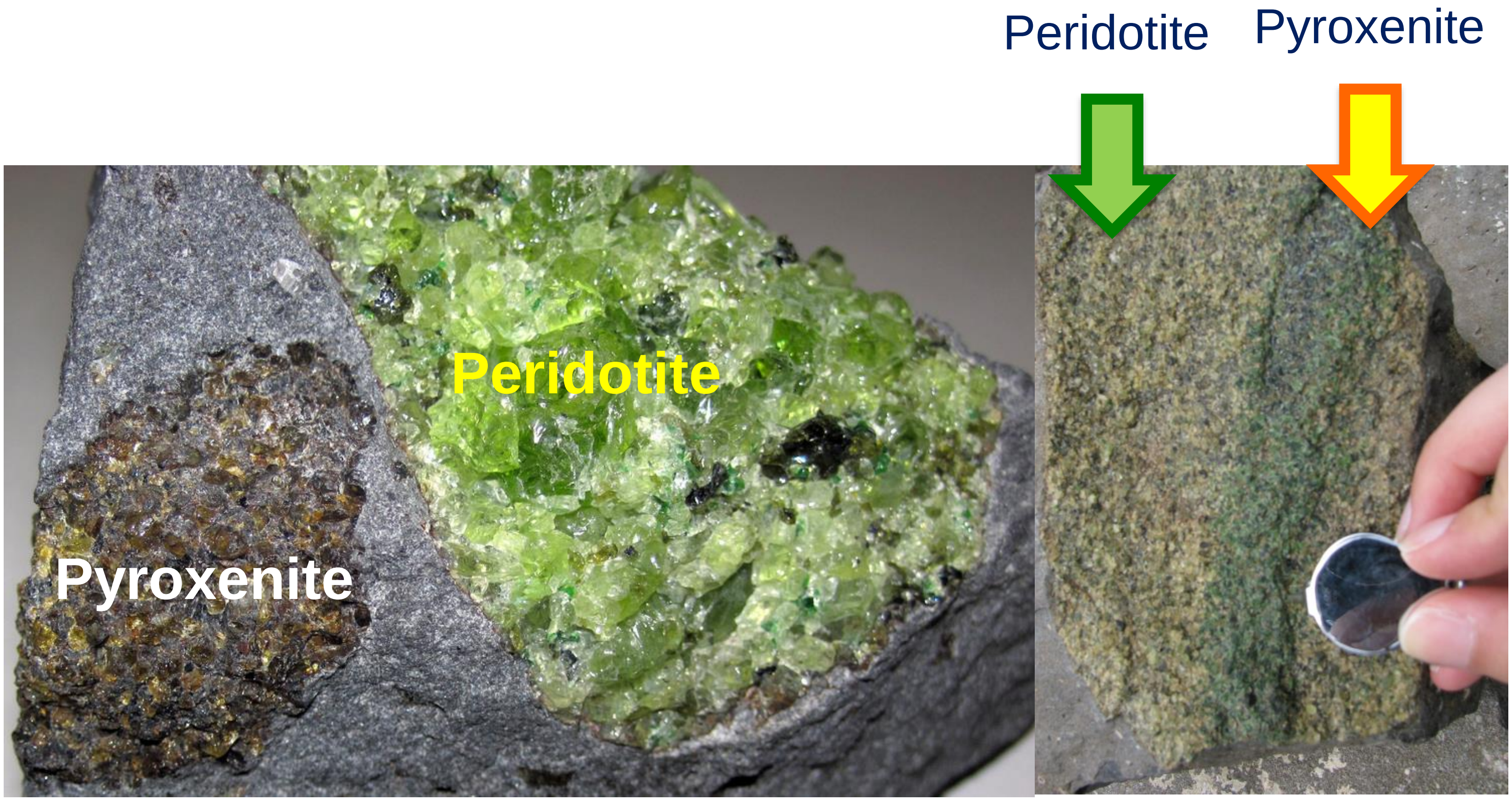
  δ^{26}Mg = -0.95 to -0.13‰; formed by reaction of low-MgO eclogite melt with peridotites



Wang et al. Geology 2015

Pyroxenites: mantle lithological heterogeneity

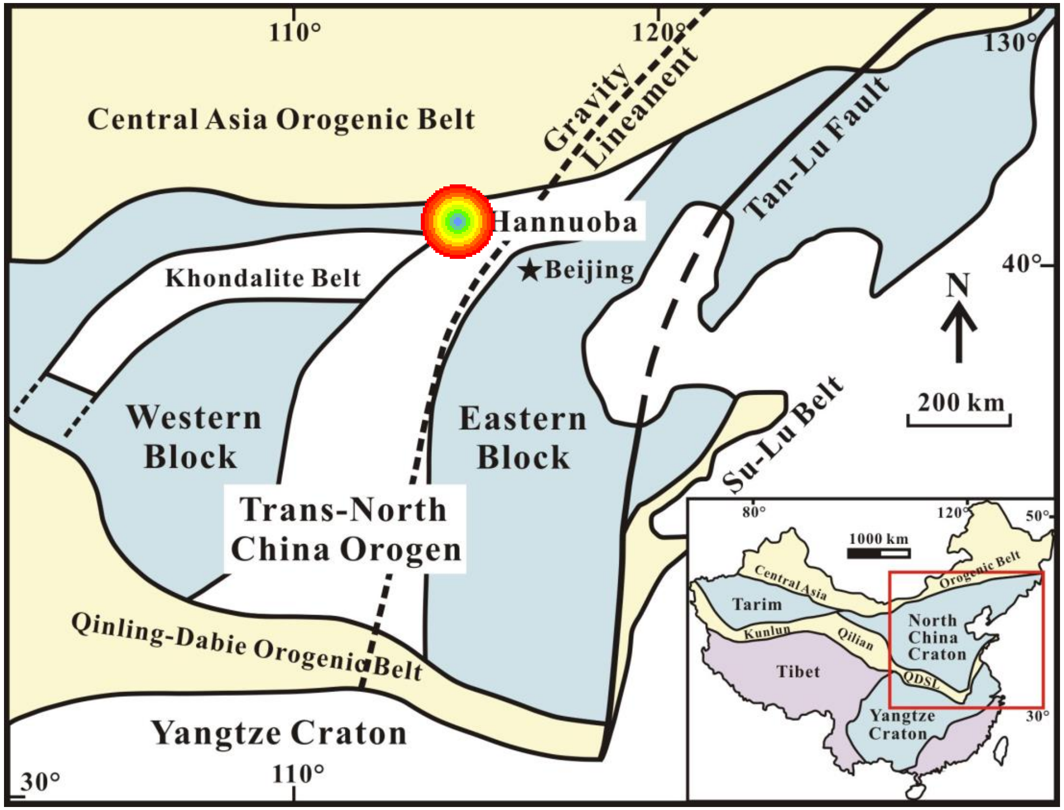
Pyroxenites represent high degree melt-peridotite interactions.

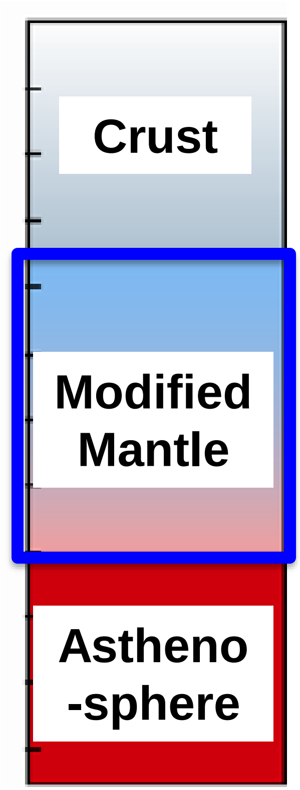


http://www.deep-earth.org/

Pyroxenites samples

A thick layer of mantle that has been strongly modified by multi-stage melt infiltration events





Crust

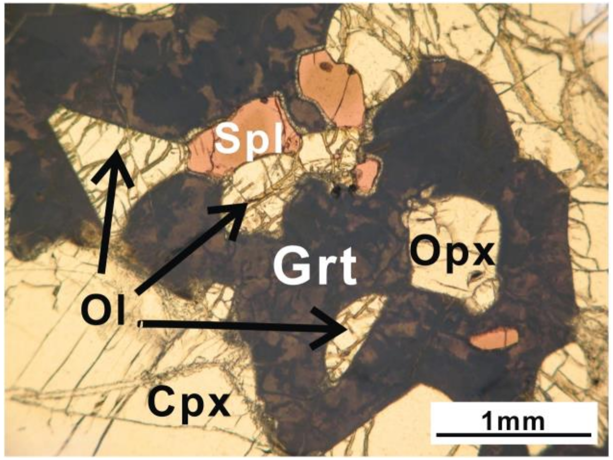
Modified Mantle

Astheno -sphere

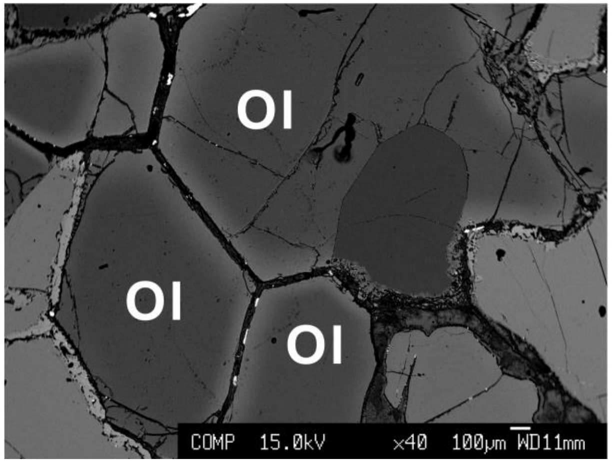
Hu et al. GCA 2016

Evidence for melt-rock interaction

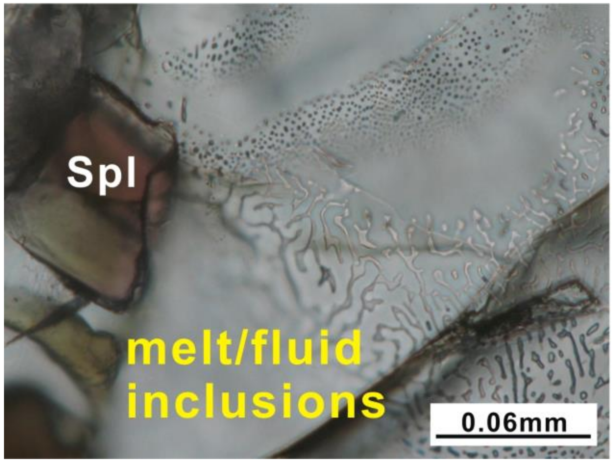
Mineral reactions



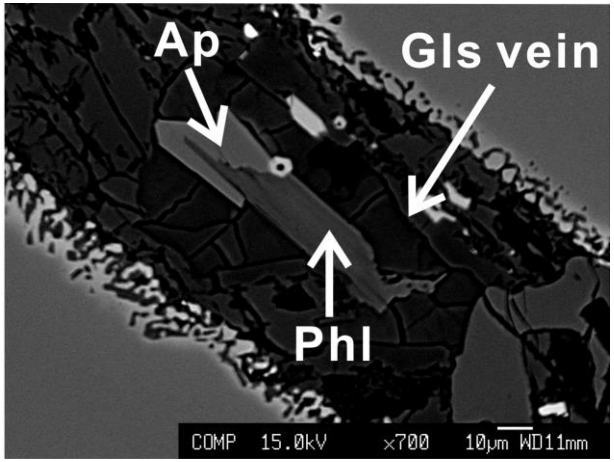
Zoned mineral



Melt/fluid inclusions

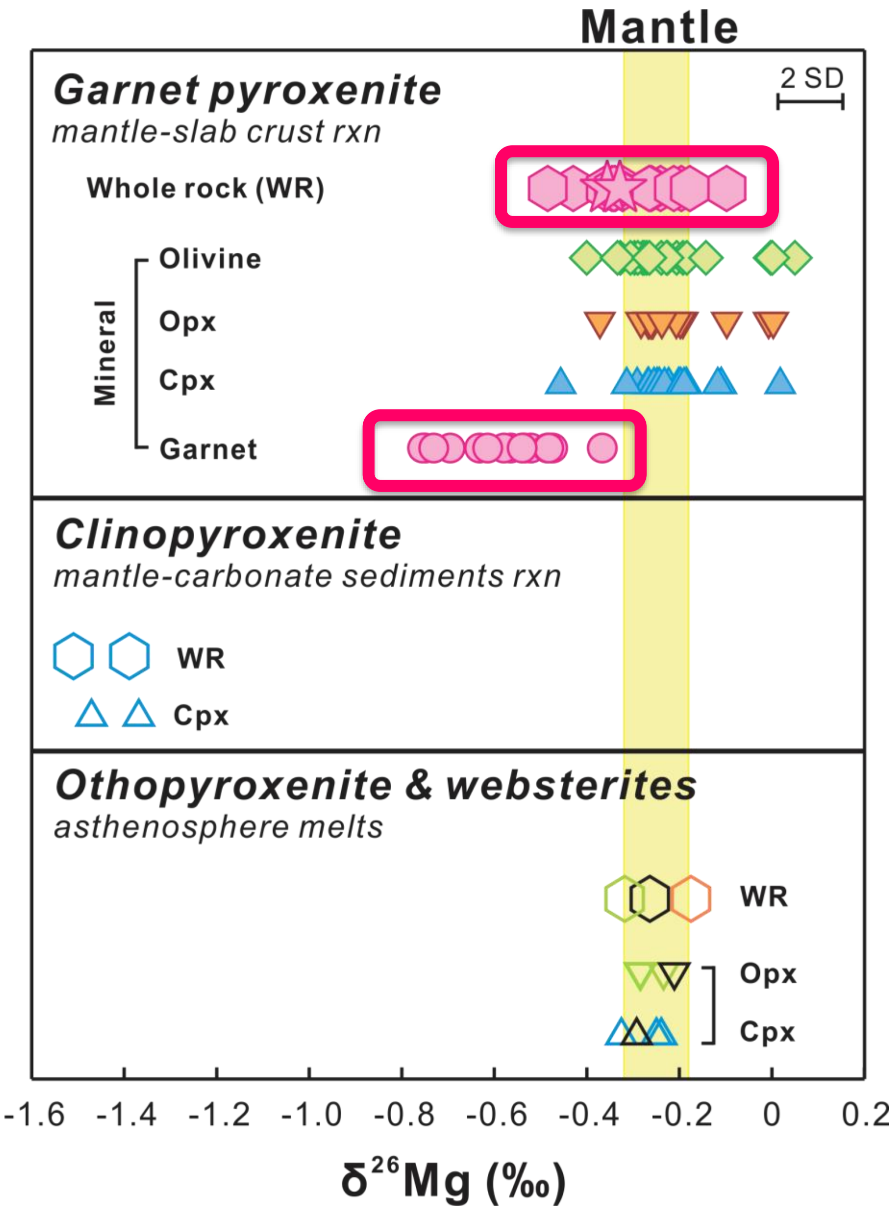


Hydrous minerals



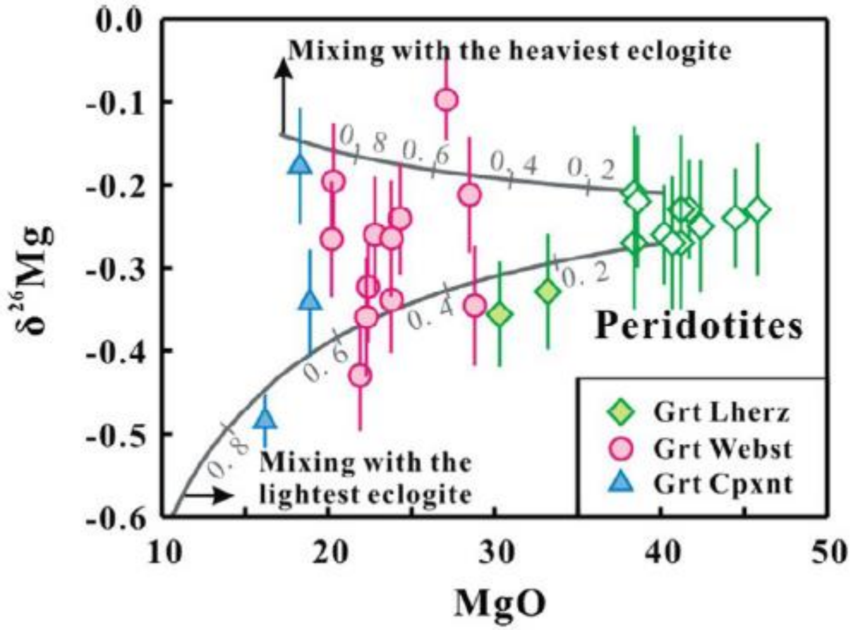
Hu et al. GCA 2016

Pyroxenite δ^{26}Mg vary with origins



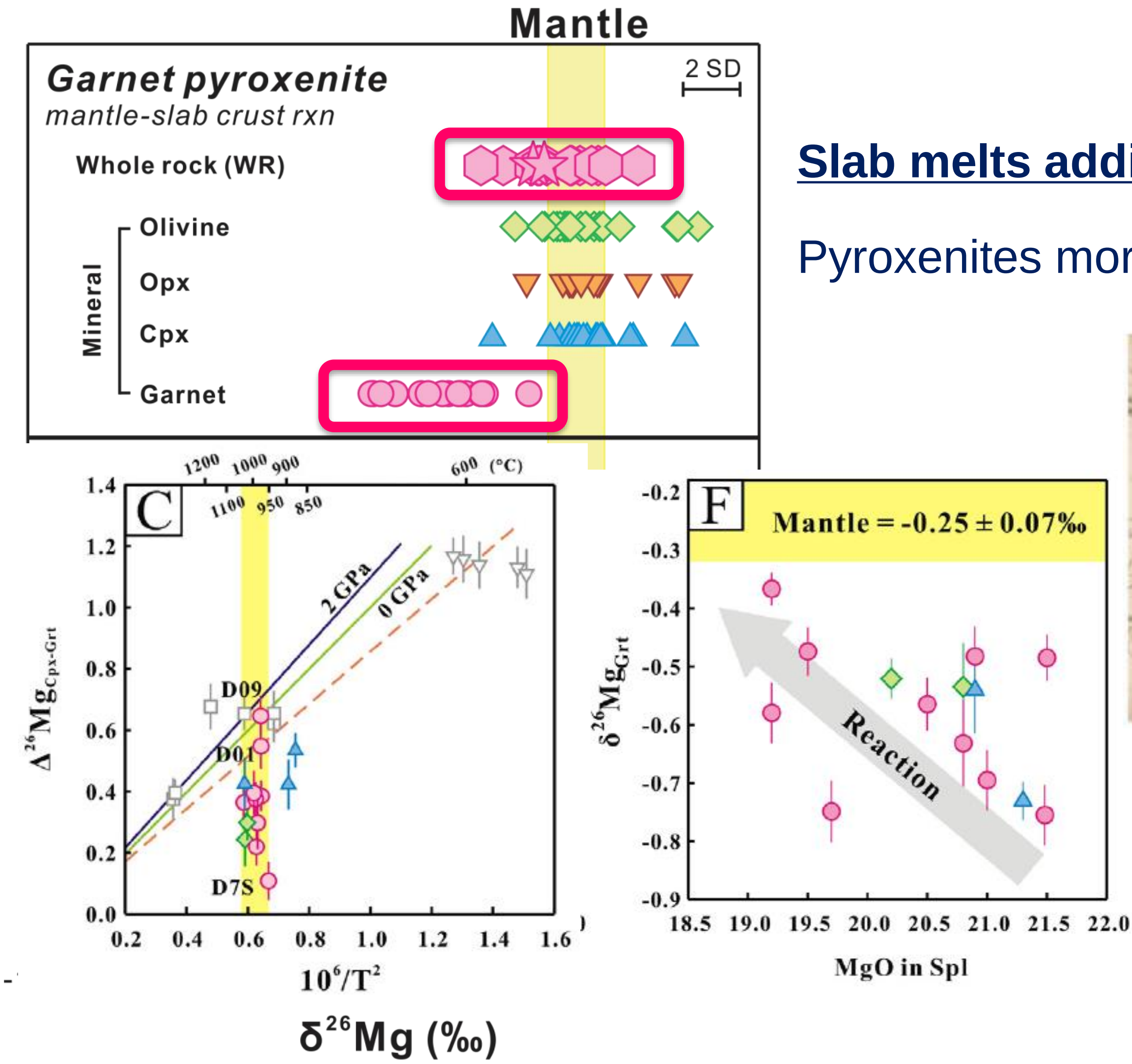
Slab melts addition

Pyroxenites more variable than mantle



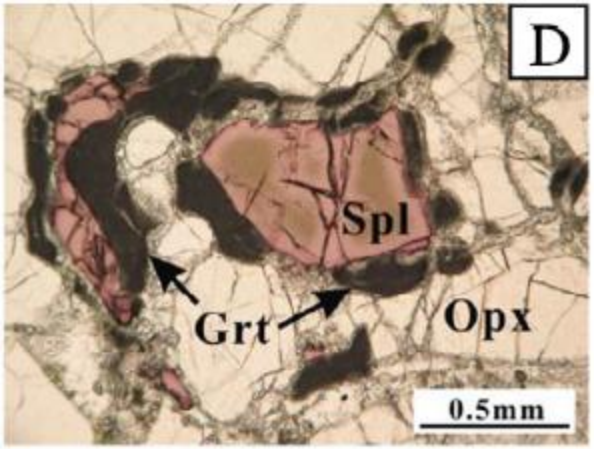
Hu et al. GCA 2016

Pyroxenite δ^{26}Mg vary with origins



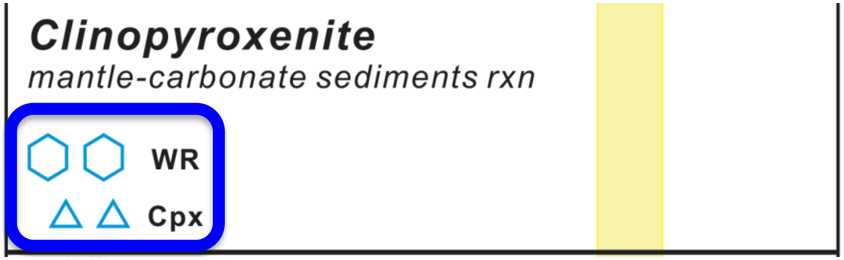
Slab melts addition

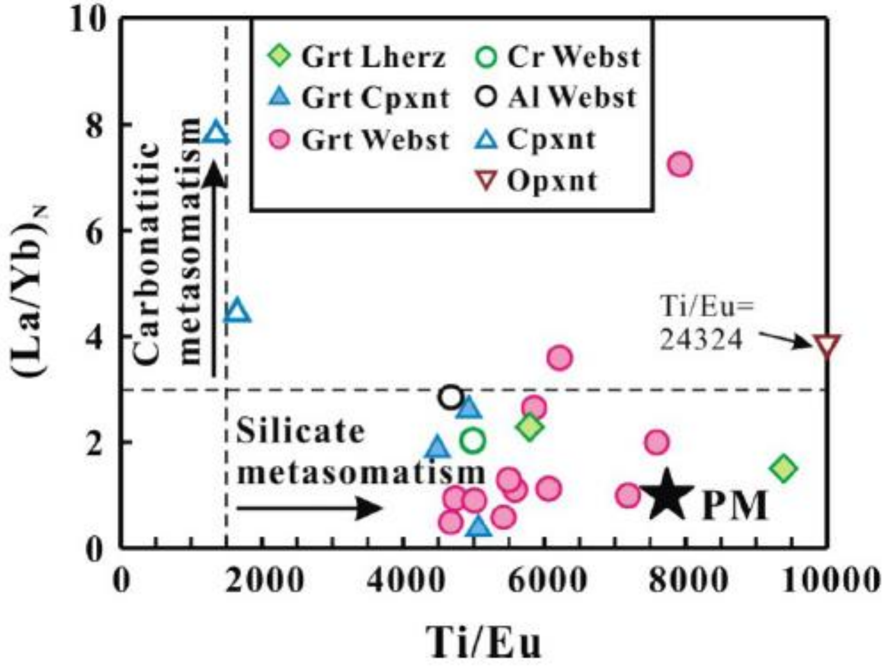
Pyroxenites more variable than mantle



Hu et al. GCA 2016

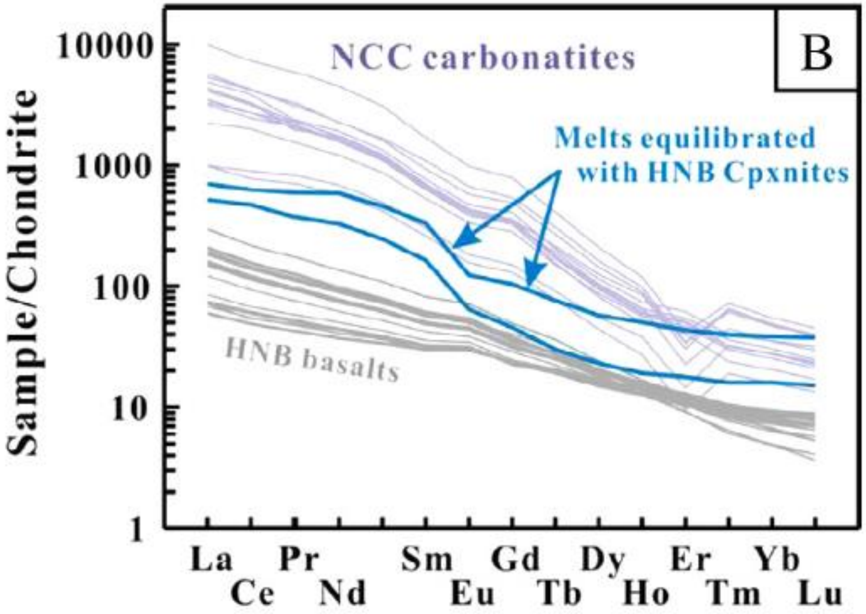
Pyroxenite δ^{26}Mg vary with origins





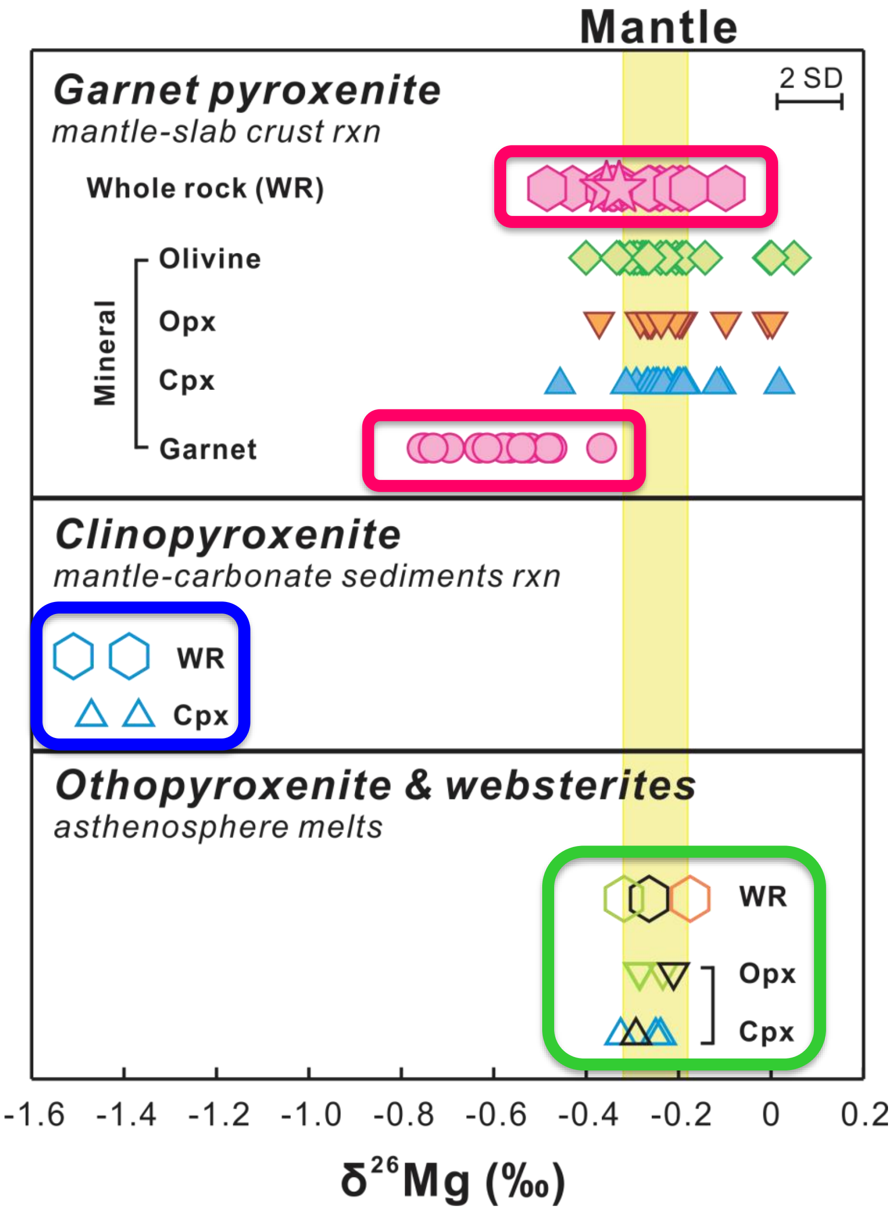
Slab carbonate sediments addition

Pyroxenites much lighter than mantle



Hu et al. GCA 2016

Pyroxenite δ^{26}Mg vary with origins



Slab melts addition

Pyroxenites more variable than mantle

Slab carbonate sediments addition

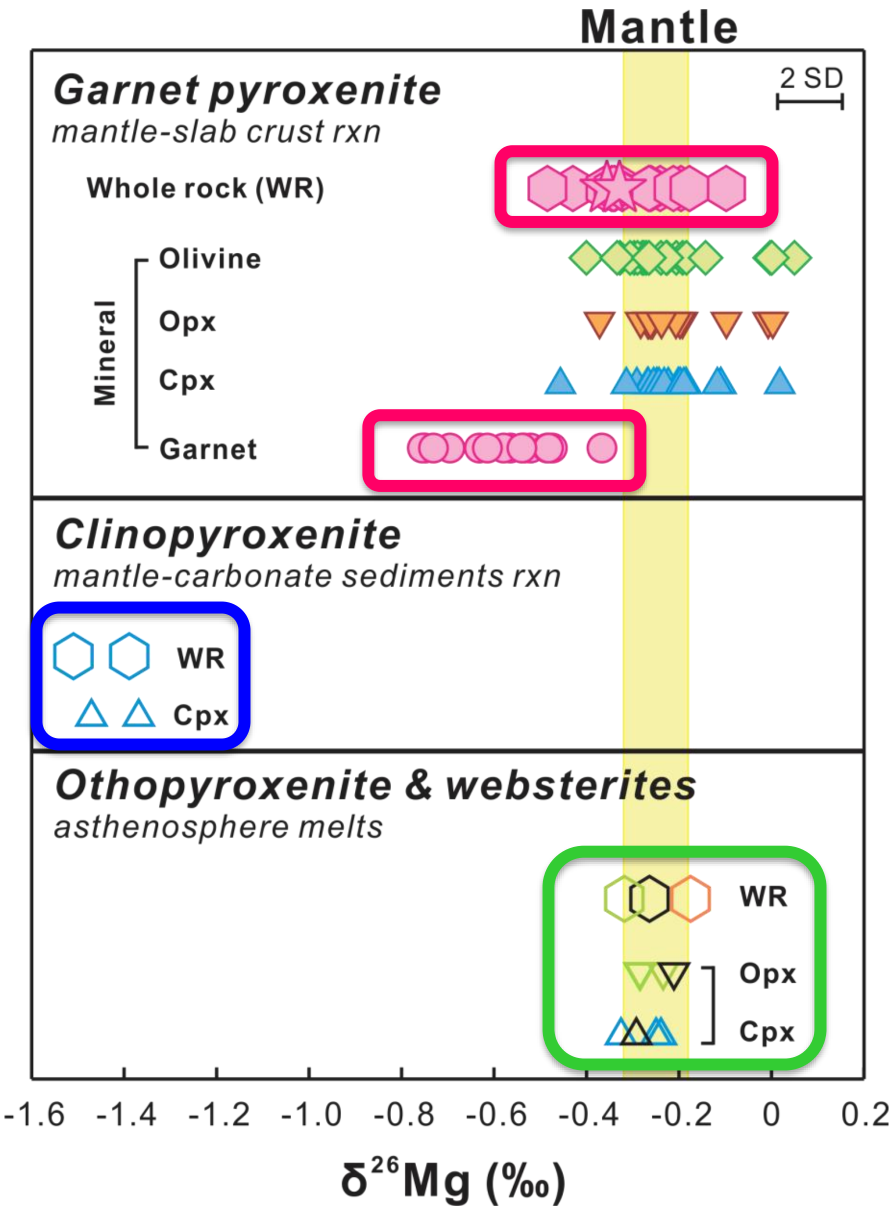
Pyroxenites much lighter than mantle

Deep basaltic melts addition

Pyroxenites = mantle

Hu et al. GCA 2016

Pyroxenite δ^{26}Mg vary with origins



Slab melts addition

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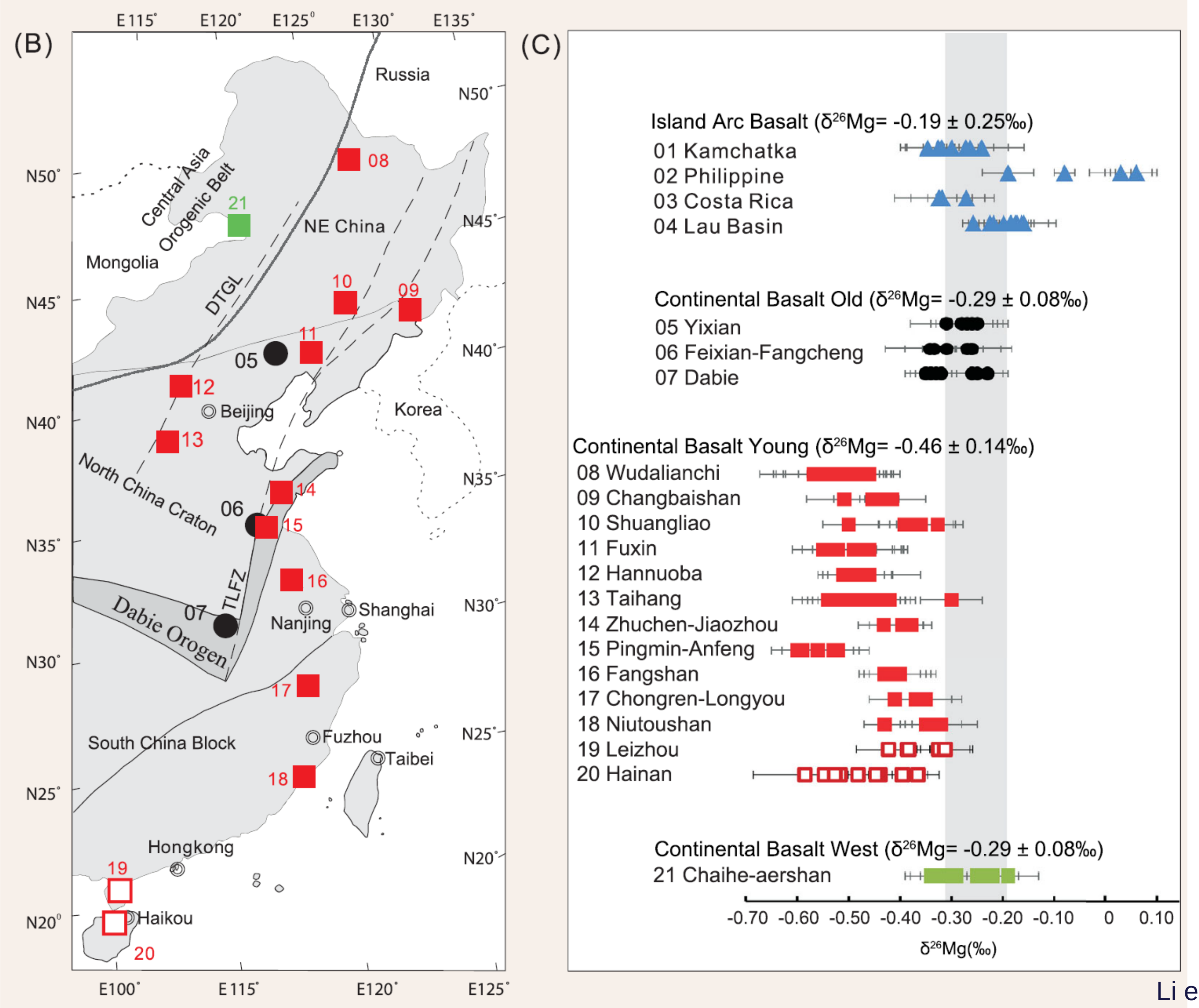
Hu et al. GCA 2016

Low-δ^{26}Mg eastern China basalts

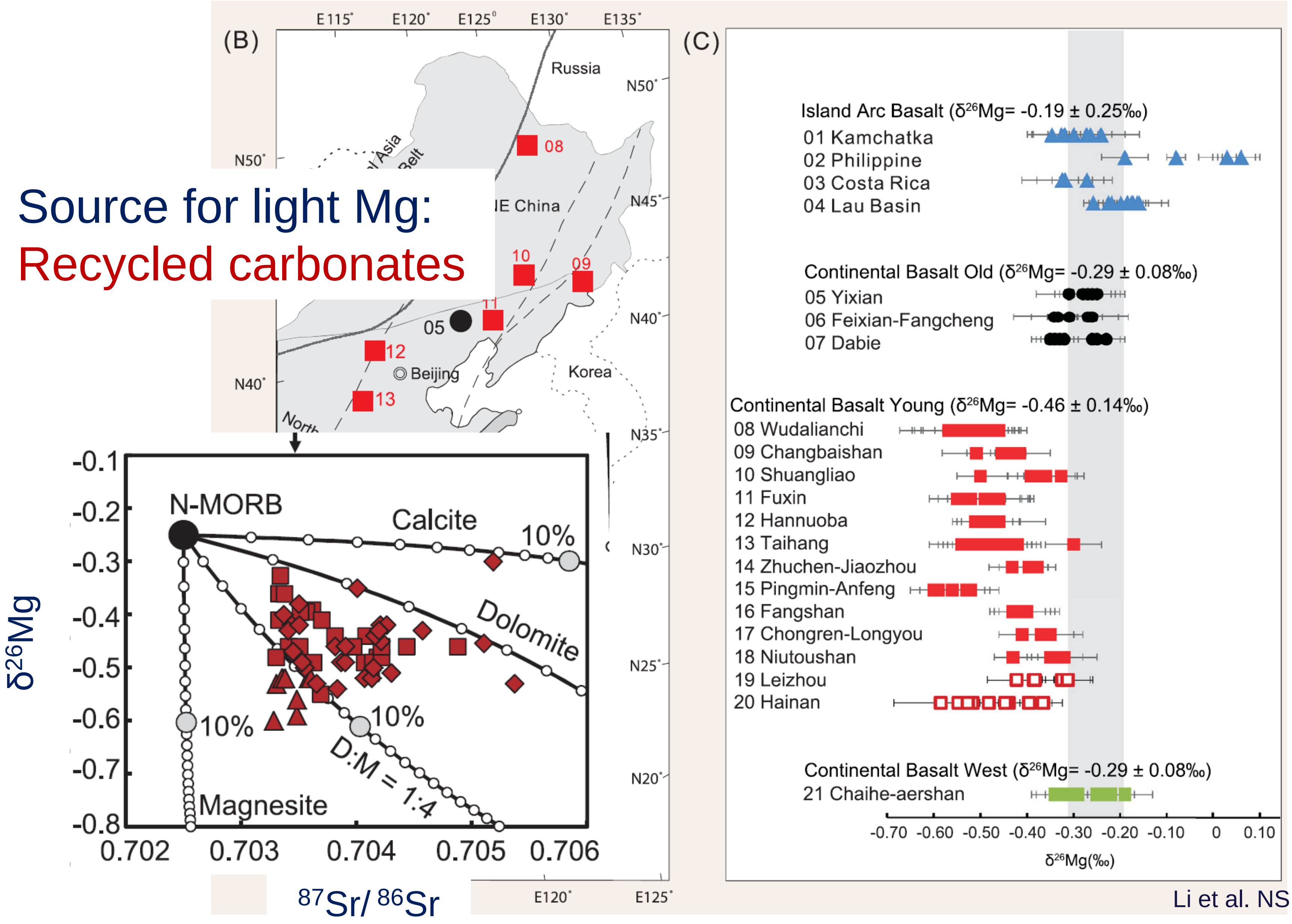


Li et al. NSR 2017

Low-δ^{26}Mg eastern China basalts

Source for light Mg:

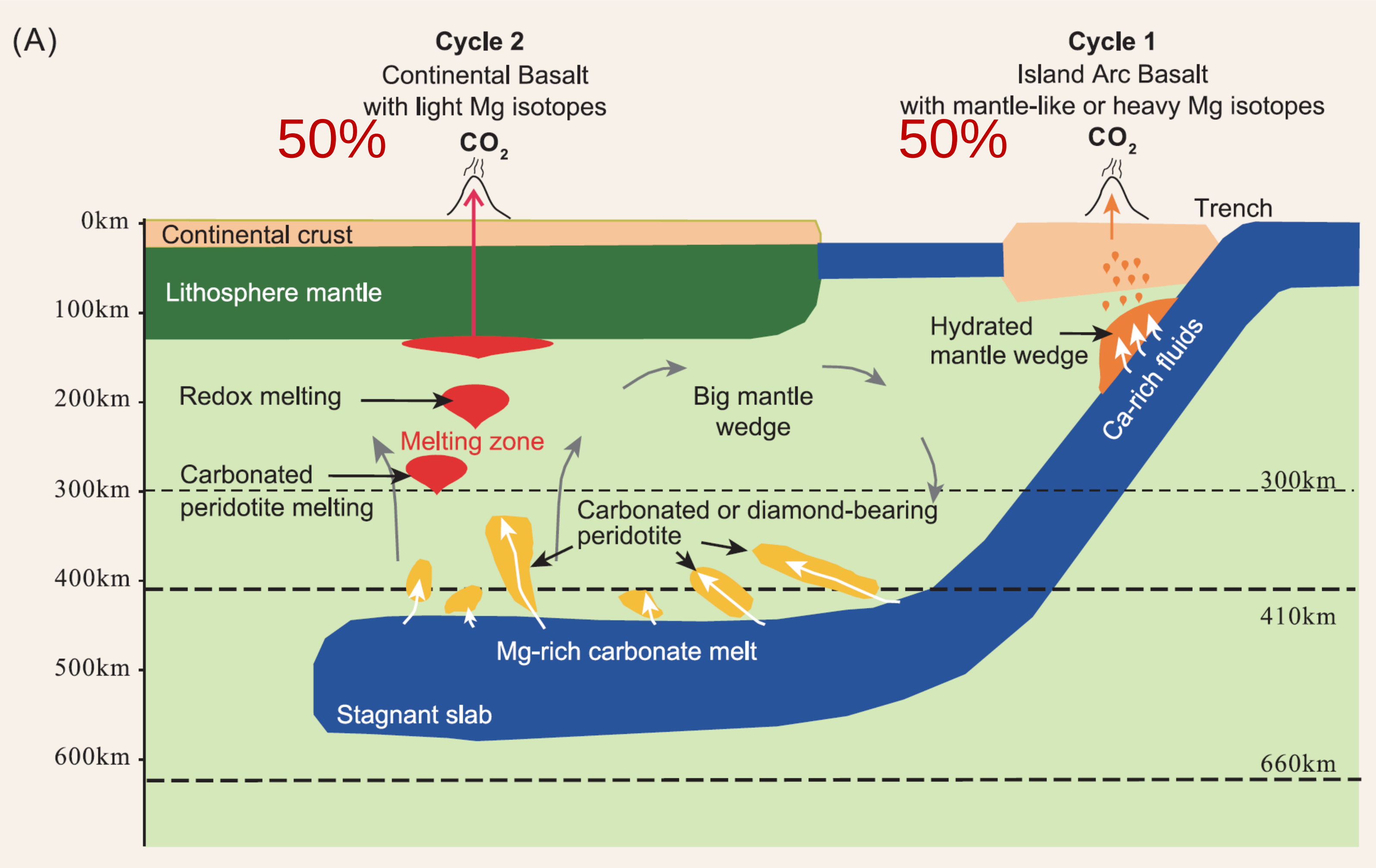
Recycled carbonates



Li et al. NSR 2017

Low-δ^{26}Mg eastern China basalts

Where mixing occurred: in the mantle source

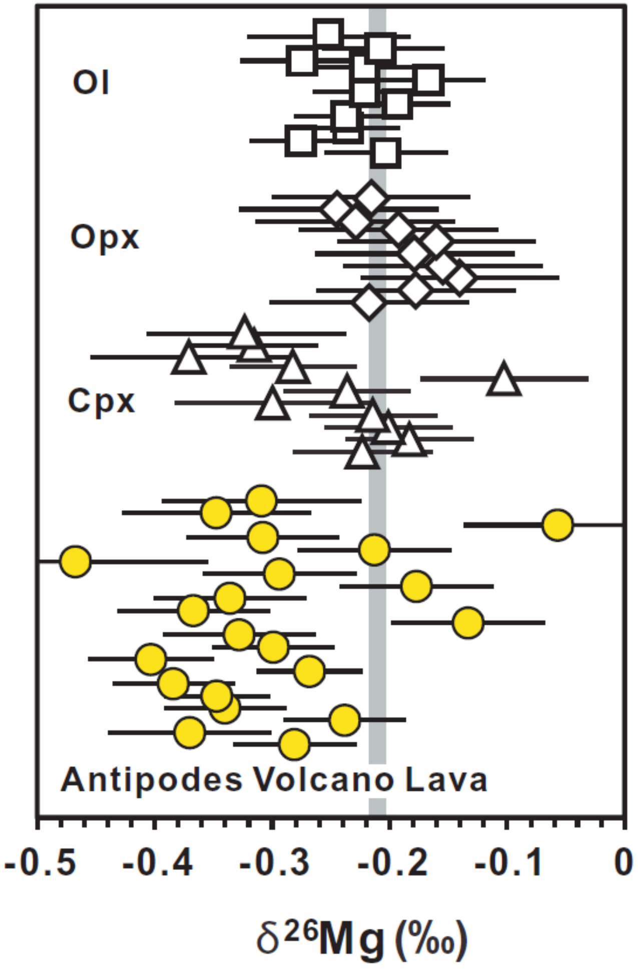


Li et al. NSR 2017

Low-δ^{26}Mg New Zealand basalts

Peridotites have mantle-like δ^{26}Mg while basalts are lighter

Other sources are involved in producing these basalts.

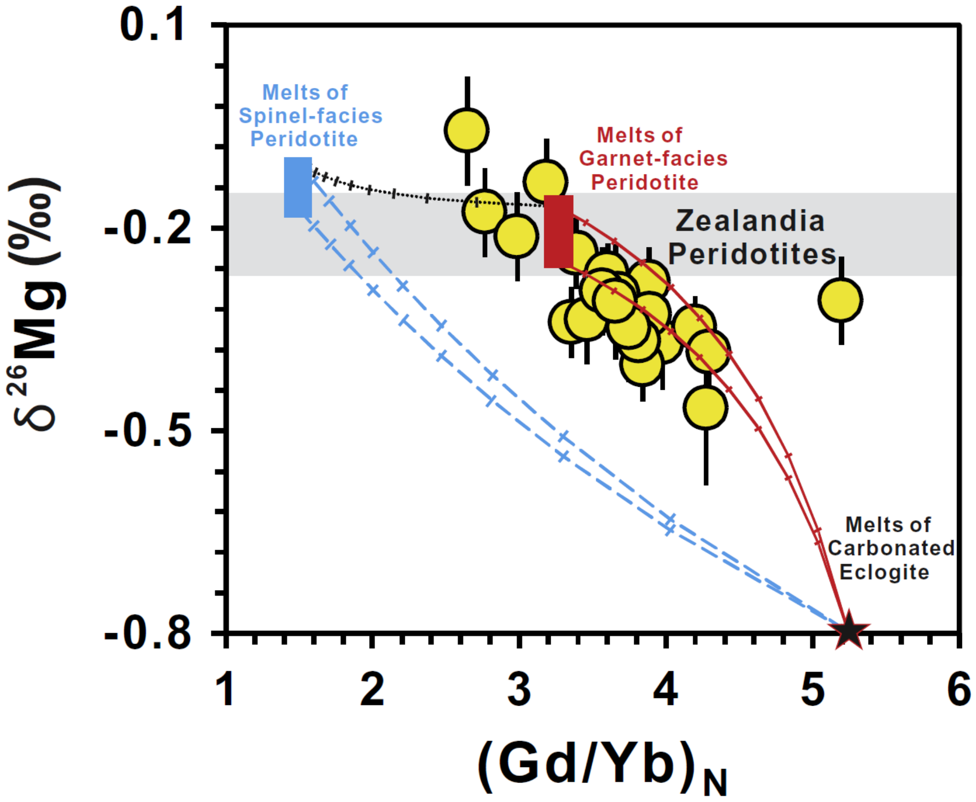


Wang et al. GCA 2016

Low-δ^{26}Mg New Zealand basalts

Source for light Mg: Recycled carbonated eclogites

Magma mixing rather than source modification



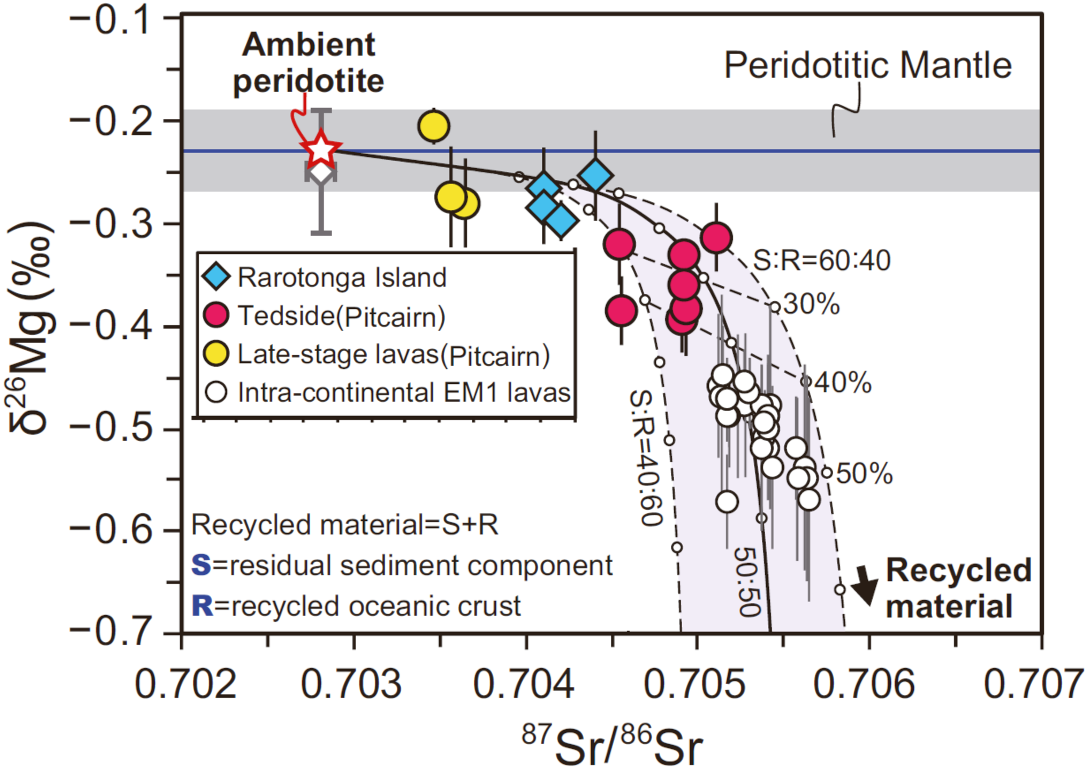
A source containing Grt

Wang et al. GCA 2016

Low-δ^{26}Mg Pitcairn OIBs

The lowest δ^{26}Mg reported in OIBs

Source of light Mg: subducted Archean dolomite

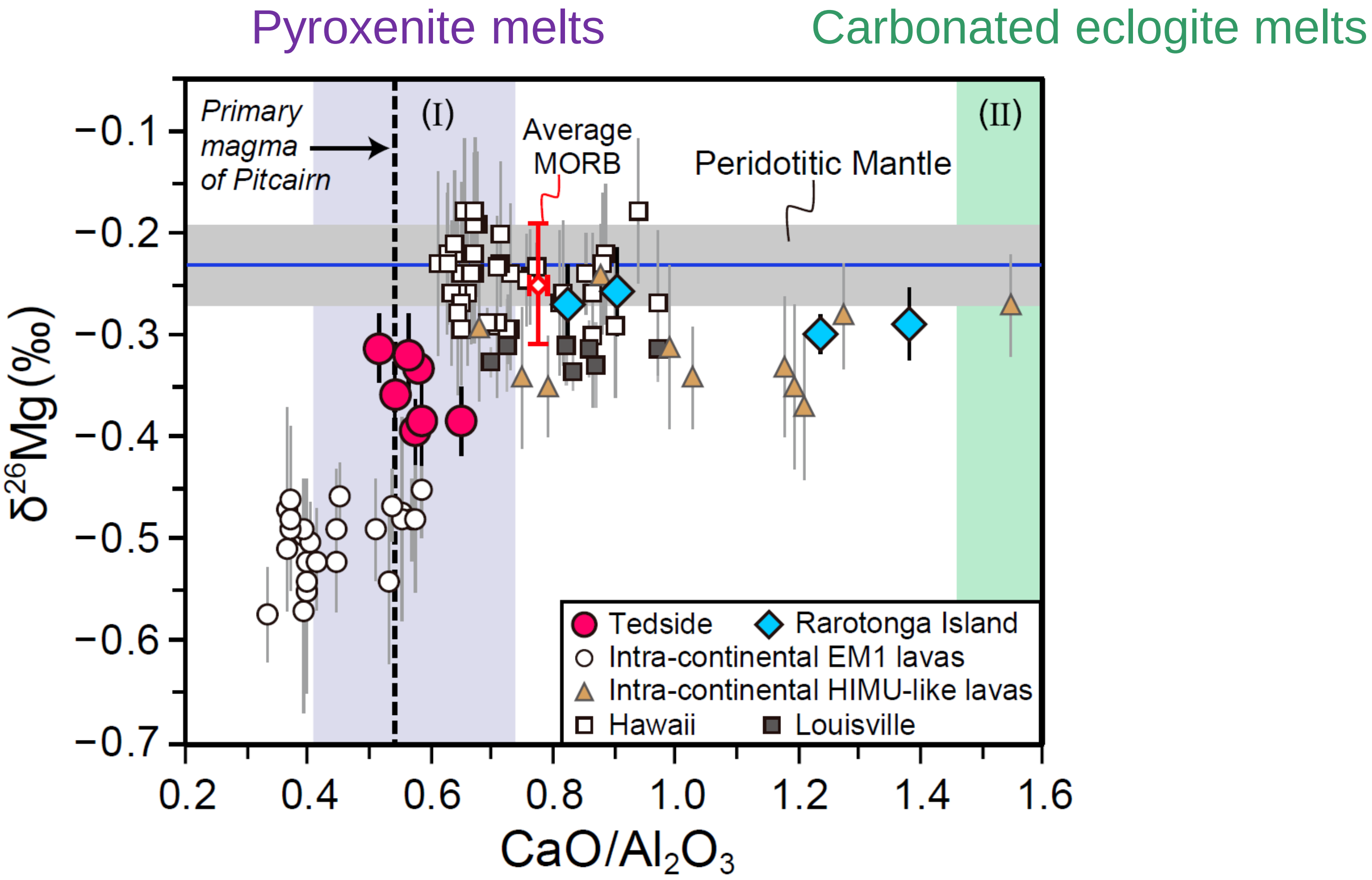


Wang et al. PNAS 2018

Low-δ^{26}Mg Pitcairn OIBs

The low CaO/Al_2O_3 is inconsistent with carbonate in their mantle source

The low δ^{26}Mg signature of dolomite is inherited by Mg-silicate



Wang et al. PNAS 2018

Low-δ^{26}Mg Pitcairn OIBs

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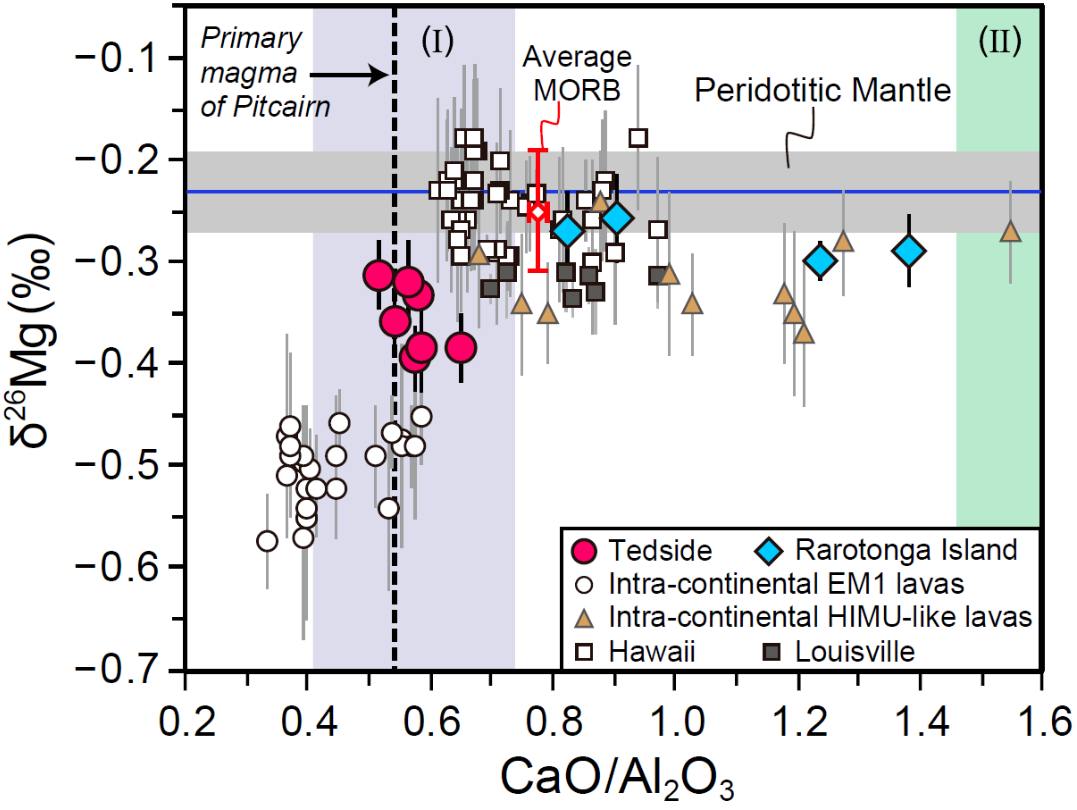
The low δ^{26}Mg signature of dolomite is inherited by Mg-silicate

Pyroxenite melts

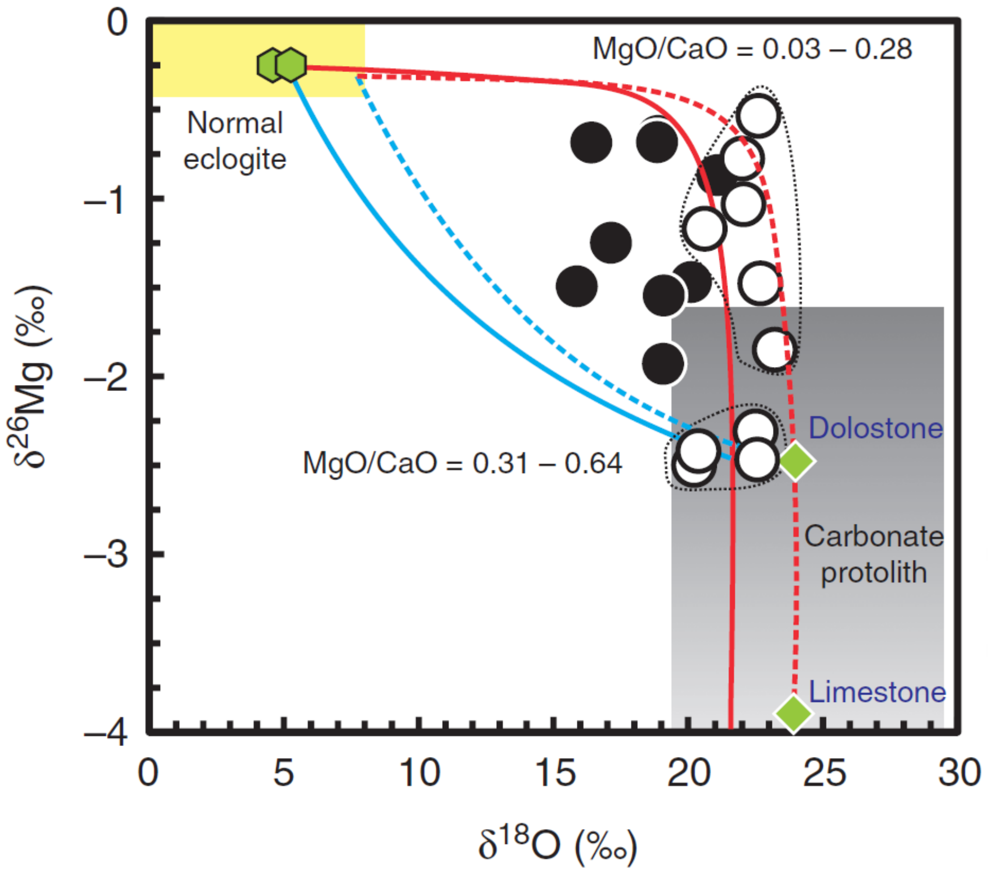
Carbonated eclogite melts



Wang et al. PNAS 2018

Mg isotope exchange between silicate and carbonate

Light Mg in marble is exchanged with heavy Mg in enclosed eclogites



Solid line: Eclogite

Dash line: Marble

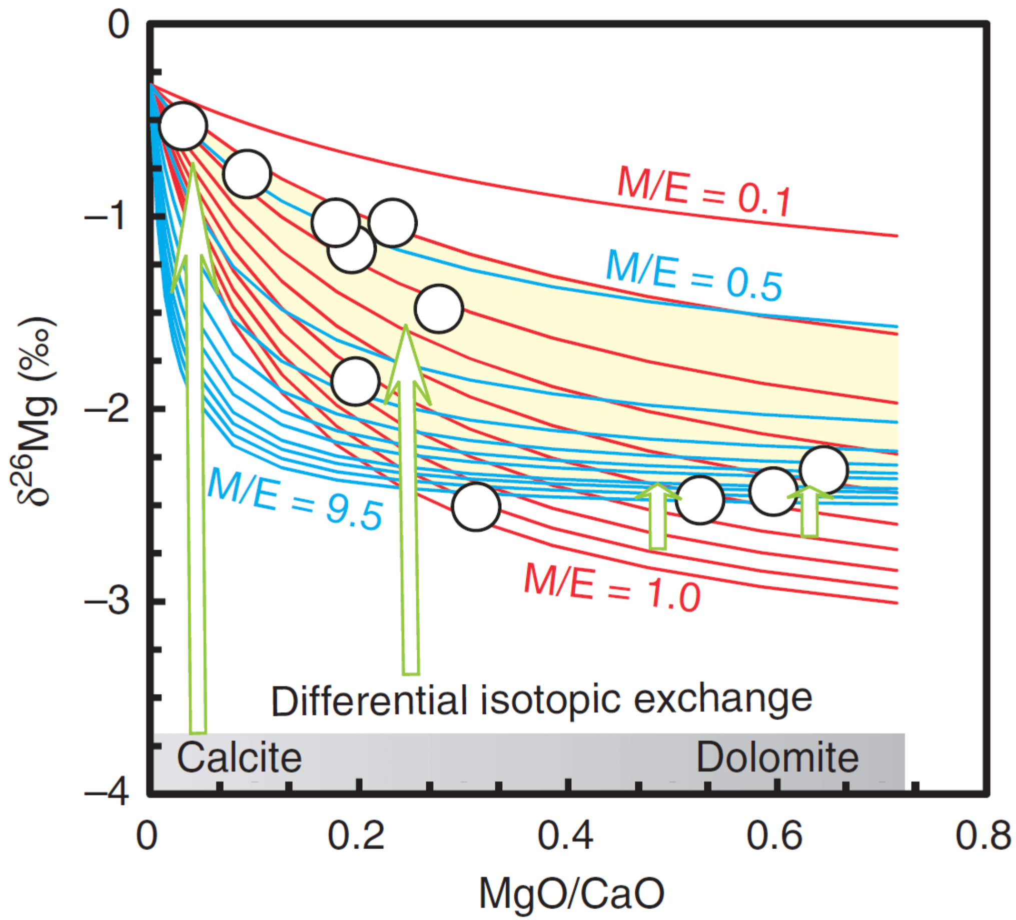
○ Marble

● Carbonated eclogite

Wang et al. Nat Commun 2014

Mg isotope exchange between silicate and carbonate

δ^{26}Mg in marble is negatively correlated with MgO/CaO



M/E = mass of marble/eclogite

Blue lines: $\delta^{26}Mg_{carb}$ = -2.5‰

Red lines: $\delta^{26}Mg_{carb}$ = -4‰

Calcite-rich carbonates shift significantly toward higher δ^{26}Mg due to their lower MgO

Wang et al. Nat Commun 2014

Summary

1. **Subduction input:** Sediments + altered oceanic crust and mantle
    - *Inputs differ significantly from mantle composition*
    - *Weathering (heavy) and carbonate (light) formation play a critical role in controlling altered slab composition*
2. **Dehydration fluids:** exhumed subduction-channel metamorphic rocks
    - *Highly heterogeneous δ^{26}Mg derived from slab dehydration*
    - *Hydrous silicates release heavy Mg; carbonates release light Mg*
3. **Subduction output:** Mantle wedge + arc magmas
    - *Dehydration of slab mantle may contribute to arc magmas*
    - *Thermal structure of a subduction zone is important for the dehydration pathway of the subducting slab*
    - *For hot subduction zones, slab melts likely dominate over fluids*
4. **Fate of subducted slabs:** Eclogite + pyroxenite + basalt
    - *Subducted slabs are identified in mantle-derived samples*
    - *How did they contribute to mantle heterogeneity is still not clear*

What is your birthstone?

https://www.gia.edu/birthstones