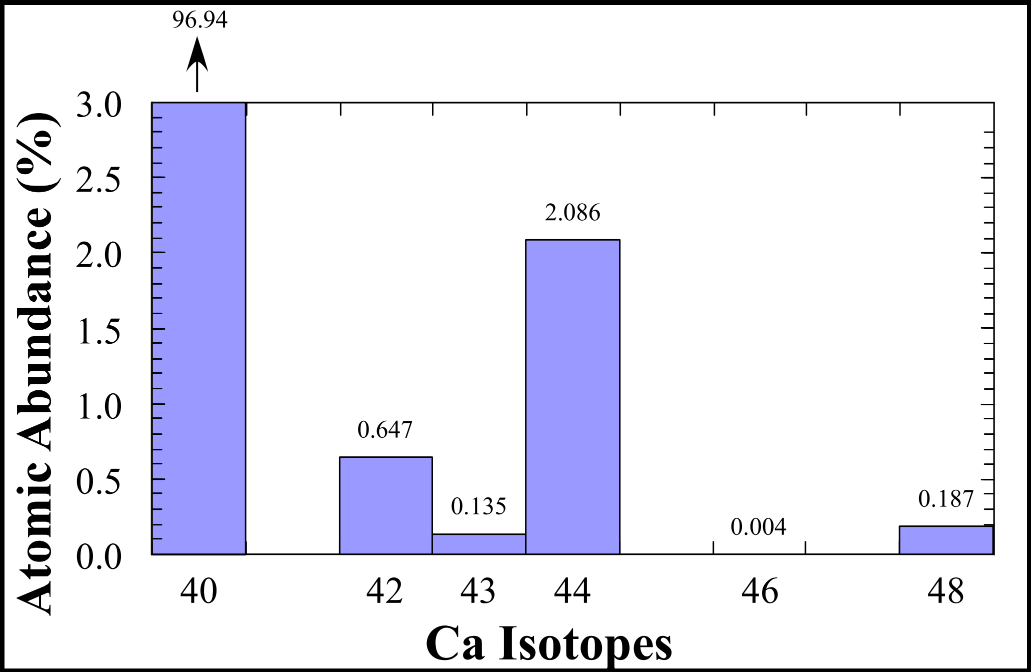
钙同位素在高温地球化学和天体化学中的应用

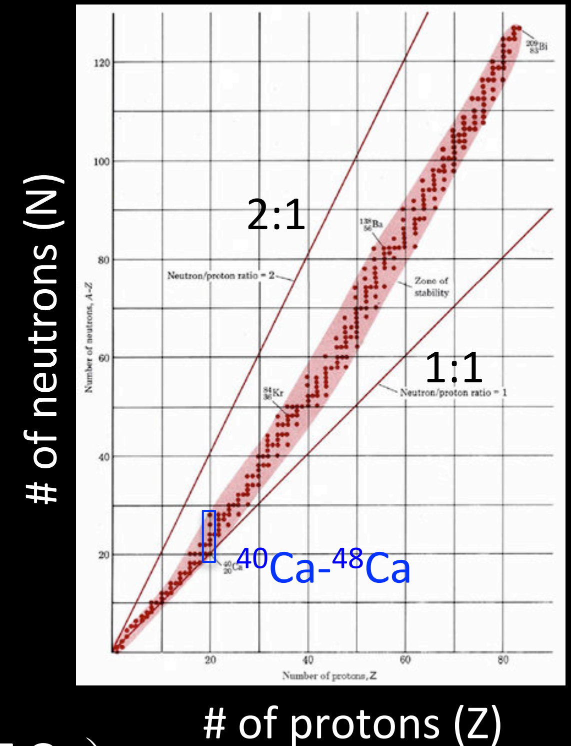
黄士春

内华达大学拉斯维加斯分校

二零二零年八月 | 第三届非传统稳定同位素暑期学校

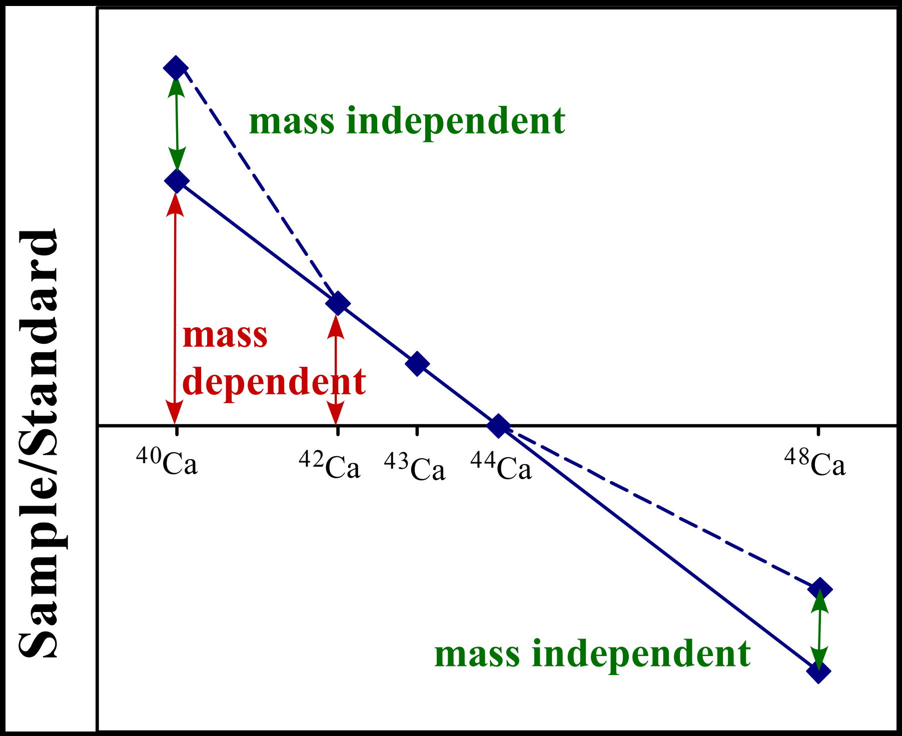
钙(Z=20)：地球上丰度第五的元素





- ^{40}Ca：氧燃烧，硅燃烧 ，^{40}K的衰变产物 （$t_{1/2}$ = 1.27 Ga）
- ^{42}Ca and ^{43}Ca：氧燃烧
- ^{44}Ca：氧燃烧，硅燃烧 -- ^{44}Ti的衰变产物 ($t_{1/2}$=60 年)
- ^{46}Ca：慢中子捕获过程（s-process）
- ^{48}Ca：富中子核合成 (neutron-rich nucleosynthesis)
  - Type Ia supernova explosions (Woosley, 1997)
  - electron-capture supernova explosions (Wanajo et al., 2013)

质量相关和非质量相关同位素变化



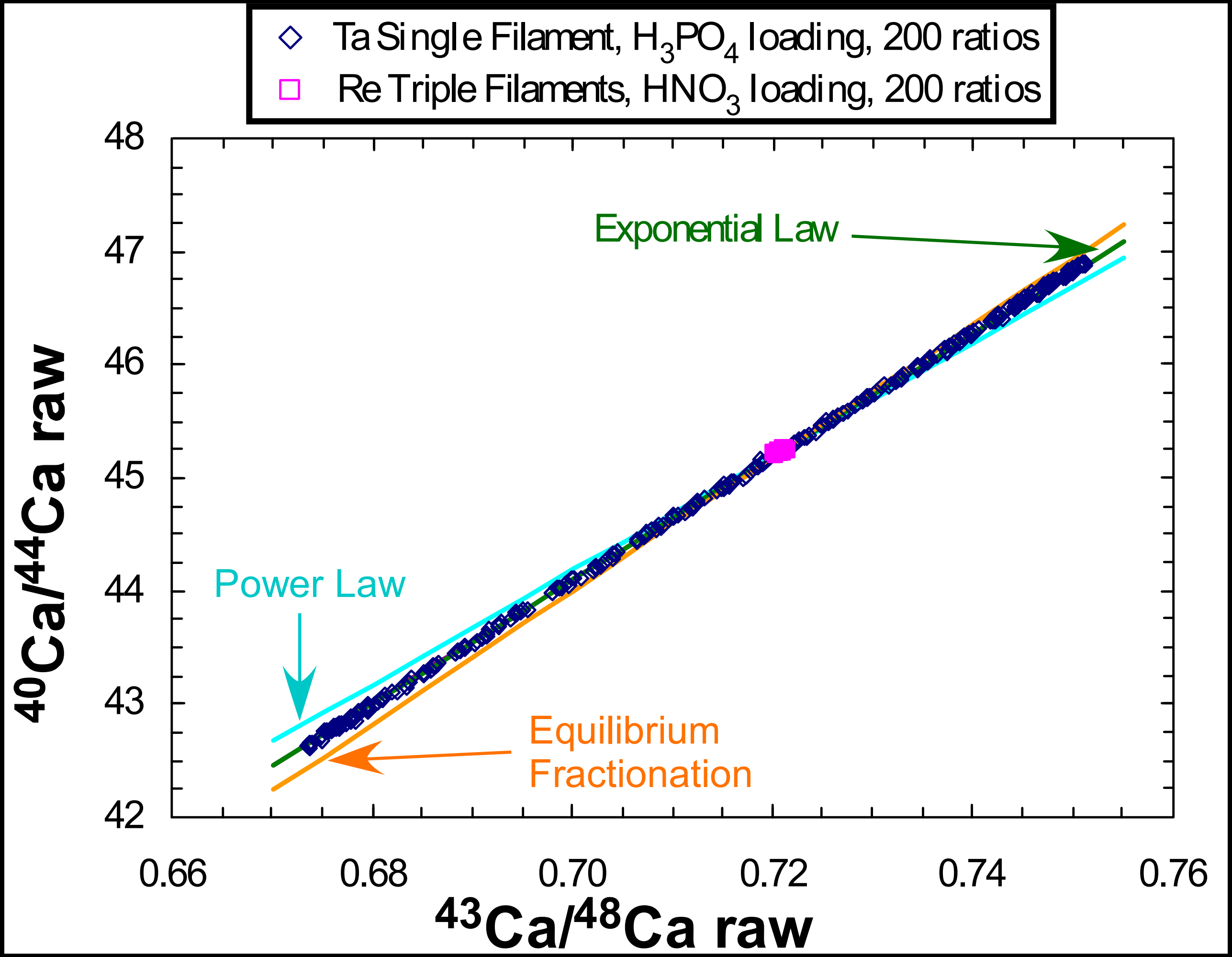
- 质量相关 **(mass dependent)**： 同位素丰度变化大小和同位素的质量差成正比
- 非质量相关 **(mass independent)**： 偏离质量相关同位素变化
  - 同位素衰变
  - 核合成异常
  - 核体积效应（见刘耘教授的报告）

钙同位素测量

- 非质量相关钙同位素变化测量
  - 仪器和自然分馏纠正至 $^{42}Ca/^{44}Ca=0.31221$（TIMS，MC-ICP-MS，SIMS）
  - $\varepsilon^{4i/44}Ca = [(^{4i}Ca/^{44}Ca_{sample\ (N)})/(^{4i}Ca/^{44}Ca_{SRM915a\ (N)}) - 1] * 10^4$
- 质量相关钙同位素变化测量
  - $\delta^{4i/4j}Ca = [(^{4i}Ca/^{4j}Ca_{sample})/(^{4i}Ca/^{4j}Ca_{SRM915a}) - 1] * 10^3$
  - TIMS：仪器分馏使用双稀释剂纠正
    - ^{43}Ca-^{48}Ca
    - ^{42}Ca-^{48}Ca
    - ^{42}Ca-^{43}Ca
  - MC-ICP-MS: standard-sample bracketing （见于慧敏教授的报告）
    - ignoring ^{40}Ca (Feng et al., 2018)
    - cool plasma (Fietzke et al., 2004)
    - collision cell MC-ICP-MS (Sapphire)

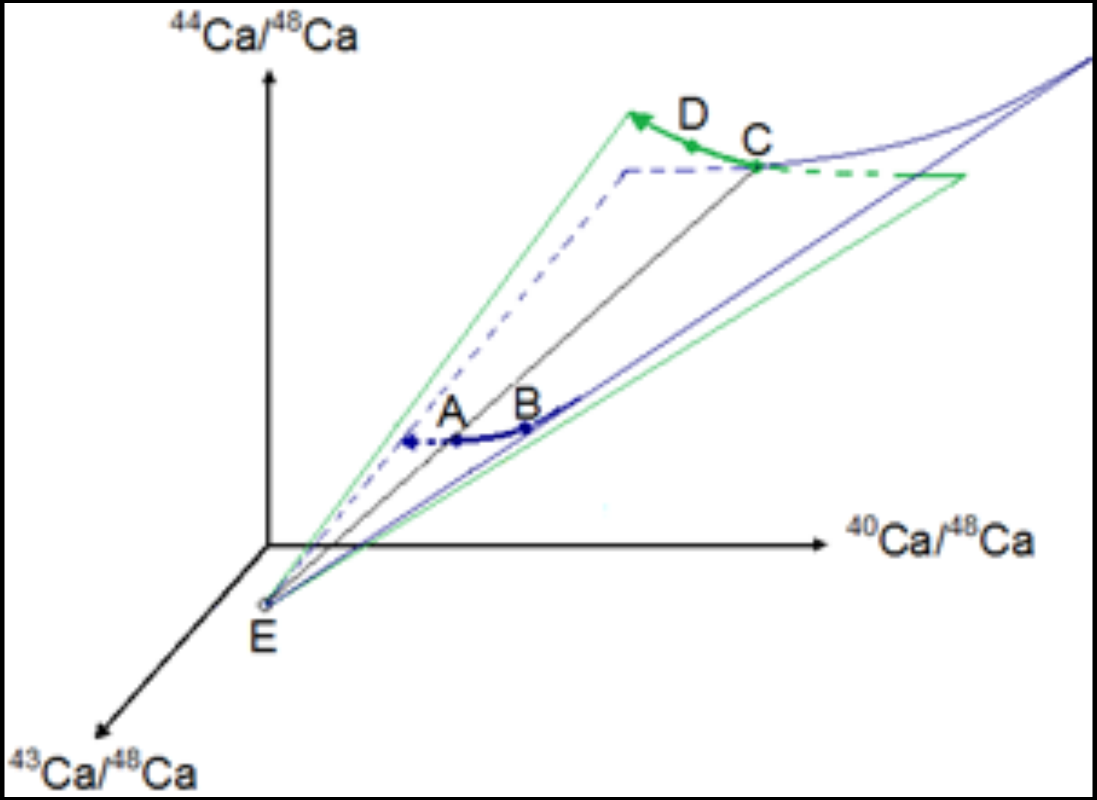
钙同位素测量

- TIMS：仪器分馏服从指数率



钙同位素测量

- 质量相关钙同位素变化测量
  - TIMS：仪器分馏使用双稀释剂纠正（e.g.，Eugster et al., 1969）
  - 必须有四个或者更多的同位素



C：样品真值

A：（样品+双稀释剂）真值

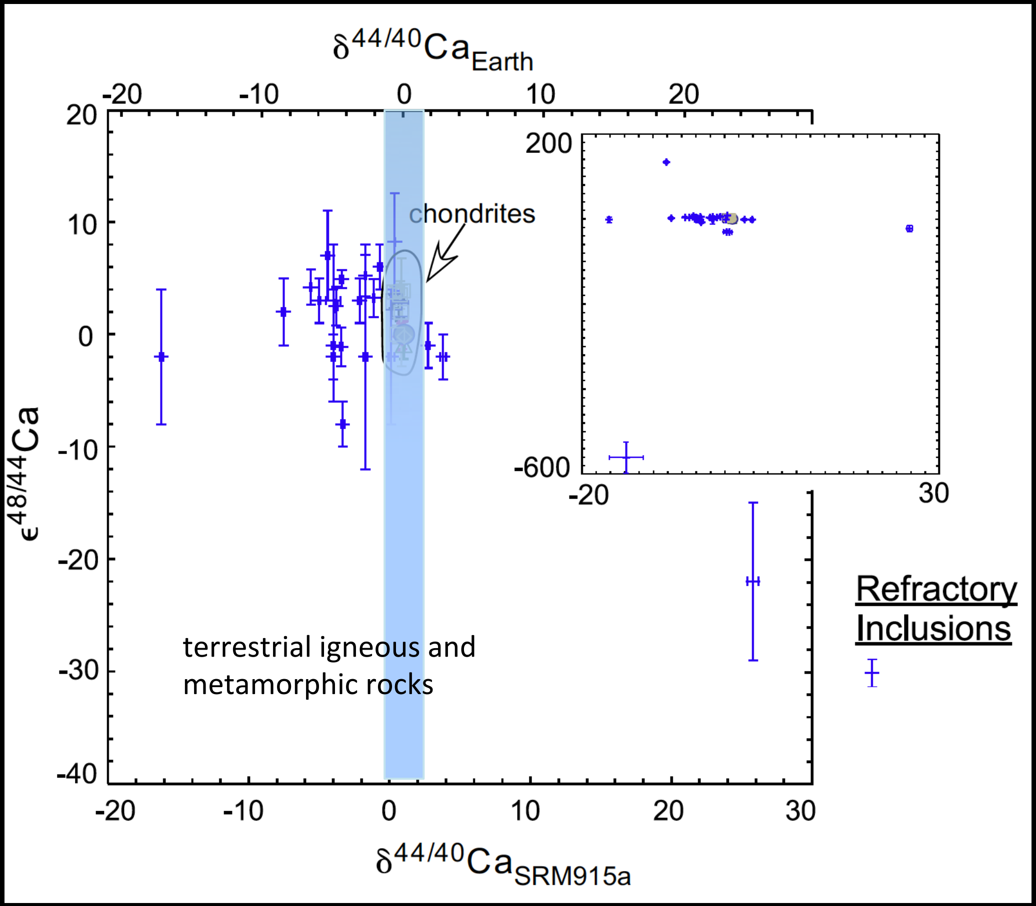
D：样品测量值

B：（样品+双稀释剂）测量值

E：双稀释剂真值

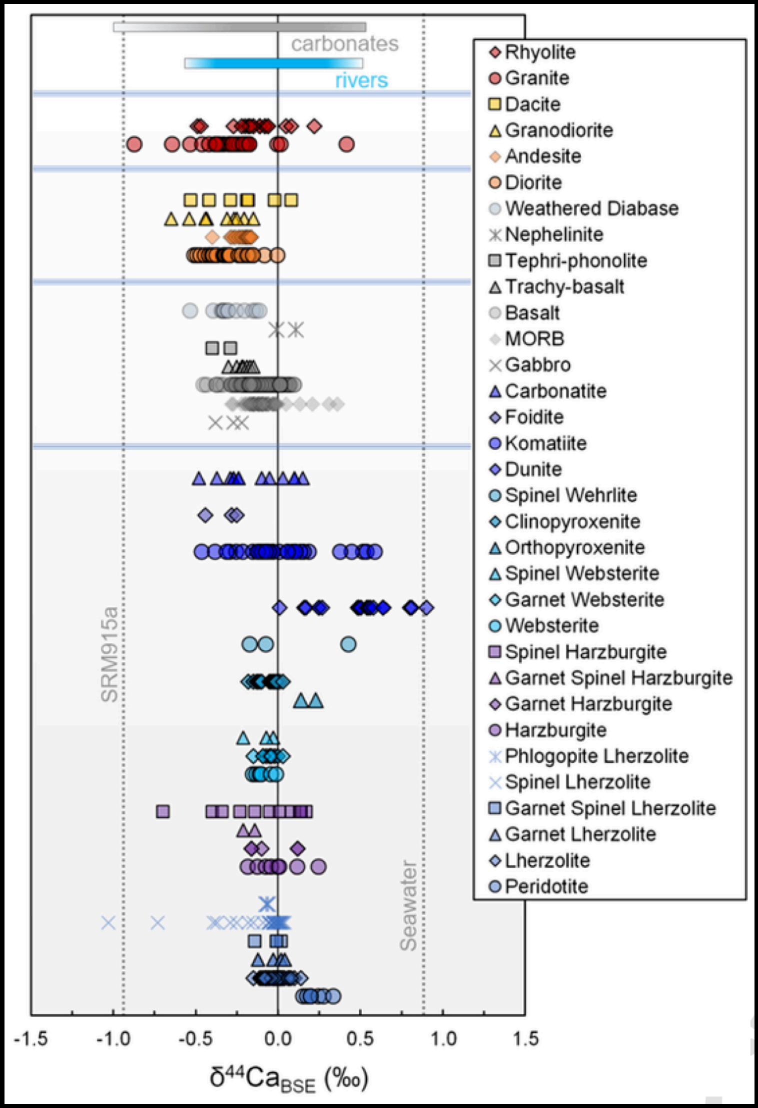
太阳系内的钙同位素变化

球粒陨石和它们的组成部分
chondrites and their components



Huang and Jacobsen (2017)

地球上的硅酸盐
terrestrial igneous and metamorphic rocks

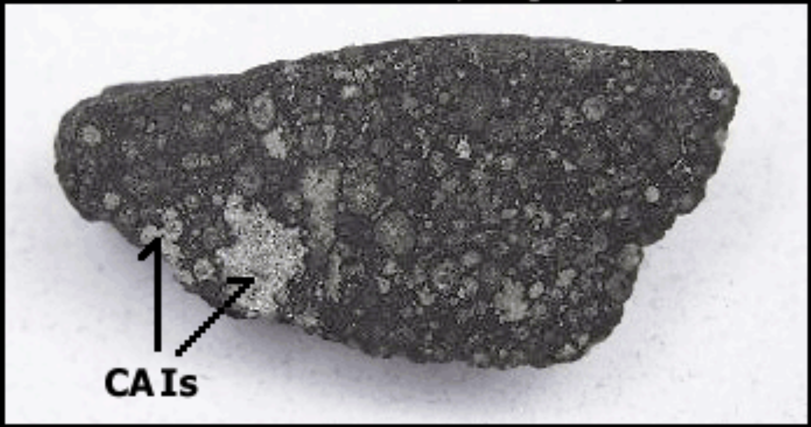


Antonelli and Simon (2020)

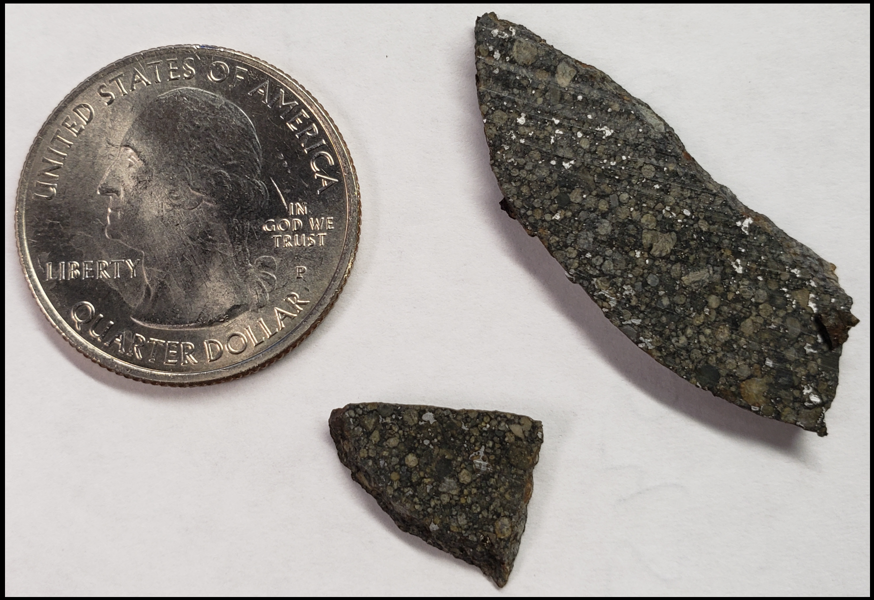
球粒陨石

- ➢球粒陨石的母体没有经历过行星尺度的分异过程（熔融）
- ➢可以代表太阳系初期星云的成份
  - ❖ carbonaceous chondrites（碳质）
  - ❖ ordinary chondrites（普通）
  - ❖ enstatite chondrites（顽火辉石）
- ➢chondrite components
  - ❖ refractory inclusions （难熔包裹体）
    - ✧ Ca-Al-rich inclusions (CAIs)
    - ✧ Amoeboid olivine aggregates (AOAs)（蠕虫状橄榄石集合体）
  - ❖ chondrules（球粒）
  - ❖ matrix（基质）

Allende CV3 meteorite, 24 gram piece

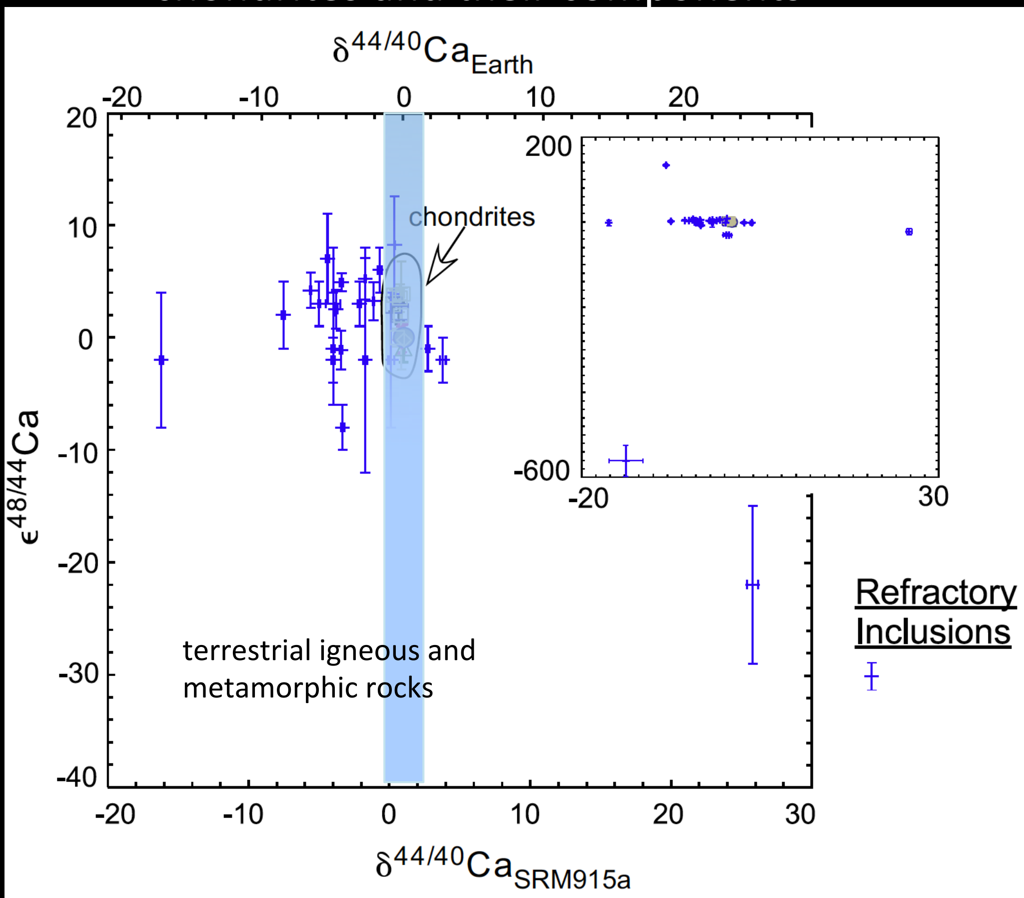


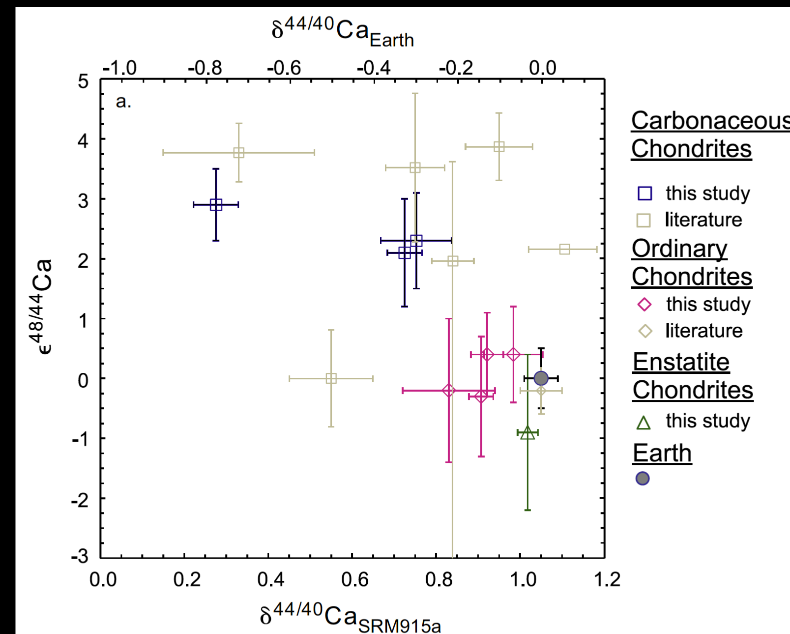
(Image courtesy of Falling Stars Inc.)



太阳系内的钙同位素变化

chondrites and their components



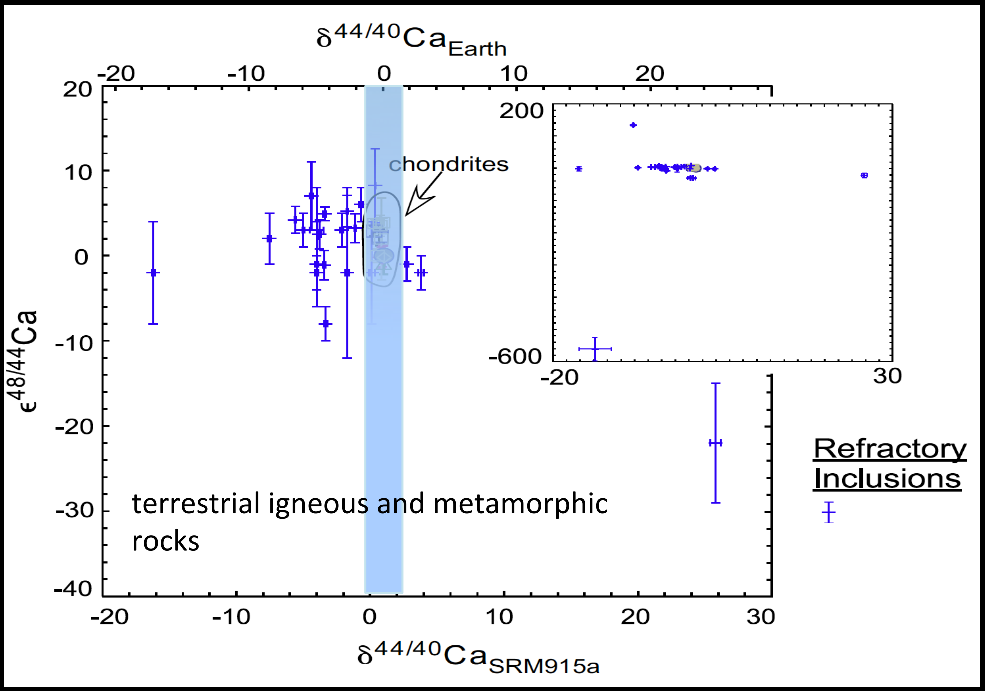


- 难熔包裹体有非常大的质量相关和非质量相关的钙同位素效应
- 球粒陨石有质量相关和非质量相关的钙同位素效应
  - 和难熔包裹体比较，尺度较小
  - $\delta^{44/40}Ca_{915a}$ = 0.2 to 1.1

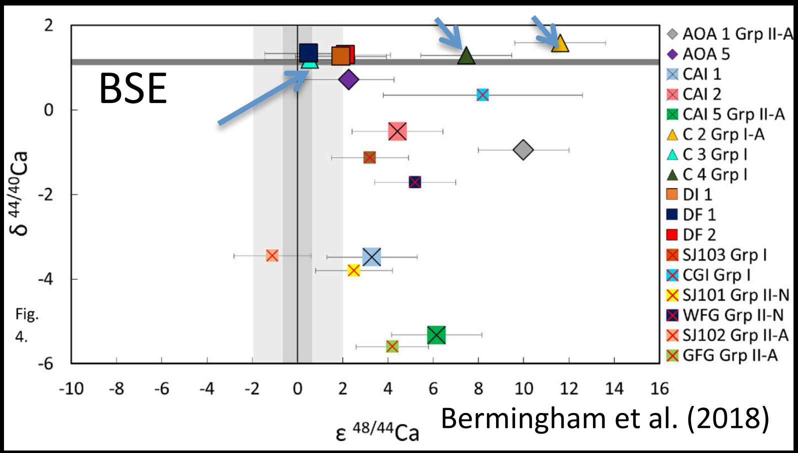
Huang and Jacobsen (2017) with data from: Jungck et al. (1984); Lee et al. (1978); Russell et al. (1978); Niederer and Papanastassiou (1984); Clayton et al. (1988); Simon et al. (2009); Moynier et al. (2010); Simon and DePaolo (2010); Huang et al. (2012); Valdes et al. (2014); Schiller et al. (2015); Bermingham et al. (2018)

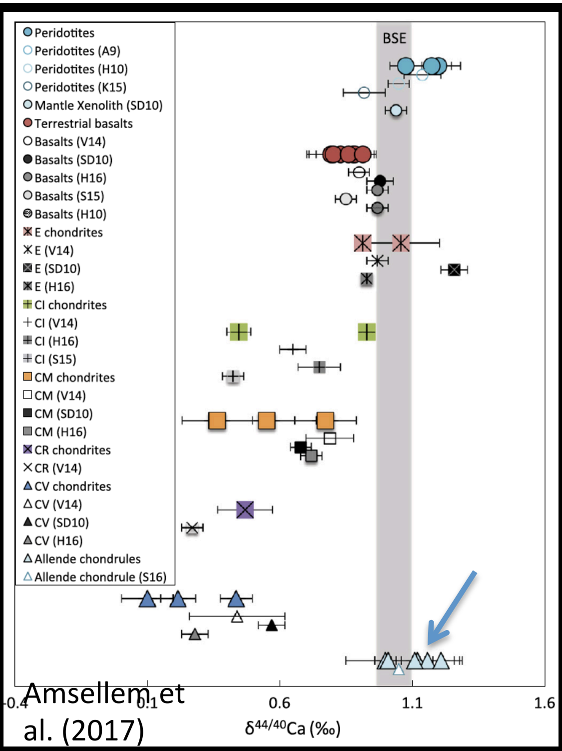
太阳系内的钙同位素变化

chondrites and their components

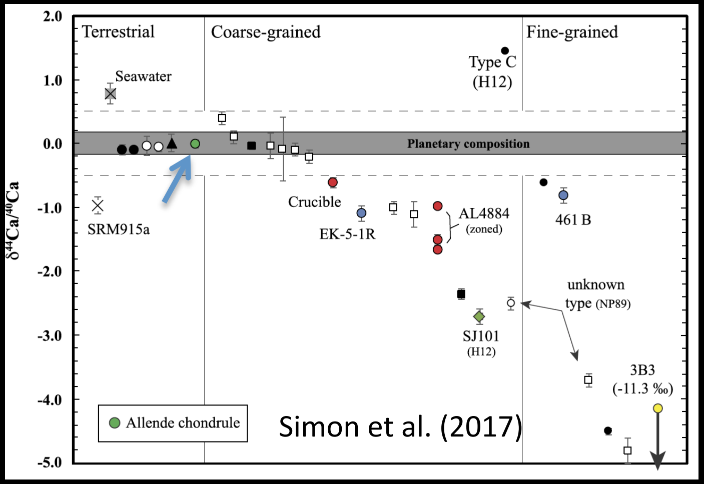


Huang and Jacobsen (2017)



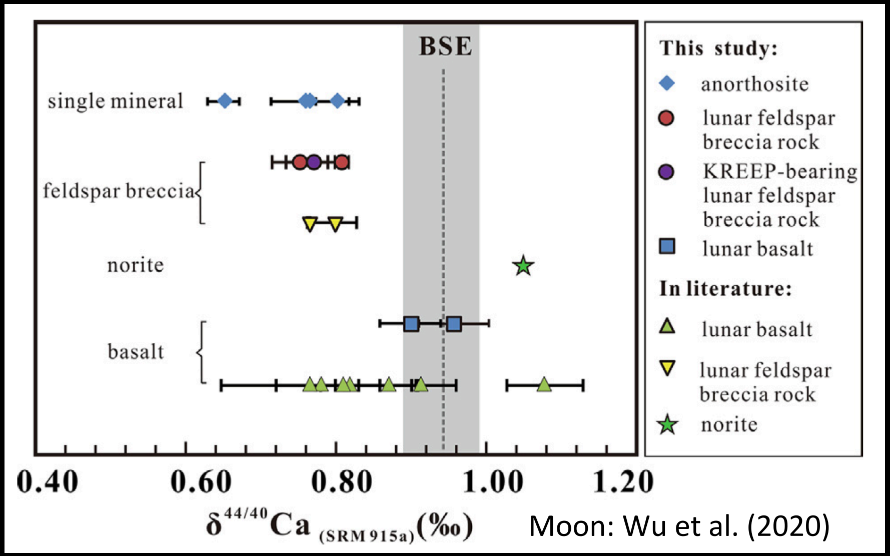


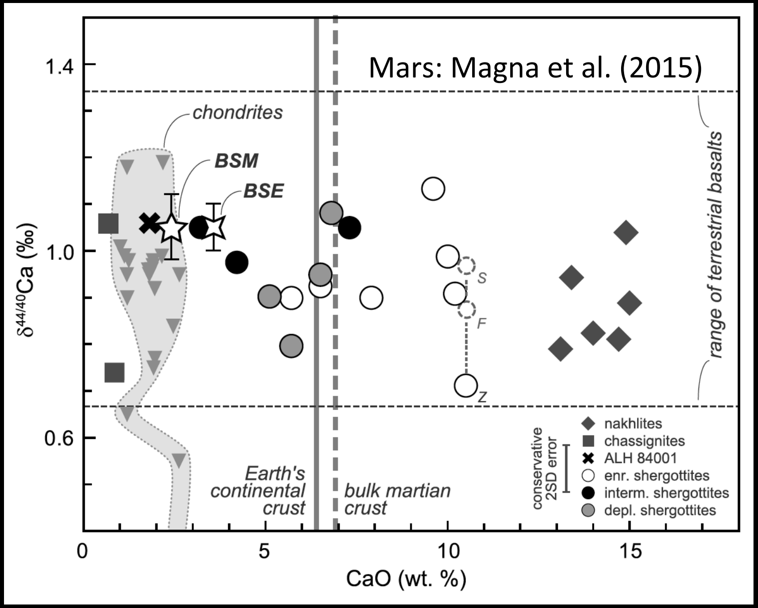
- 球粒有质量相关和非质量相关的钙同位素效应

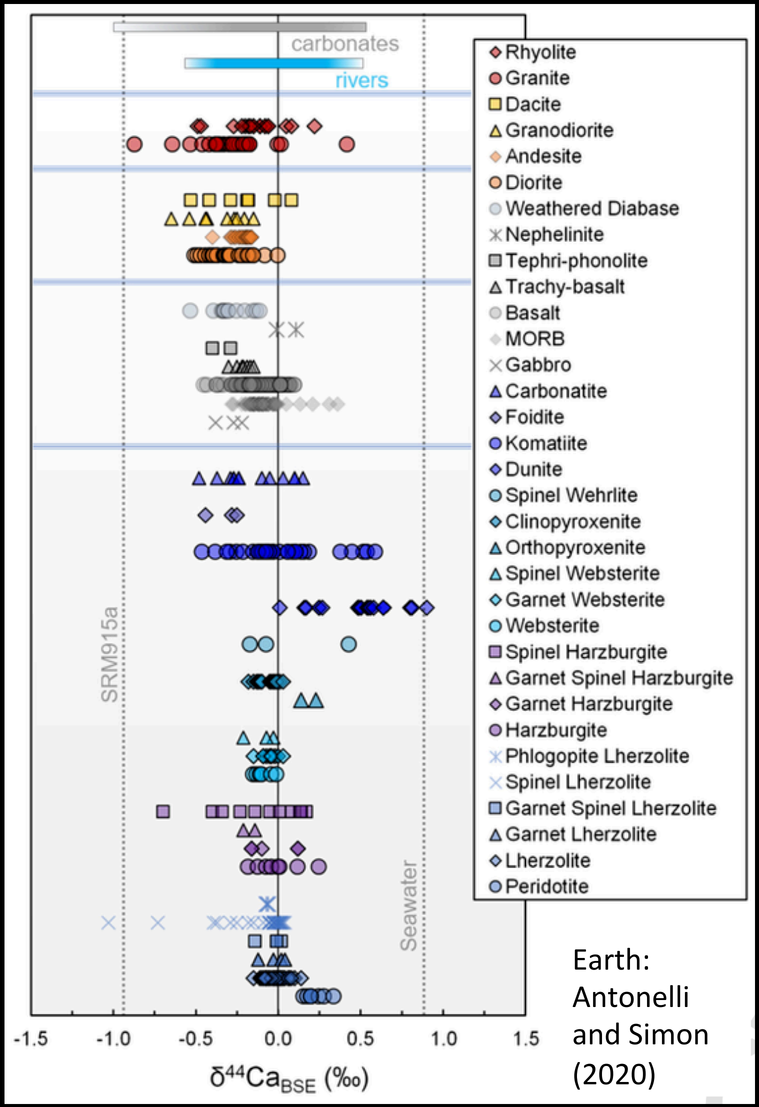


- $\delta^{44/40}Ca_{915a}$ = 0.53 to 1.59

太阳系内的钙同位素变化

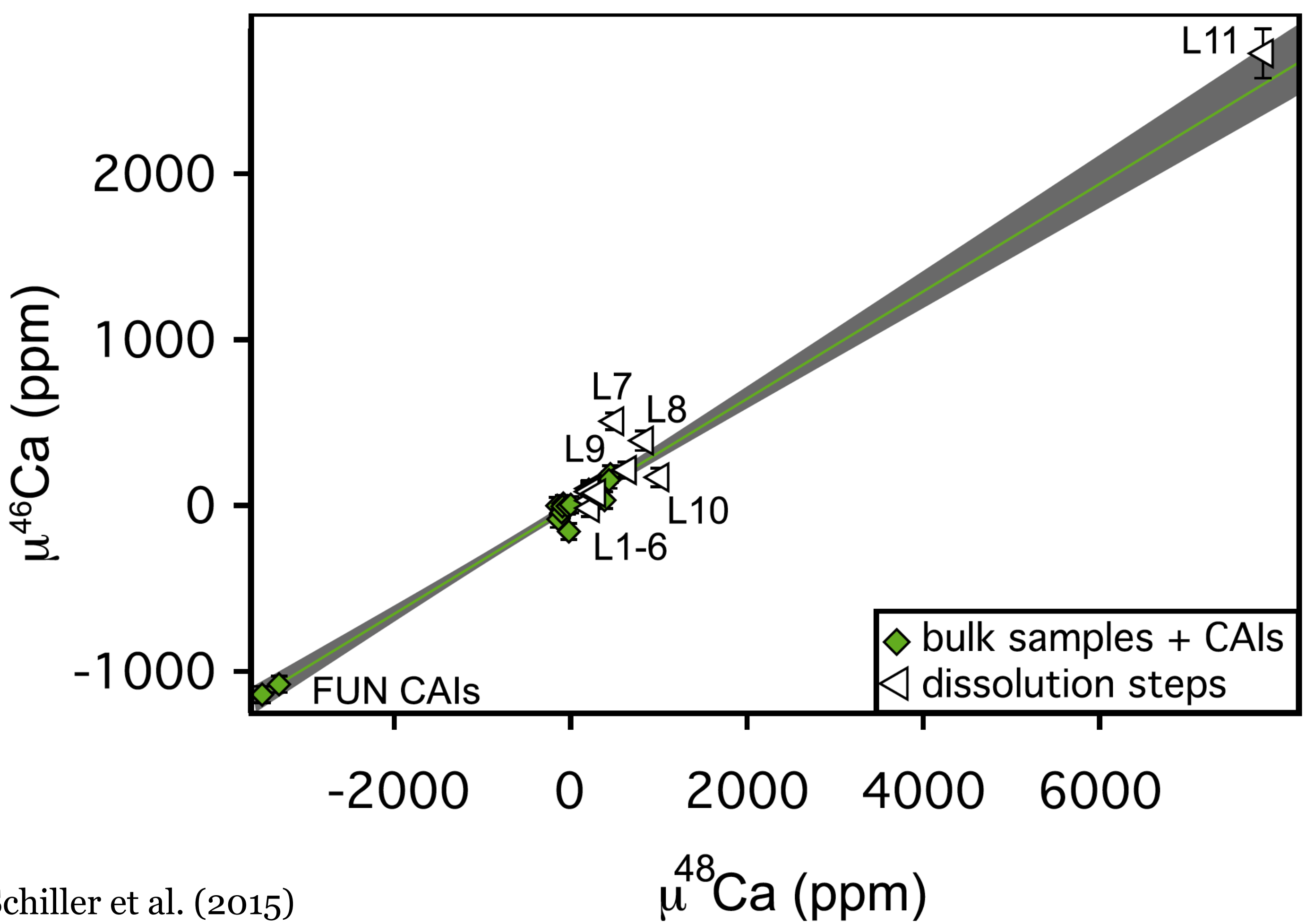






- Earth, Moon, Mars: $\delta^{44/40}Ca_{915a}$ = -0.1 to 1.9

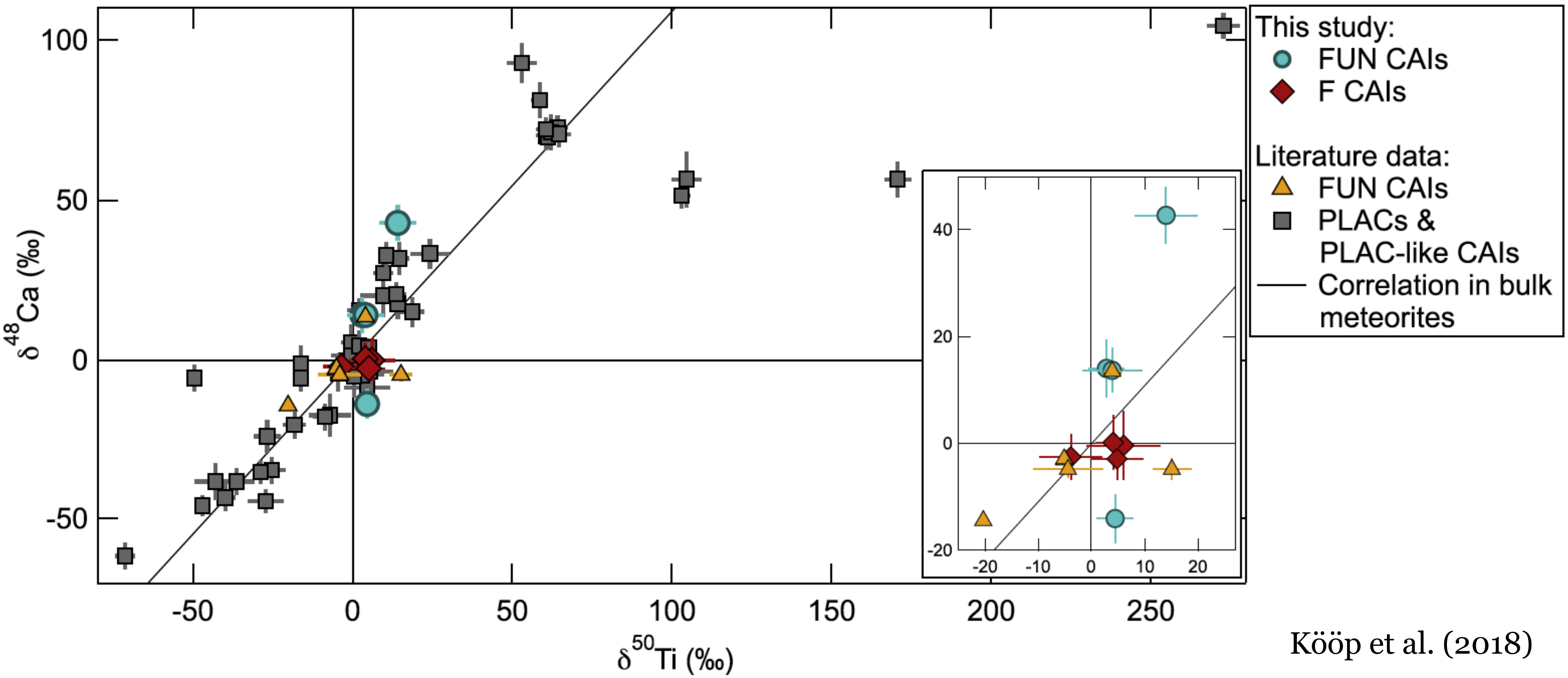
难熔包裹体和球粒陨石全岩中的^{46}Ca异常



Schiller et al. (2015)

- 在文献里，质量不相关同位素变化有时候用μ-notation来表示
- 因为低丰度的原因，^{46}Ca异常的测量不多

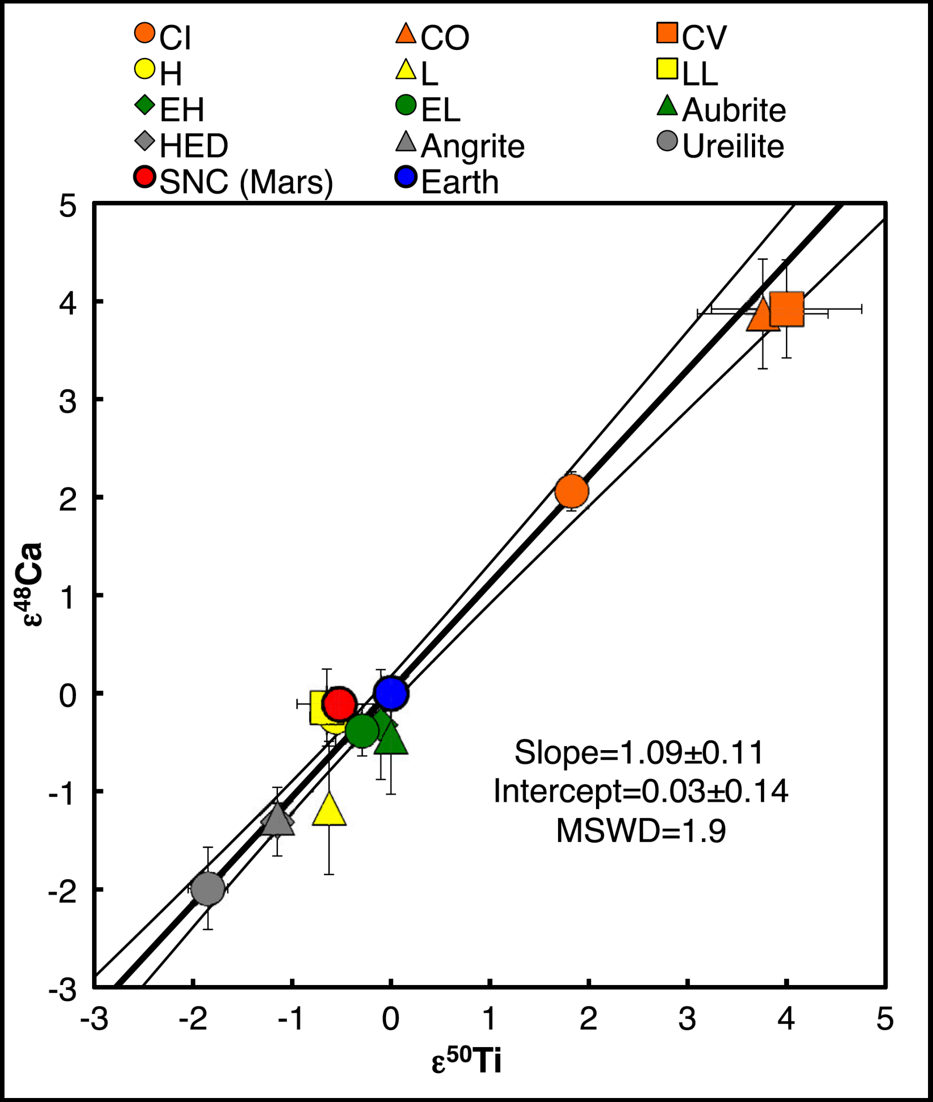
难熔包裹体中的富中子同位素(^{48}Ca, ^{50}Ti)异常



Kööp et al. (2018)

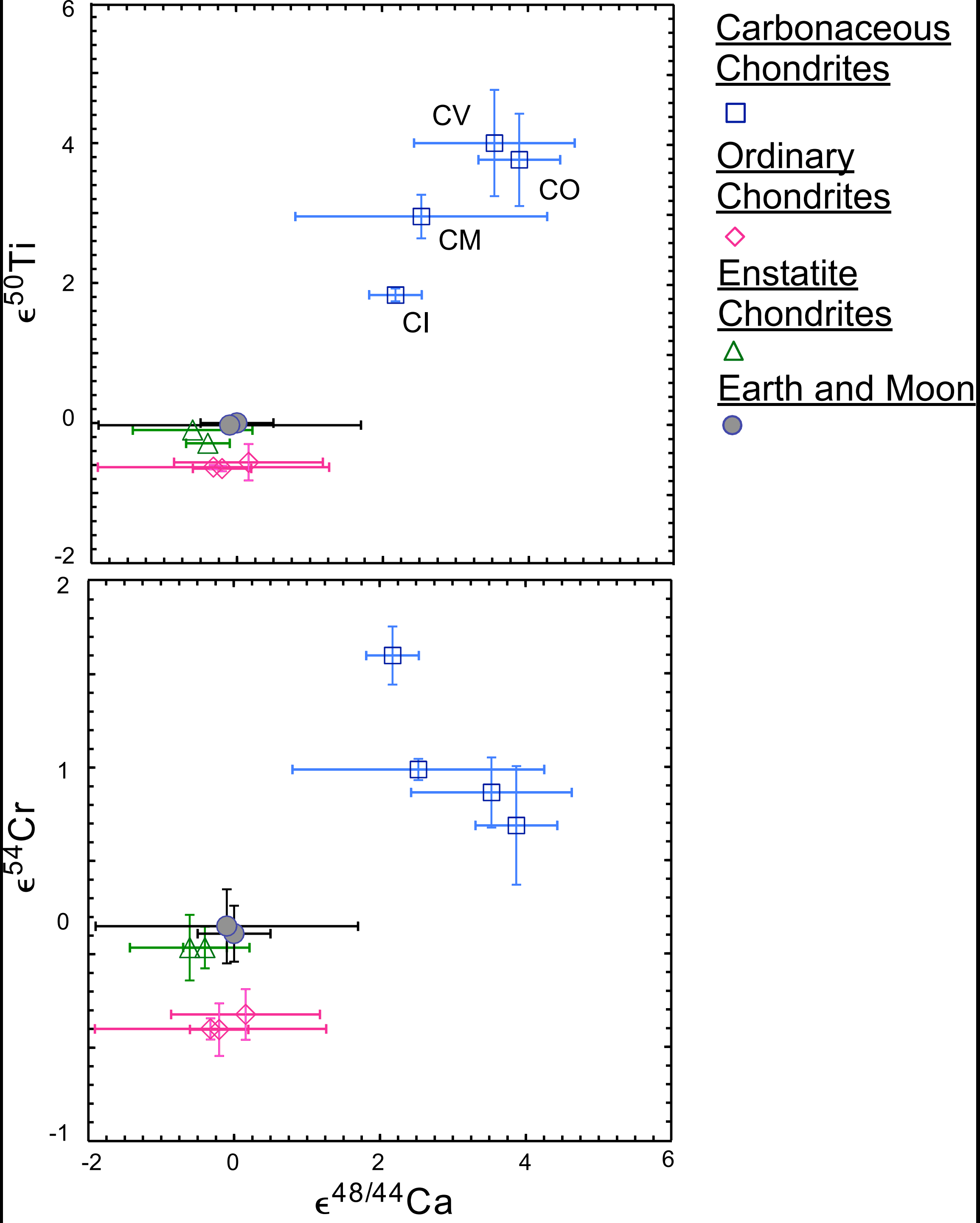
- 在文献里，质量不相关同位素变化有时候用δ-notation来表示

陨石中的富中子同位素(^{48}Ca, ^{50}Ti)异常



Dauphas et al. (2014)

- ^{48}Ca和^{50}Ti异常线性相关

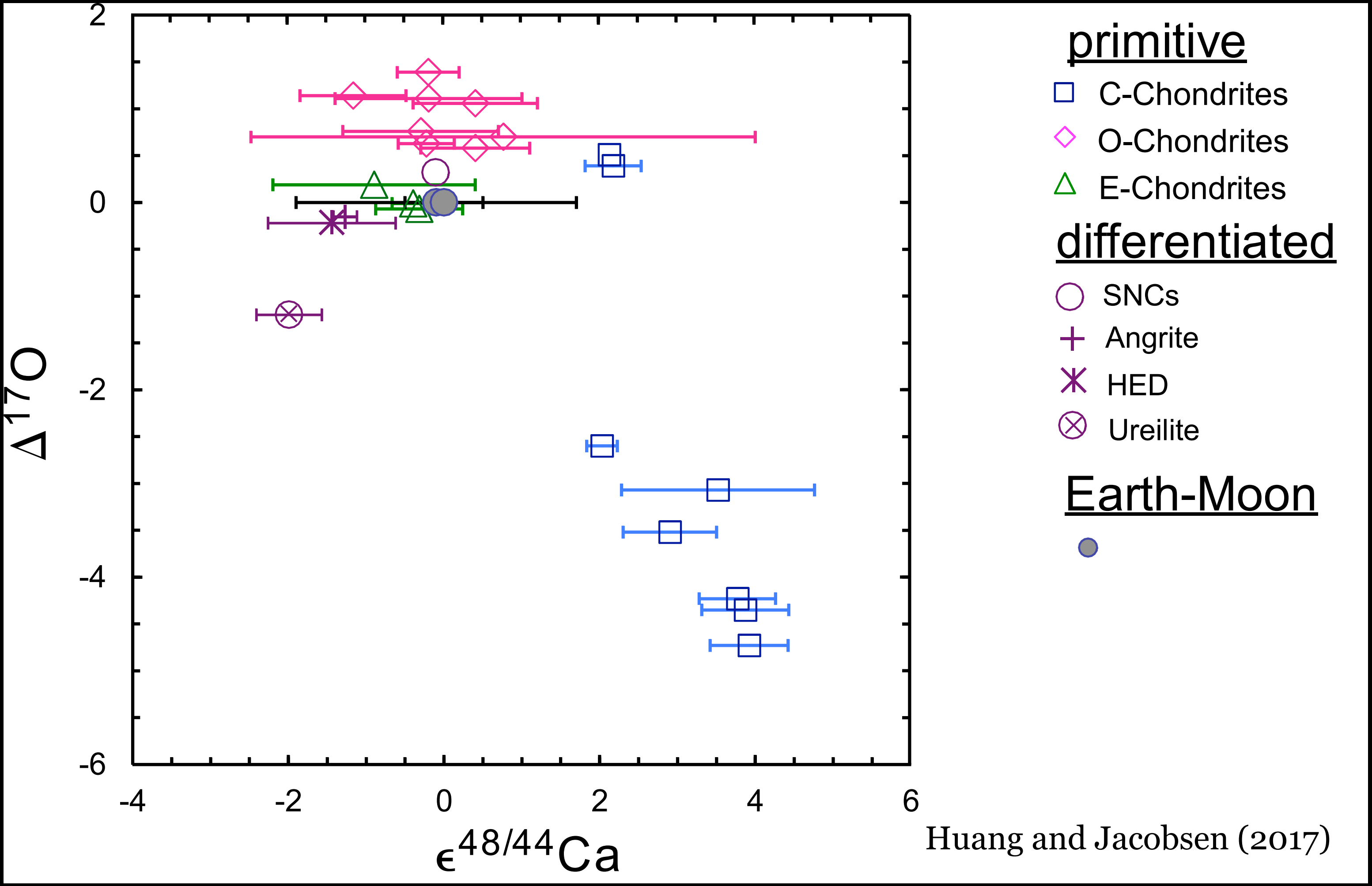


球粒陨石中的富中子同位素(^{48}Ca, ^{50}Ti, ^{54}Cr)异常

- 至少有三个端元
- 多个超新星爆发来源

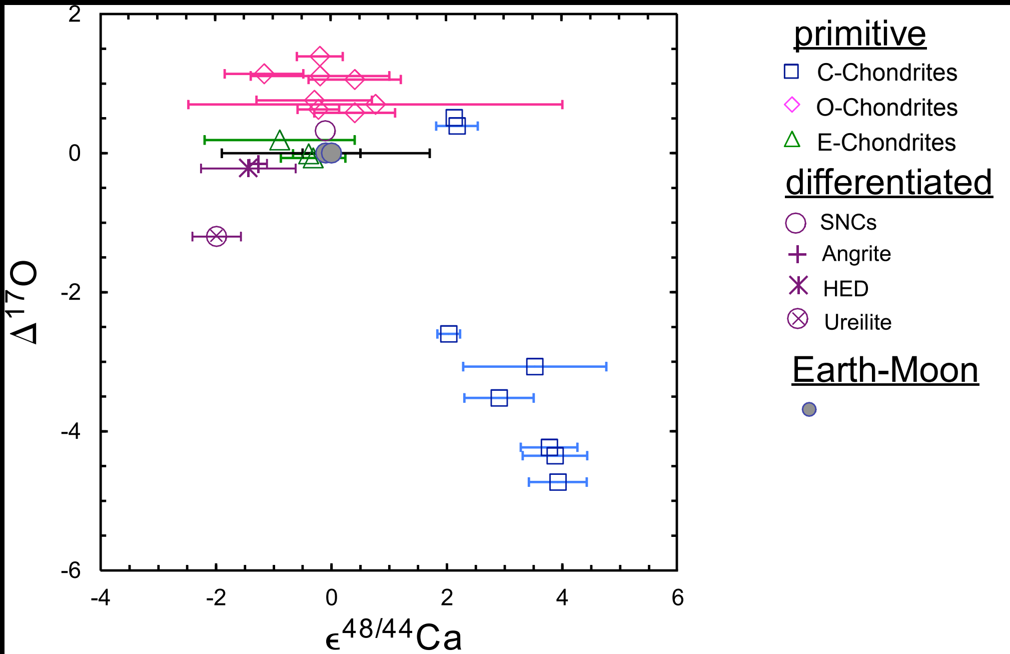
Huang and Jacobsen (2017)

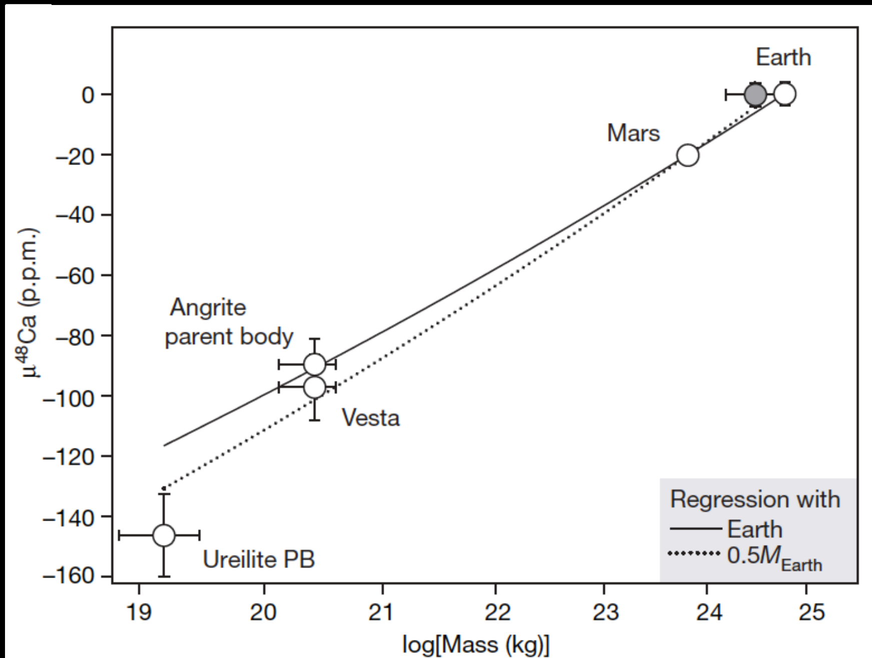
陨石全岩中质量不相关钙-氧同位素异常



- ➢ ^{48}Ca异常和$\Delta^{17}O$异常的相关性
- ➢ 可能用来推测太阳系星云中CO自屏蔽效应 （self-shielding） 发生的时间
- ➢ 或者说，$\Delta^{17}O$ 异常来源与核合成异常(Krot et al., 2010; Koop et al., 2016a; b)

陨石全岩中质量不相关钙-氧同位素异常



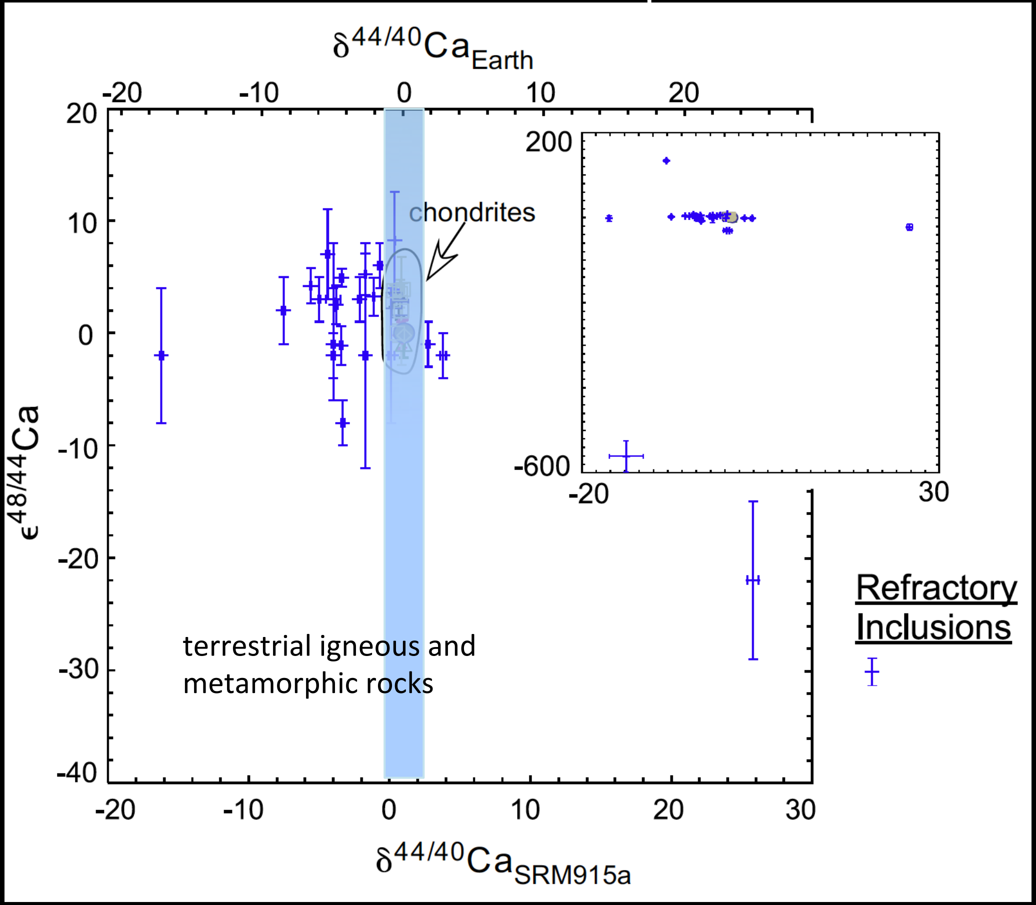


Schiller et al. (2018)

➢ ^{48}Ca 异常广泛地分布在太阳系内的行星中（e.g., Lee et al., 1978; Chen et al., 2011; Huang and Jacobsen, 2017; Schiller et al., 2018）

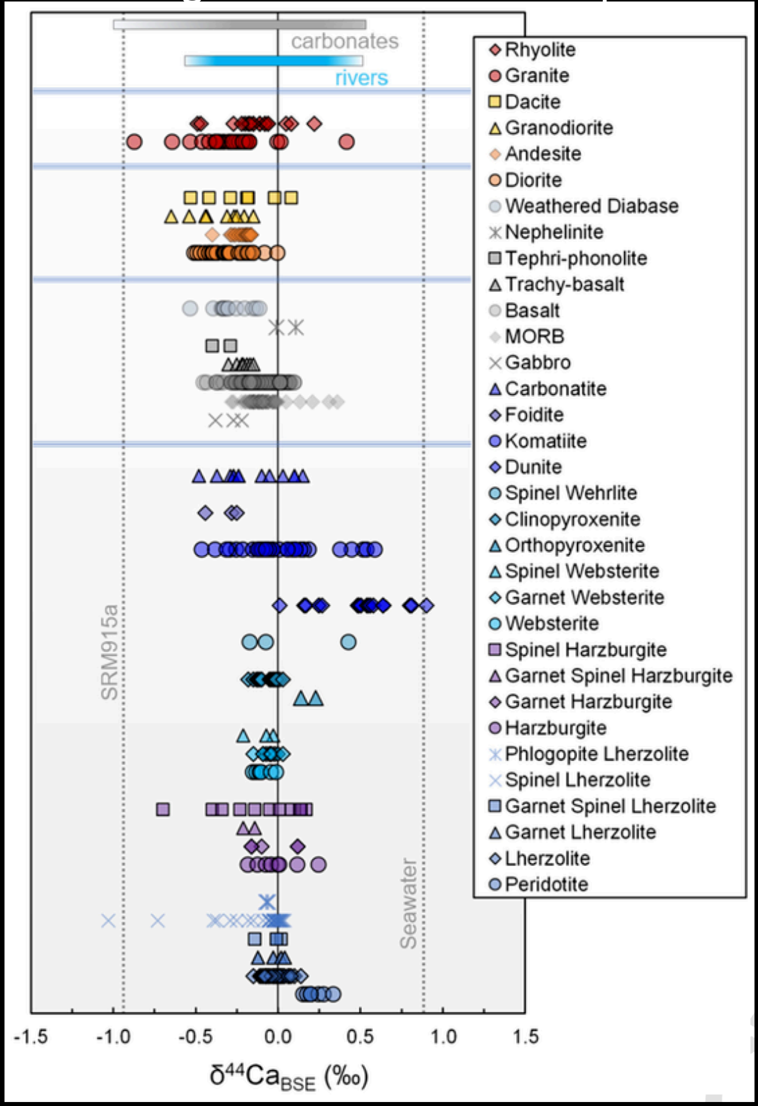
钙同位素的分馏

chondrites and their components



Huang and Jacobsen (2017)

terrestrial igneous and metamorphic rocks



Antonelli and Simon (2020)

钙同位素的分馏：质量相关分馏率

isotopes *i, j, k*

R_{ik}: isotope ratio of *i* and *k*

${}^{T}R_{ik}$: true isotope ratio

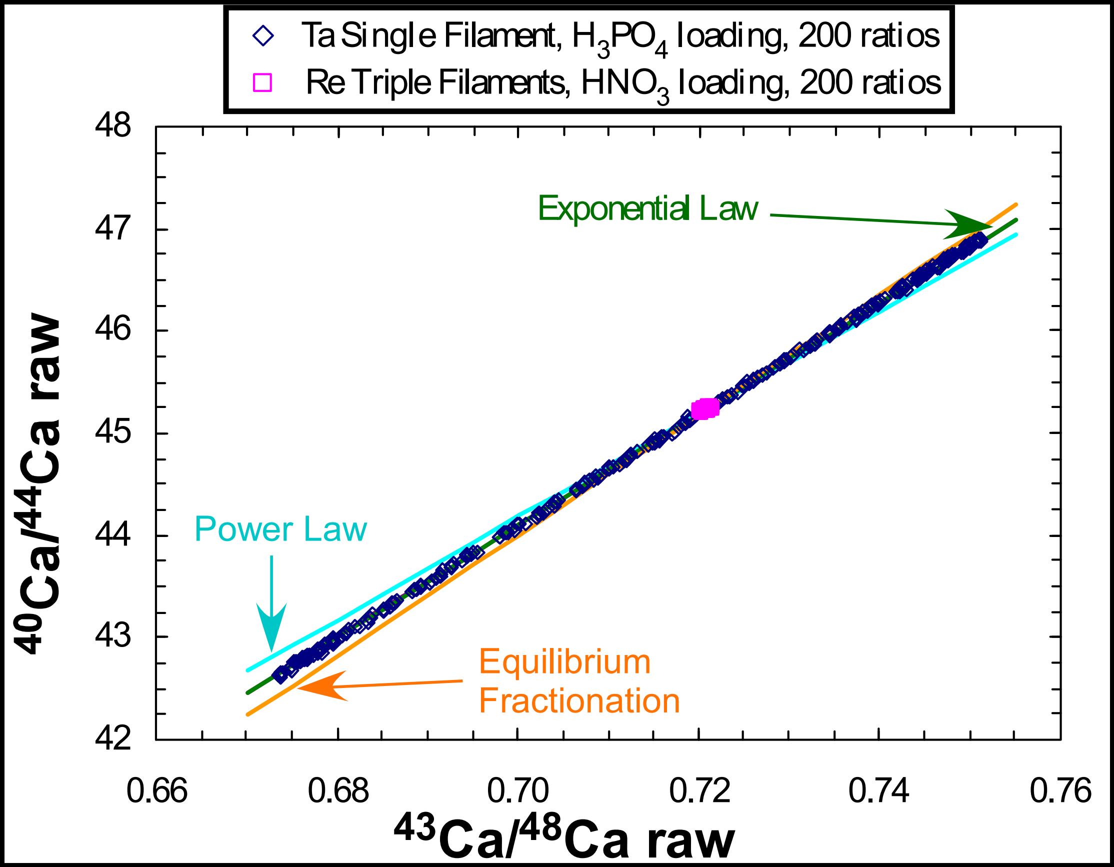
${}^{F}R_{ik}$: fractionated isotope ratio

${}^{F}R_{ik}/{}^{T}R_{ik} = ({}^{F}R_{jk}/{}^{T}R_{jk})^{\beta}$

$\beta = (m_k^n - m_i^n)/(m_k^n - m_j^n)$

m: mass of isotopes *i, j, k*

n = -1	equilibrium law
n = +1	power law
n -> 0	exponential law
n = -0.5	Rayleigh law



钙同位素的分馏：瑞利分馏

isotopes *i*, *j*, *k*
R_{ik}: isotope ratio of *i* and *k*
$^{T}R_{ik}$: true isotope ratio
$^{F}R_{ik}$: fractionated isotope ratio
$^{F}R_{ik}/^{T}R_{ik} = (^{F}R_{jk}/^{T}R_{jk})^{\beta}$

$\beta = (m_k^n - m_i^n)/(m_k^n - m_j^n)$

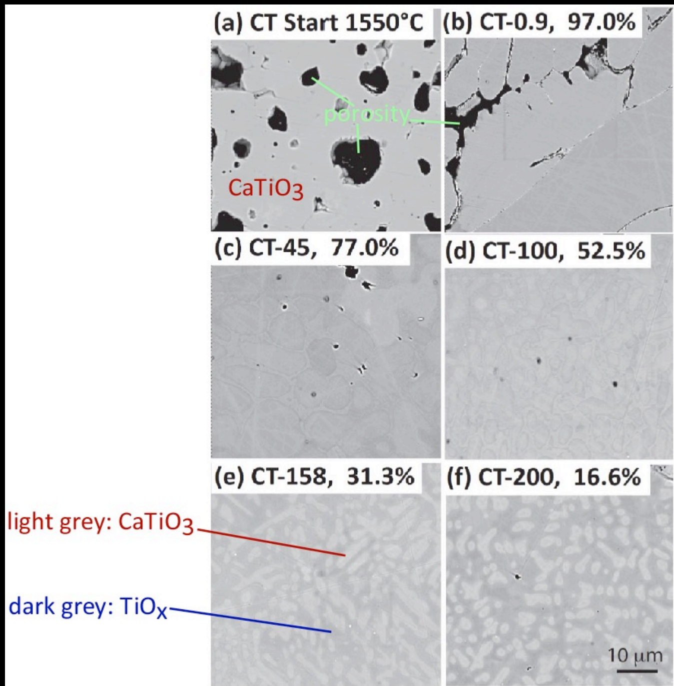
m: masses of isotopes *i*, *j*, *k*

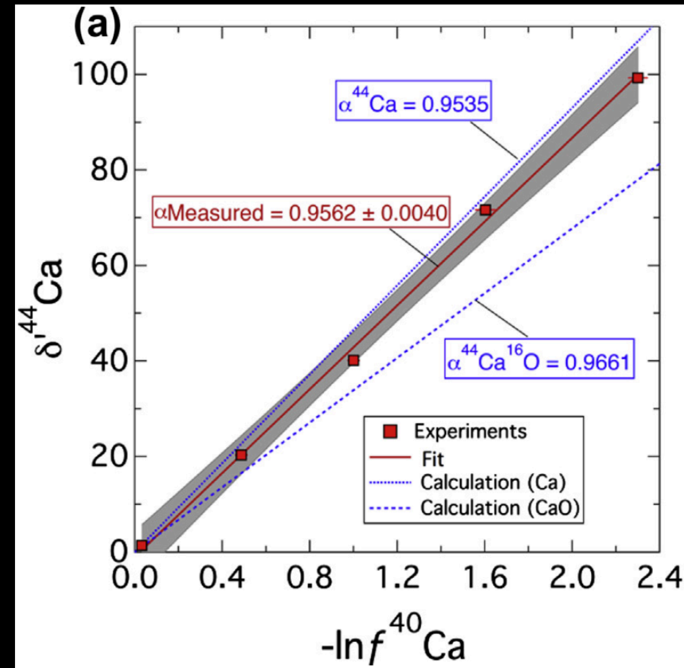
n = -0.5 Rayleigh law

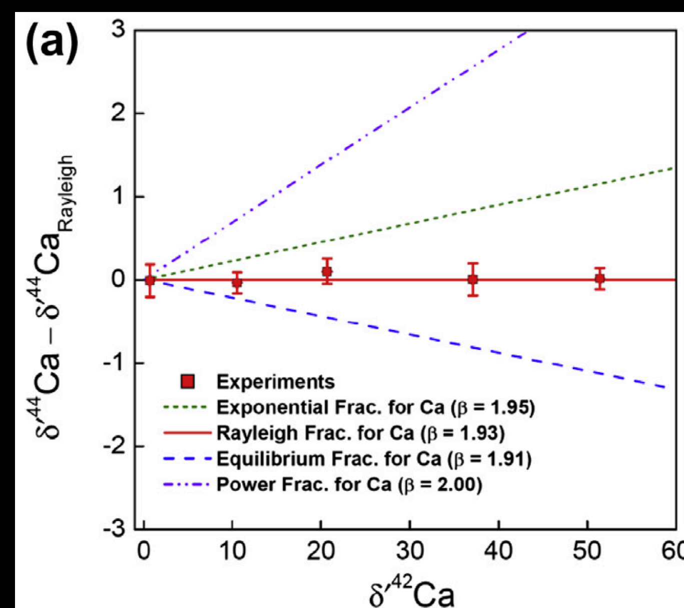
- 开放体系
- 反应生成物形成后，马上离开体系
- $R_{ik}/R_{ik,o} = f^{(\alpha ik-1)}$
- f = 0-1, 残余量
- $\alpha ik = (m_k/m_i)^{0.5}$

- 考虑三个同位素（两个同位素比值）R_{ik}, R_{jk}
- $R_{ik}/R_{ik,o} = f^{(\alpha ik-1)}$
- $R_{jk}/R_{jk,o} = f^{(\alpha jk-1)}$
- $R_{ik}/R_{ik,o} = (R_{jk}/R_{jk,o})^{\beta}$
- $\beta = (\alpha ik-1)/(\alpha jk-1) = (m_k^{0.5} - m_i^{0.5})/(m_k^{0.5} - m_j^{0.5})$

高温蒸发过程中钙同位素的分馏





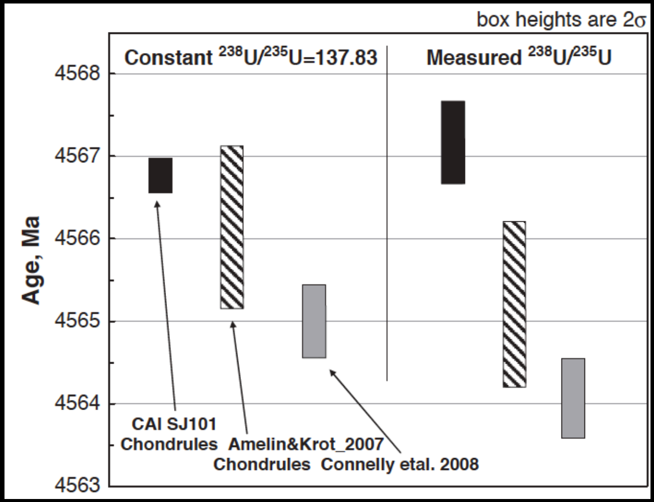


- 初始材料: $CaTiO_3$ 钙钛矿
- 真空炉内2005 °C下蒸发 (钙钛矿的熔点是 ~1975 °C)
- 非常大的钙同位素分馏
- 蒸发残留物含重钙
- 符合瑞利分馏关系： $R_{ik}/R_{ik,o} = f^{(\alpha ik-1)}$
- 蒸发种类：单原子Ca

Davis et al. (1995)
Zhang et al. (2014)

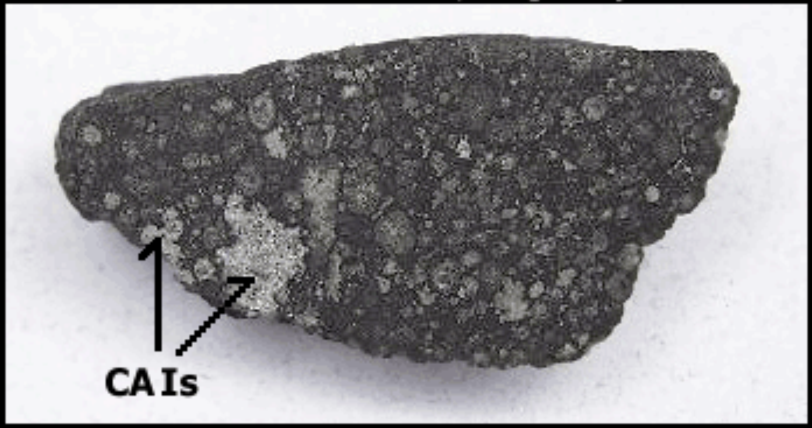
钙同位素的分馏：来自难熔包裹体的故事

- 球粒陨石没有经历过母天体的熔融分异 ， 代表了太阳系的原始成分
- 球粒陨石内的难熔包裹体包括富钙富铝包裹体（CAIs）和蠕虫状橄榄石集合体（AOAs）：太阳系内最老的固体

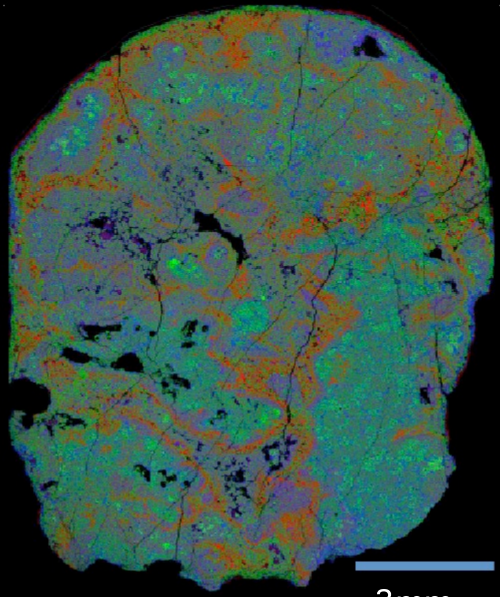


Amelin et al. (2010)

Allende CV3 meteorite, 24 gram piece



(Image courtesy of Falling Stars Inc.)

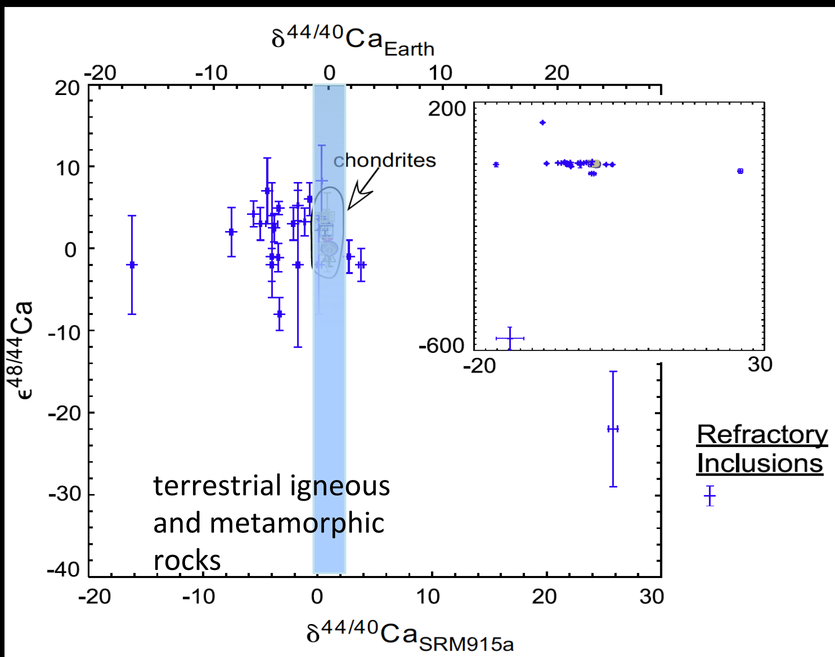


SJ101: 6.2 g

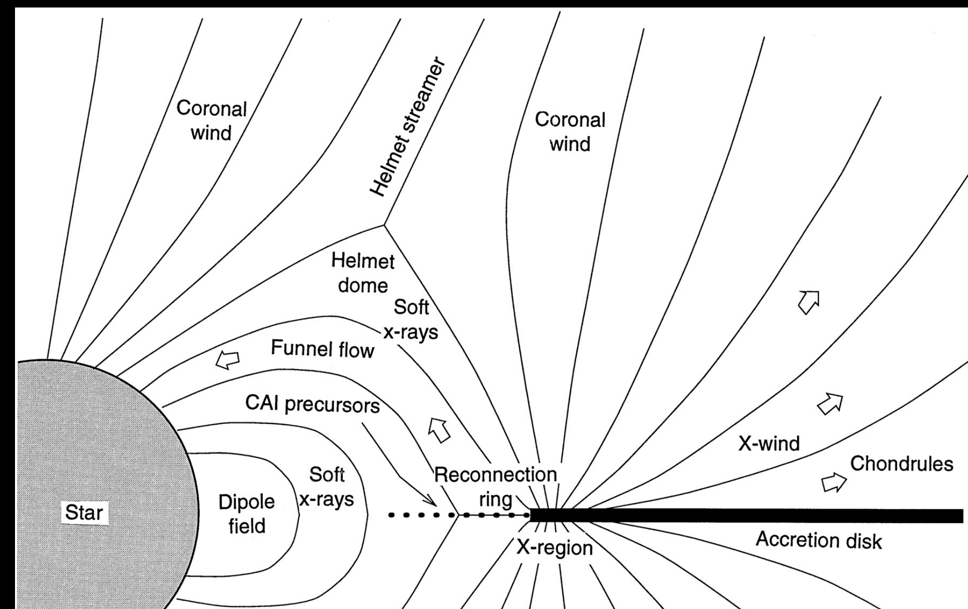
- Al-rich clinopyroxene (dark green)
- Mg-rich melilite (bright green)
- anorthite (blue)
- spinel (purple)
- forsterite (red)

难熔包裹体的钙同位素变化

chondrites and their components



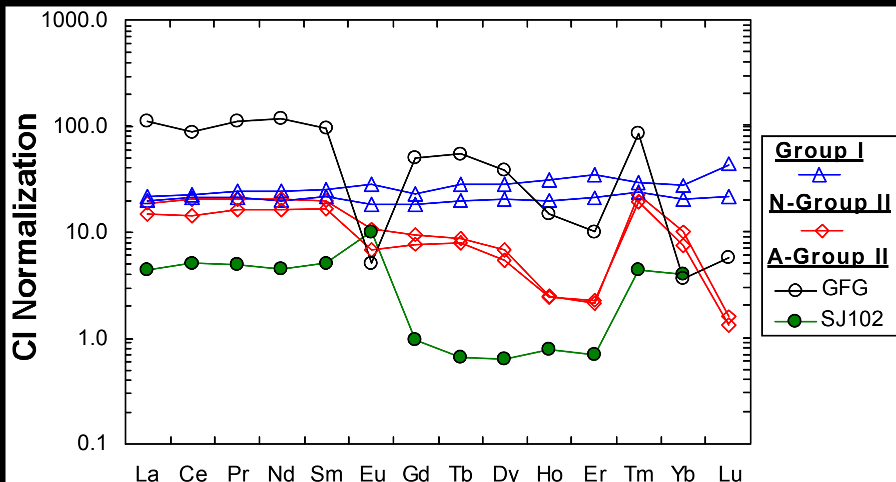
Huang and Jacobsen (2017)



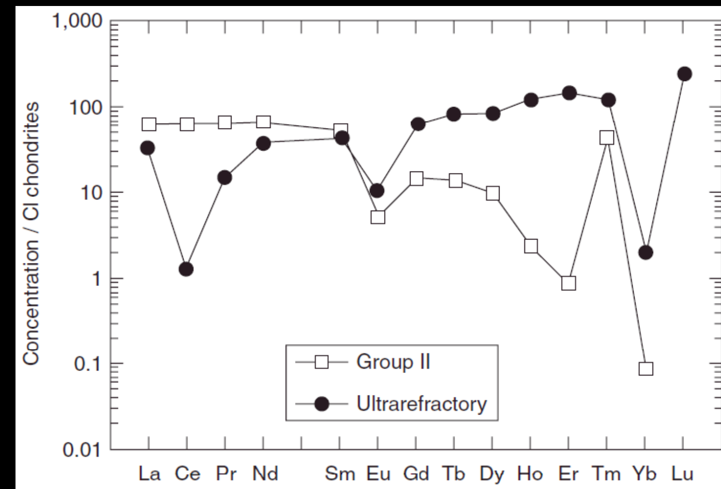
Shu et al. (1997)

- x-wind model for refractory inclusion formation: 高温低压
- 绝大多数难熔包裹体的钙同位素偏轻
- 为什么？

难熔包裹体的稀土元素分布模式



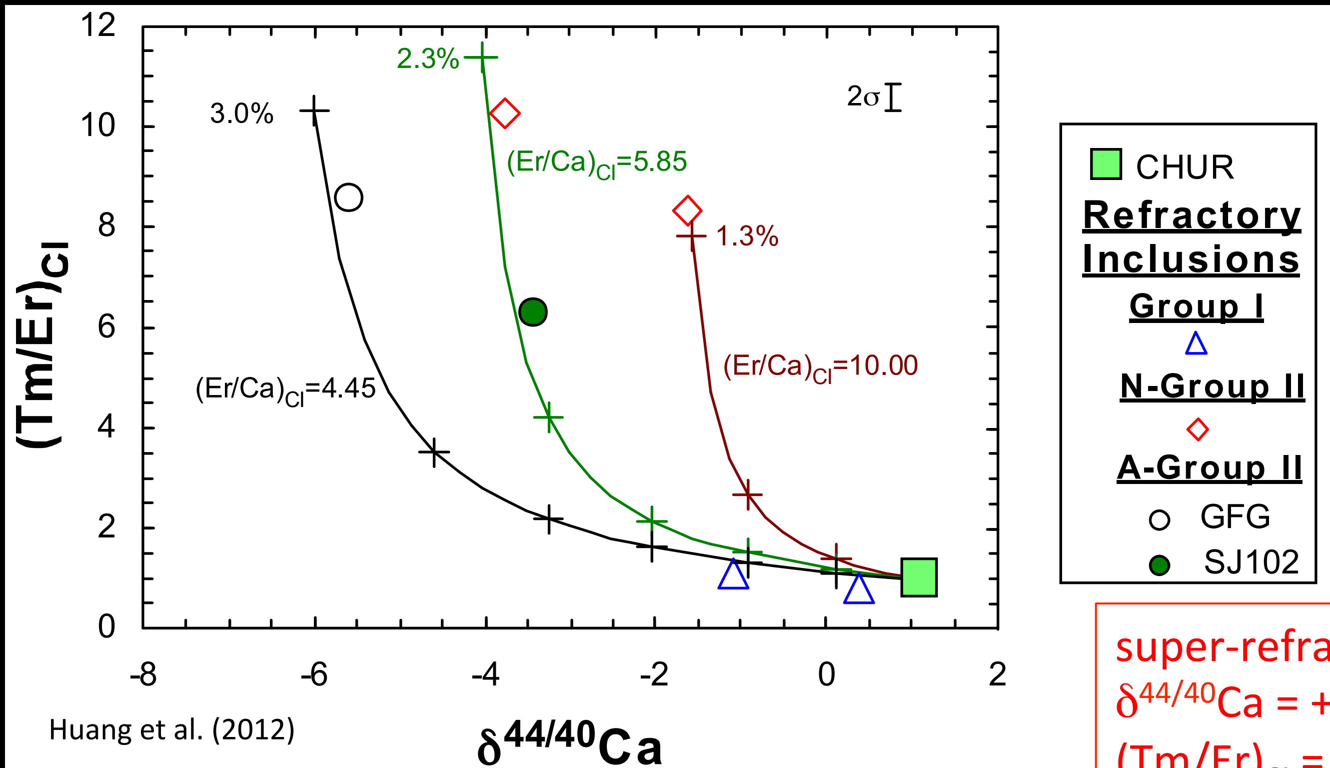
Huang et al. , 2012



Macpherson, 2004

- 太阳系内最老的固体
- 其成因很太阳系早期星云内的蒸发和凝结过程相关
- 不同的稀土元素分馏分布模式
  - Group I: 水平
  - Group II: 正Tm异常， 高Tm/Er
  - 超难熔（Ultrarefractory）：和 Group II 互补(低Tm/Er)，非常罕见

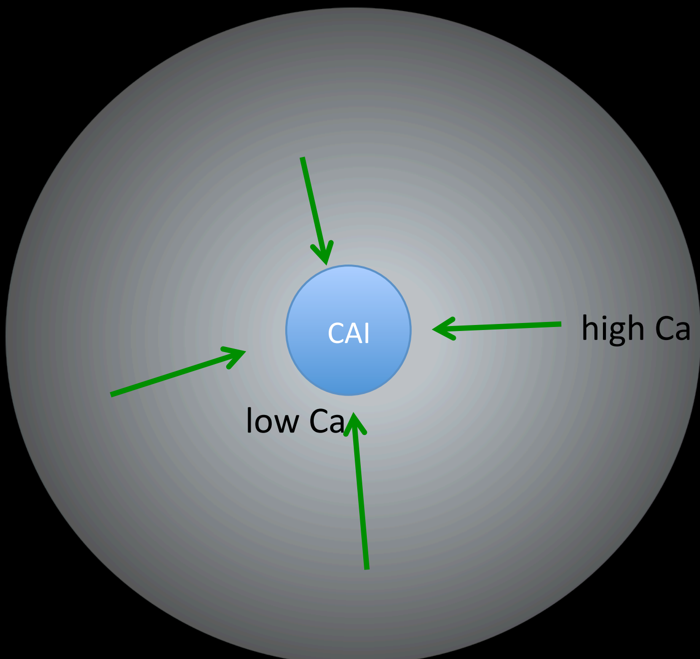
难熔包裹体中$\delta^{44/40}$Ca-Tm/Er的相关性

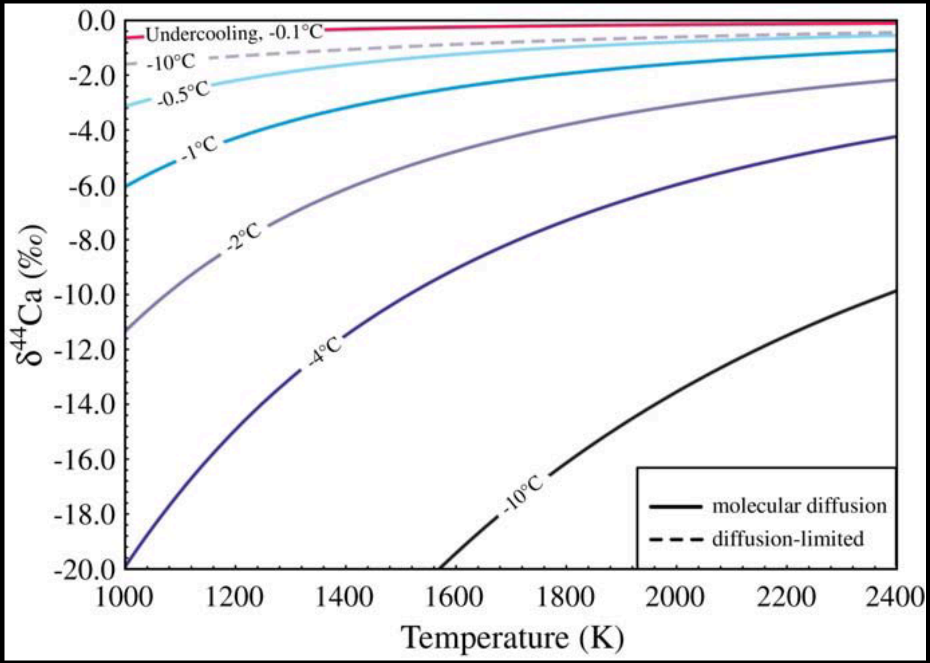


super-refractory residue
$\delta^{44/40}$Ca = +28
$(Tm/Er)_{CI}$ = 0.25

- $\delta^{44/40}$Ca和Tm/Er负相关
- 有Group II稀土元素分布模式的难熔包裹体有更低的$\delta^{44/40}$Ca
- 高温蒸发后的残余物（super-refractory residue）应该有高$\delta^{44/40}$Ca和低Tm/Er值, 和难熔包裹体的特征相反
- 从一个具有球粒陨石特征的储库中分离出去高温蒸发后的残余物后，可以得到观察到的低$\delta^{44/40}$Ca-高$(Tm/Er)_{CI}$特征

难熔包裹体的钙同位素变化: super cooling



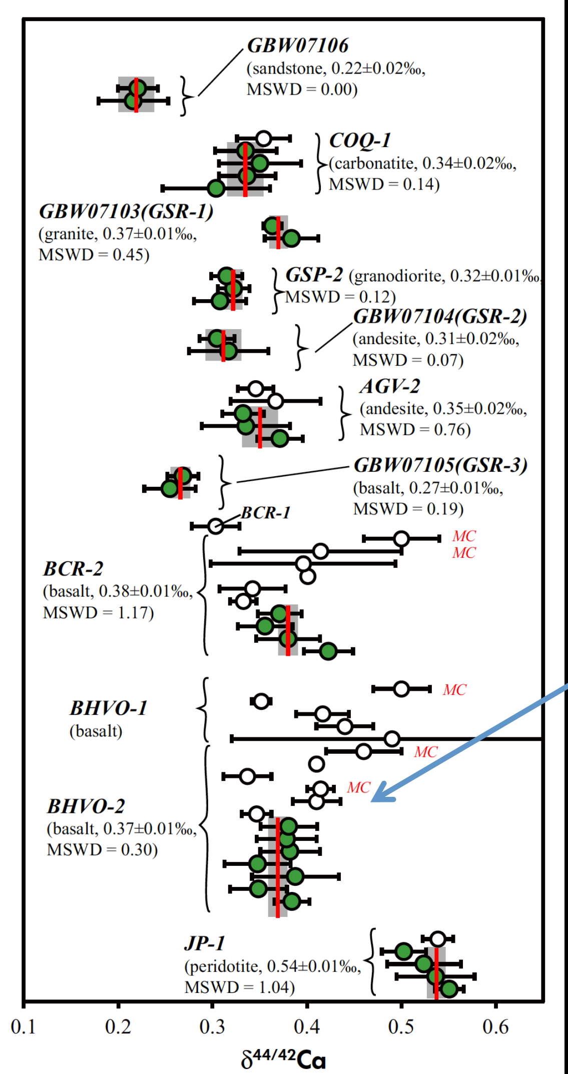


Simon and DePaolo (2010)

- 难熔包裹体在过冷（super cooling）的太阳系星云中凝结出来
- 动力学效应（kinetic isotope effect）: Ca diffusion in the solar nebula

钙同位素的分馏

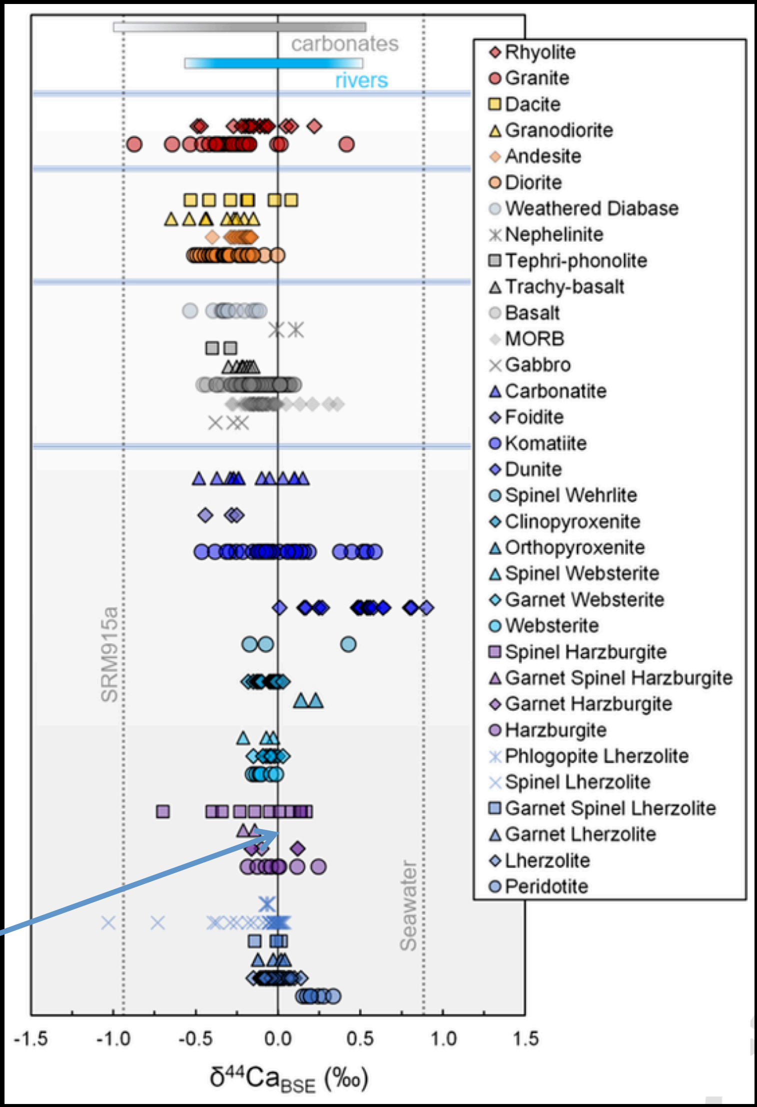
terrestrial igneous and metamorphic rocks
2‰ variation in $^{44/40}$Ca



He et al. (2017)

inter-lab difference: 0.2 in $\delta^{44/40}$Ca

$\delta^{44/40}Ca_{915a}$ = 0.95



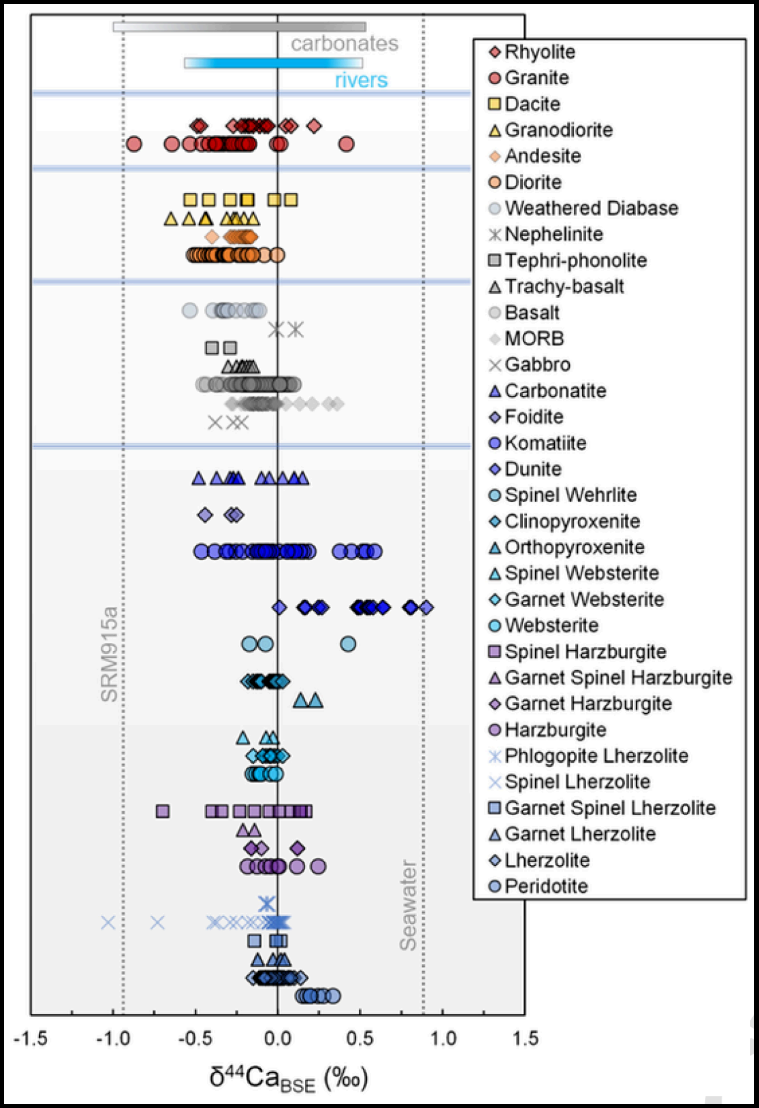
Antonelli and Simon (2020)

钙同位素的分馏

- condensation/evaporation
- inter-mineral fractionation
- partial melting / crystal fractionation
- recycling of surface material
- Soret effect: thermal diffusion
- chemical diffusion

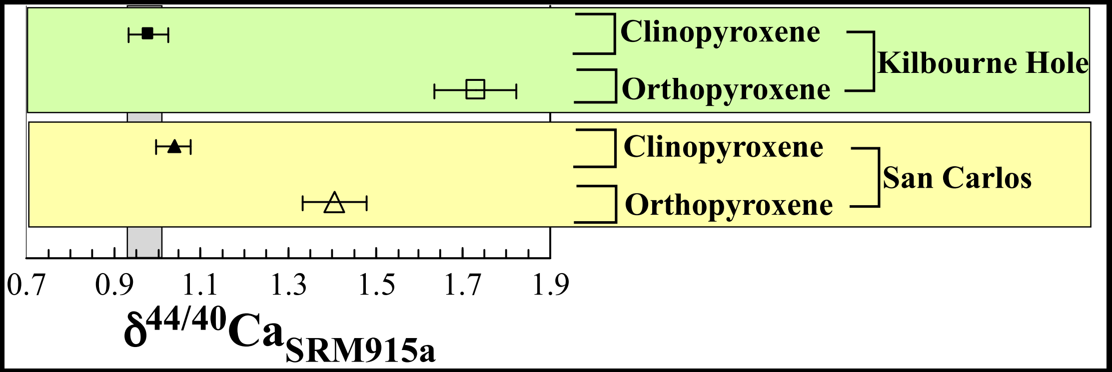
- 凝结和蒸发
- 矿物间分馏
- 部分熔融和结晶分异
- 表层物质再循环
- 热扩散: Soret effect:
- 化学扩散

terrestrial igneous and metamorphic rocks
2‰ variation in $^{44/40}Ca$



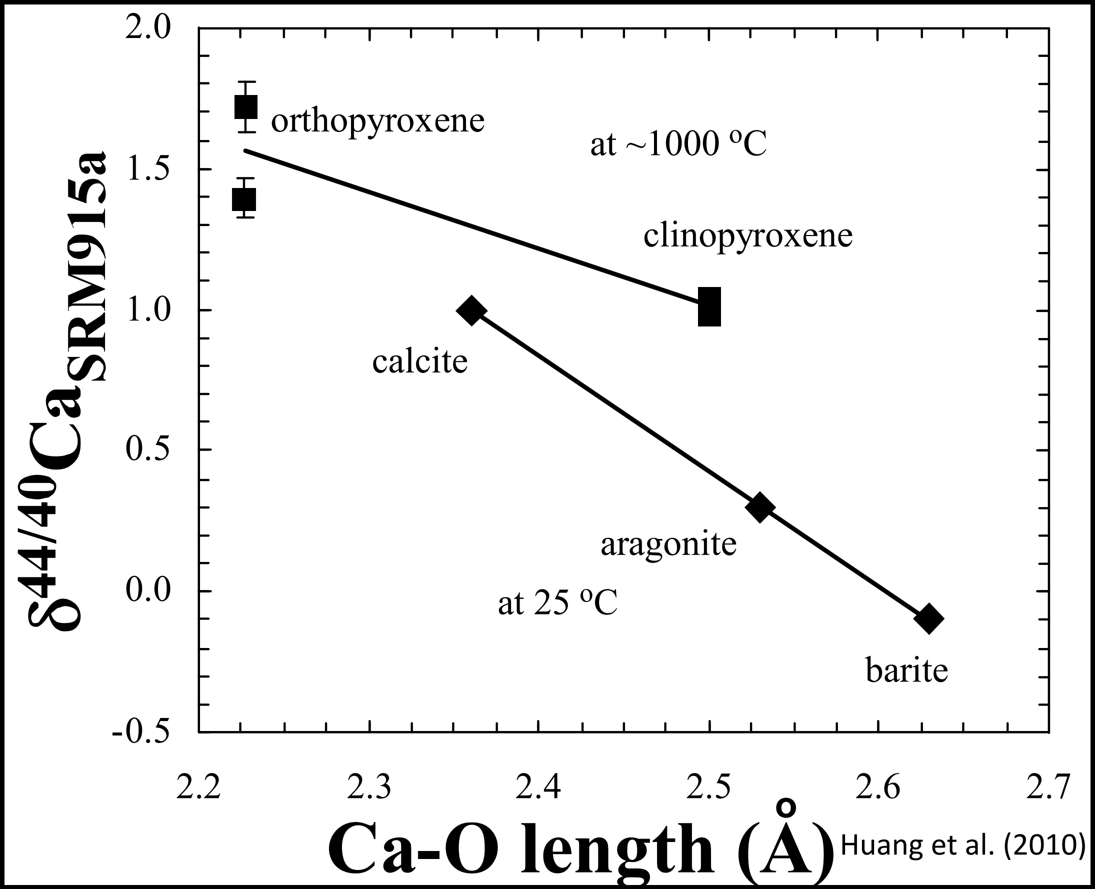
Antonelli and Simon (2020)

钙同位素在辉石间的分馏: 观察和第一性原理计算结果



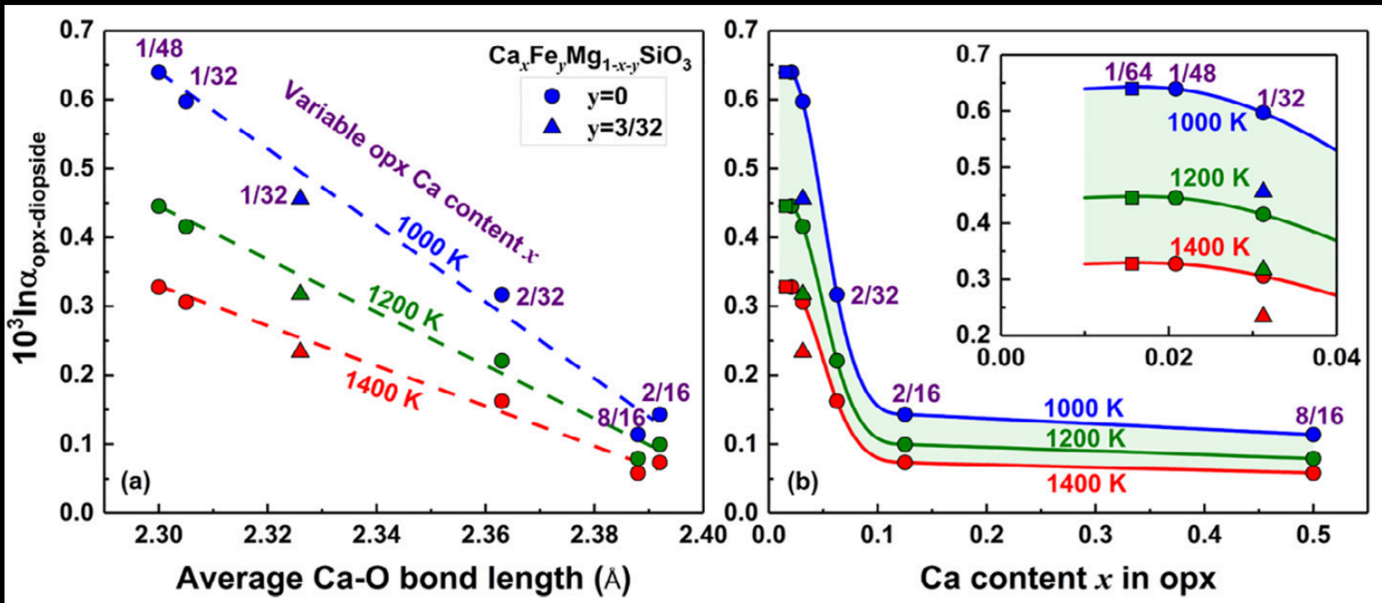
- 尖晶石相橄榄岩: olivine, orthopyroxene, clinopyroxene, spinel
- Ca isotopic measurement of orthopyroxene-clinopyroxene pairs from Kilbourne Hole and San Carlos spinel peridotites

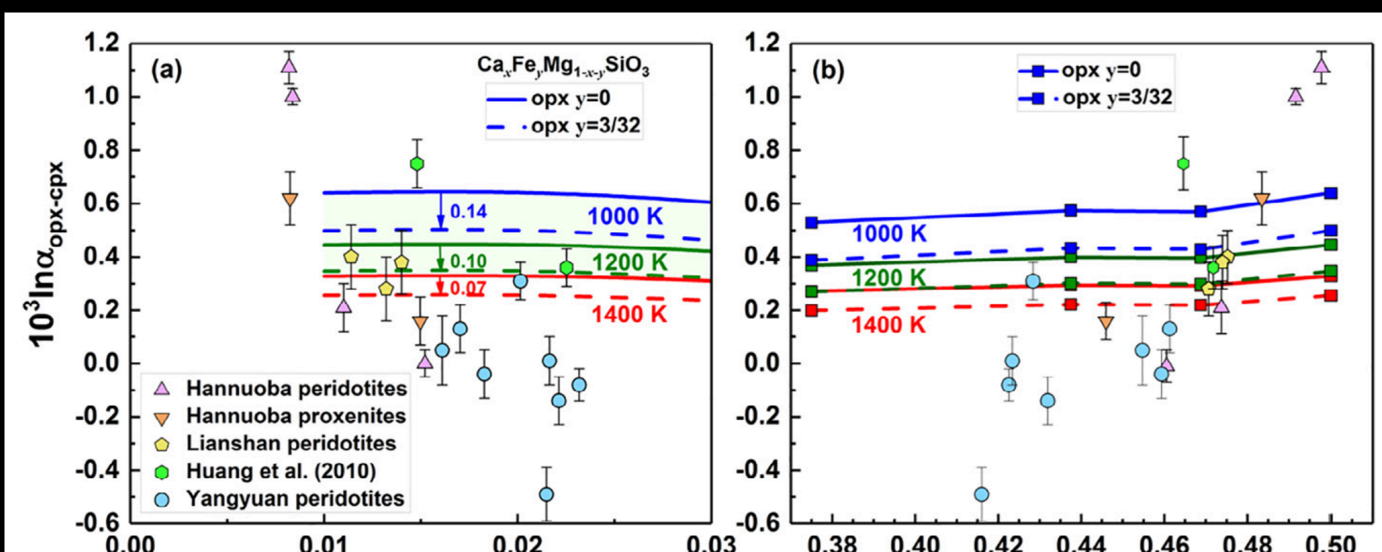
矿物间的钙同位素分馏与Ca-O键长的关系



- Ca isotopic fractionation between CPX-OPX is comparable to low T inter-mineral fractionation
- Ca isotopic fractionation between minerals is controlled by their Ca-O bond lengths: mineral with shorter Ca-O bond tends to have heavier Ca isotopes

矿物间钙同位素分馏和矿物成份的关系

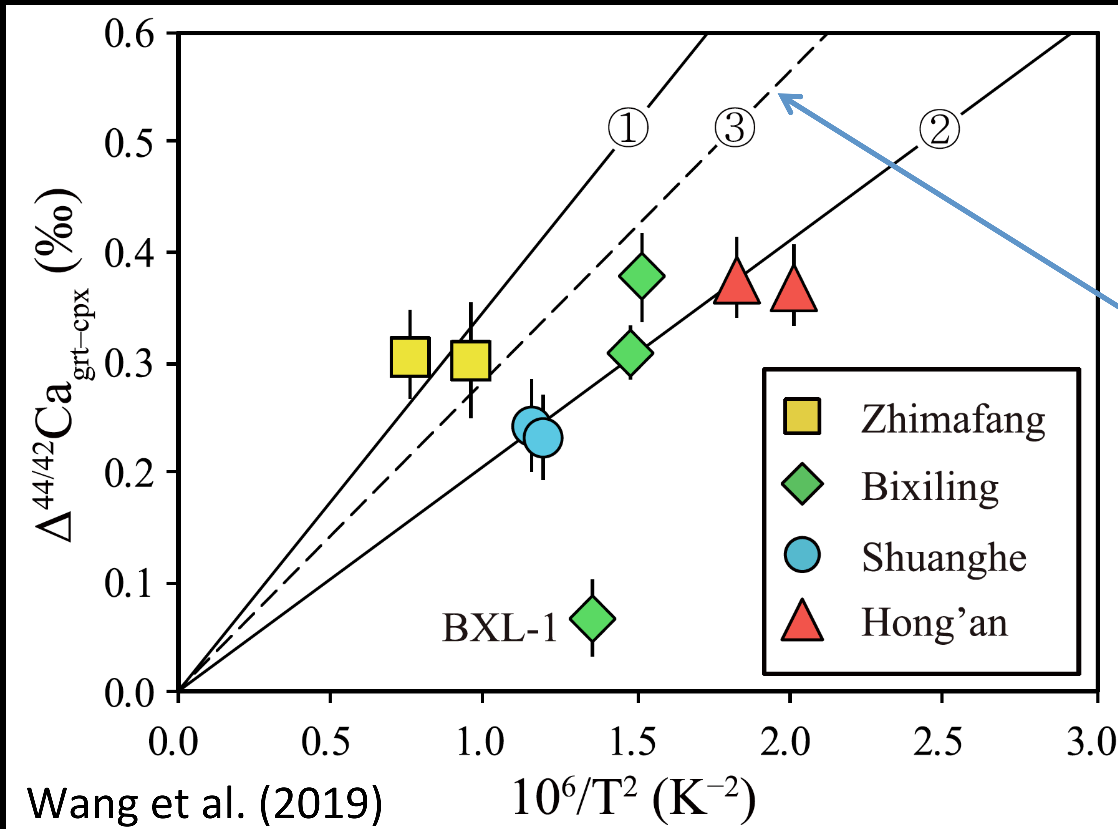




Wang et al. (2017)

- 平衡分馏
  - 浓度效应？
- 动力学分馏？
- 更多见王文忠博士的报告

石榴子石和单斜辉石间的钙同位素分馏



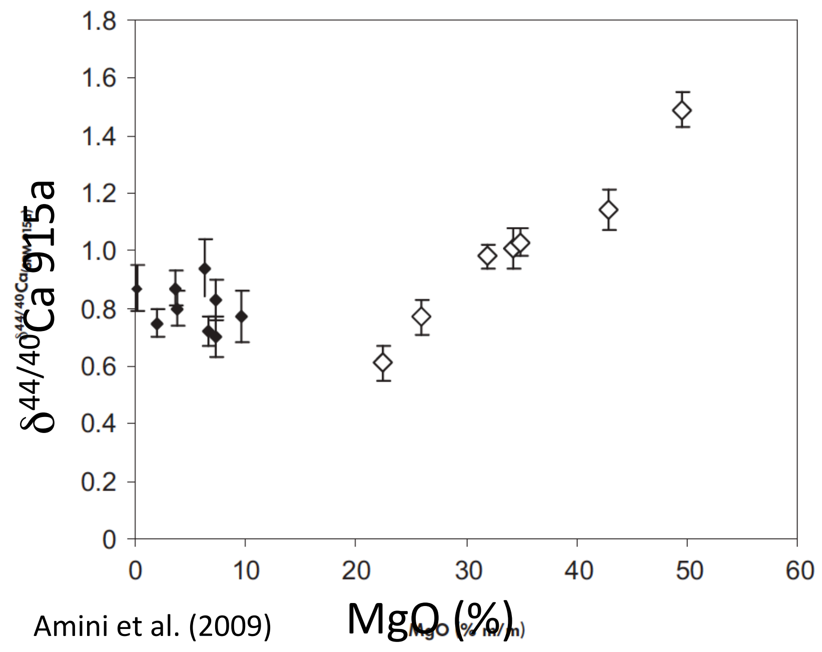
第一性原理计算结果（黄方等2019）

- 石榴子石比单斜辉石更重

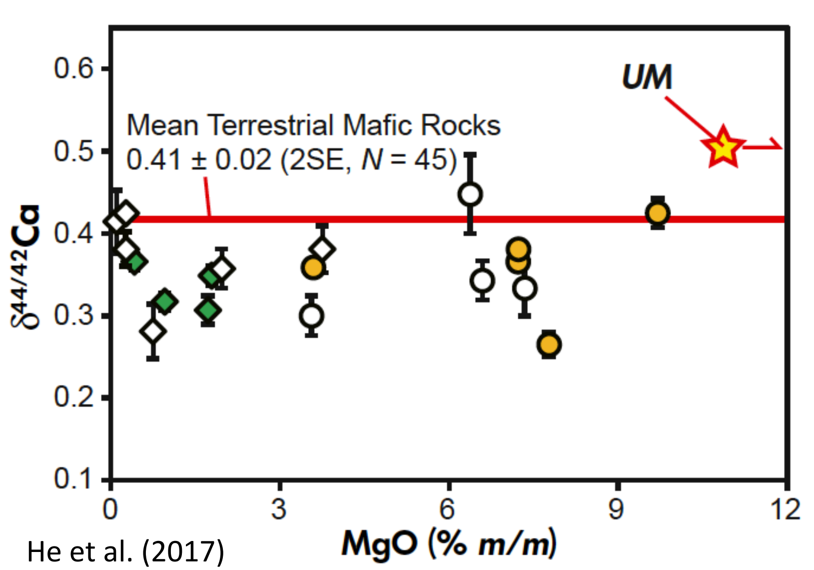
钙同位素的分馏：部分熔融效应

terrestrial igneous and metamorphic rocks

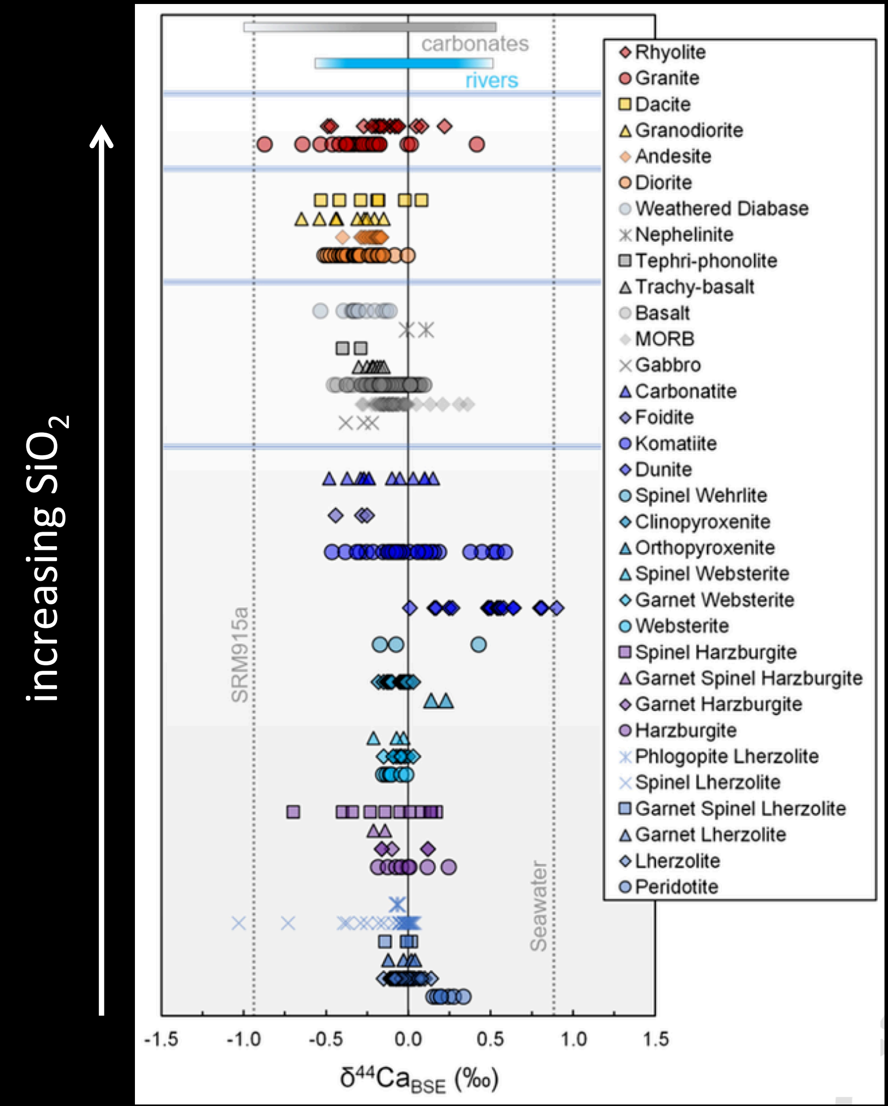
2‰ variation in $^{44/40}Ca$



Amini et al. (2009)

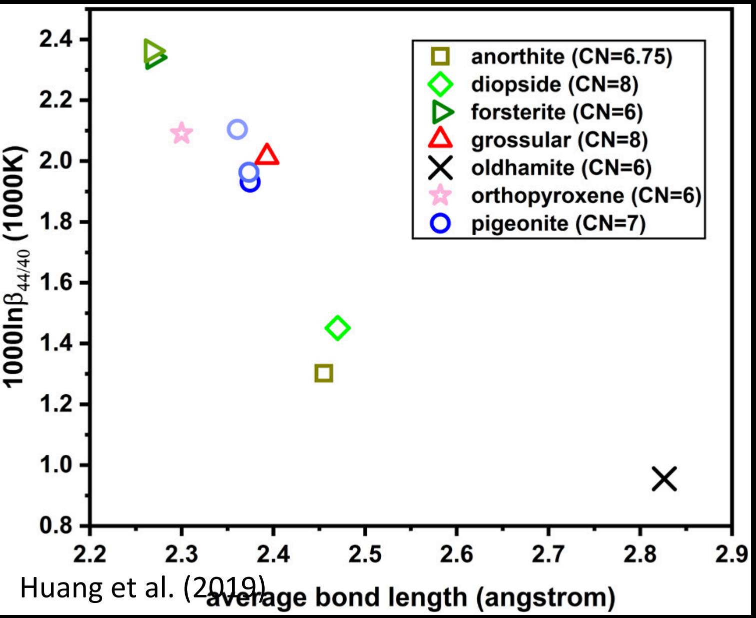


He et al. (2017)

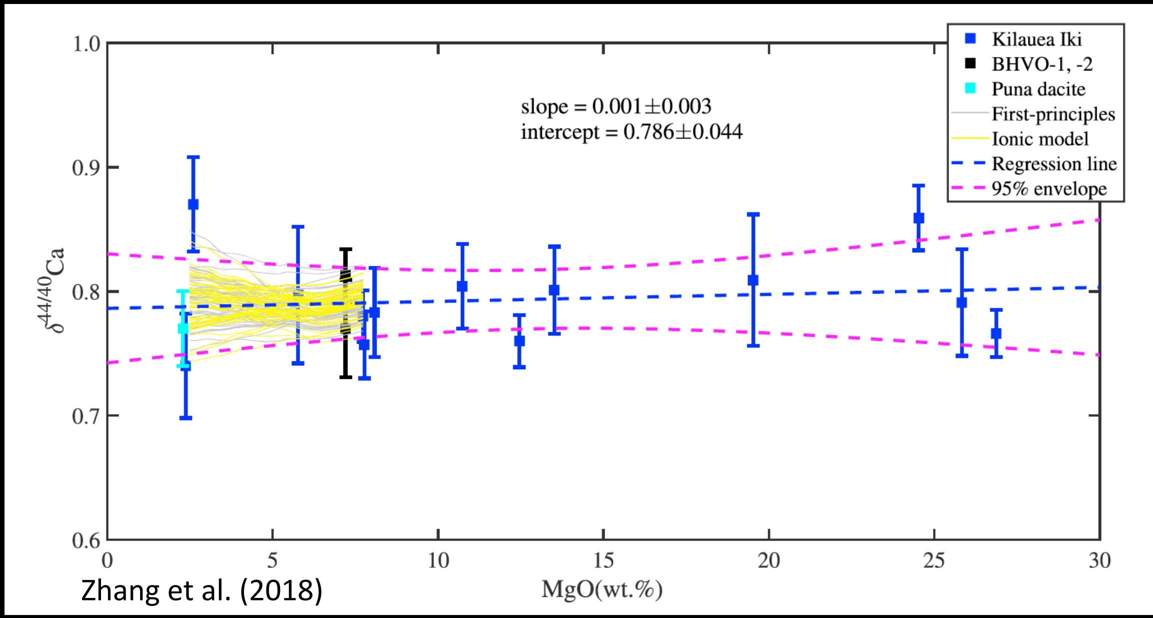


Antonelli and Simon (2020)

钙同位素的分馏：矿物-熔体的分馏系数



Huang et al. (2019)



Zhang et al. (2018)

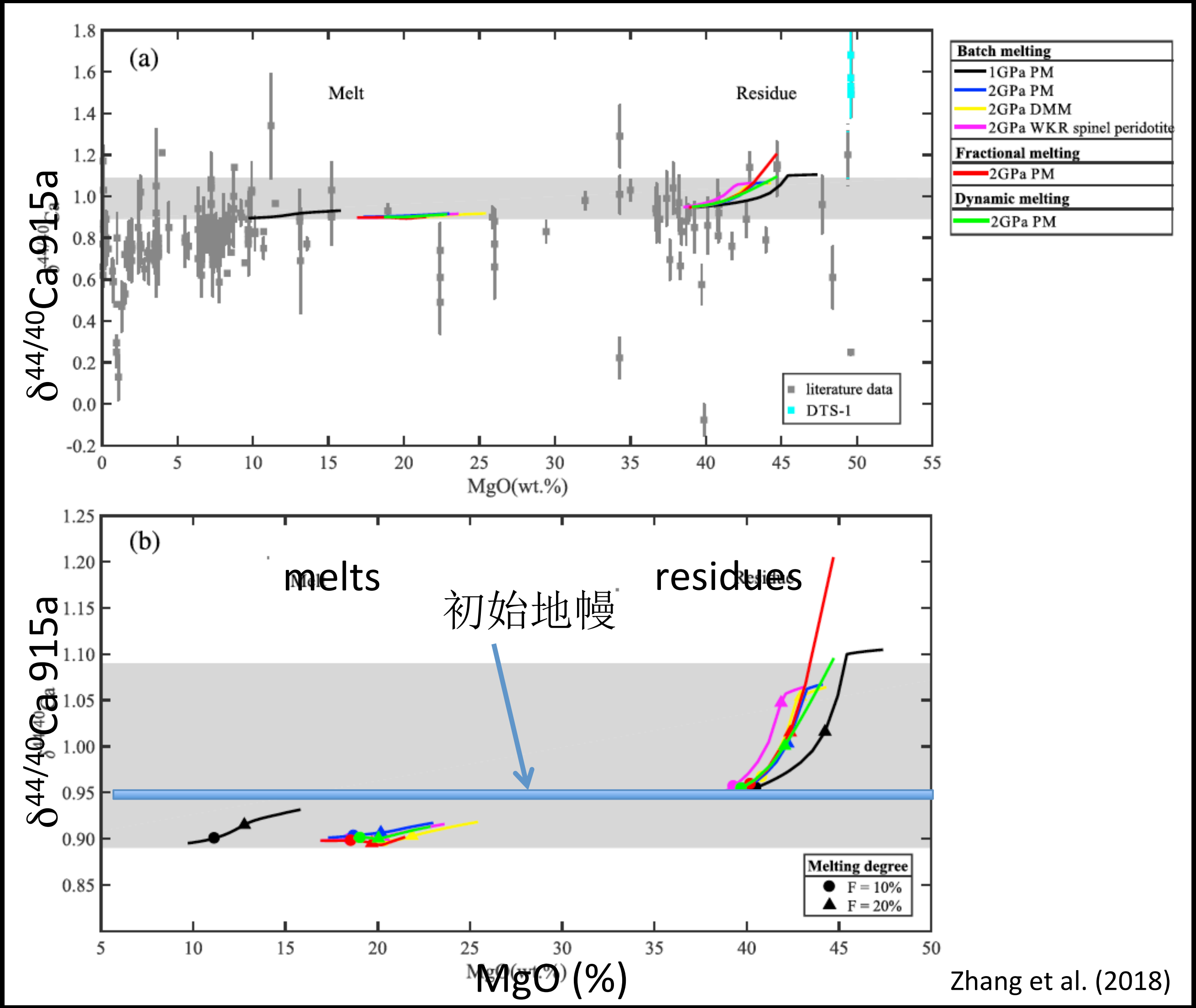
Estimated Mineral-Melt Ca Fractionation Factors

Minerals	Formula	*a*					
		First principles	2 SD	Ionic model	2 SD	Average	2 SD
Clinopyroxene	$Ca_{15/32}Mg_{17/32}SiO_3$	0.07	0.05	0.11	0.05	0.09	0.07
Plagioclase	$CaAl_2Si_2O_8$	−0.12	0.06	−0.17	0.07	−0.15	0.08
Pigeonite	$Ca_{1/8}Mg_{7/8}SiO_3$	0.49	0.08	0.39	0.07	0.44	0.13
Orthopyroxene	$Ca_{1/32}Fe_{3/32}Mg_{7/8}SiO_3$	0.49	0.08	0.55	0.08	0.52	0.10

$\Delta^{44/40}Ca^{mineral\text{-}melt} = a/(T/1{,}000)^2$, where T is the temperature in kelvin.

- 矿物间的分馏系数：first principles calculations （大多数来自USTC，UCLA）
- 斜长石，单斜辉石与熔体的分馏系数：Kilauea Iki lava series （Zhang et al., 2018）

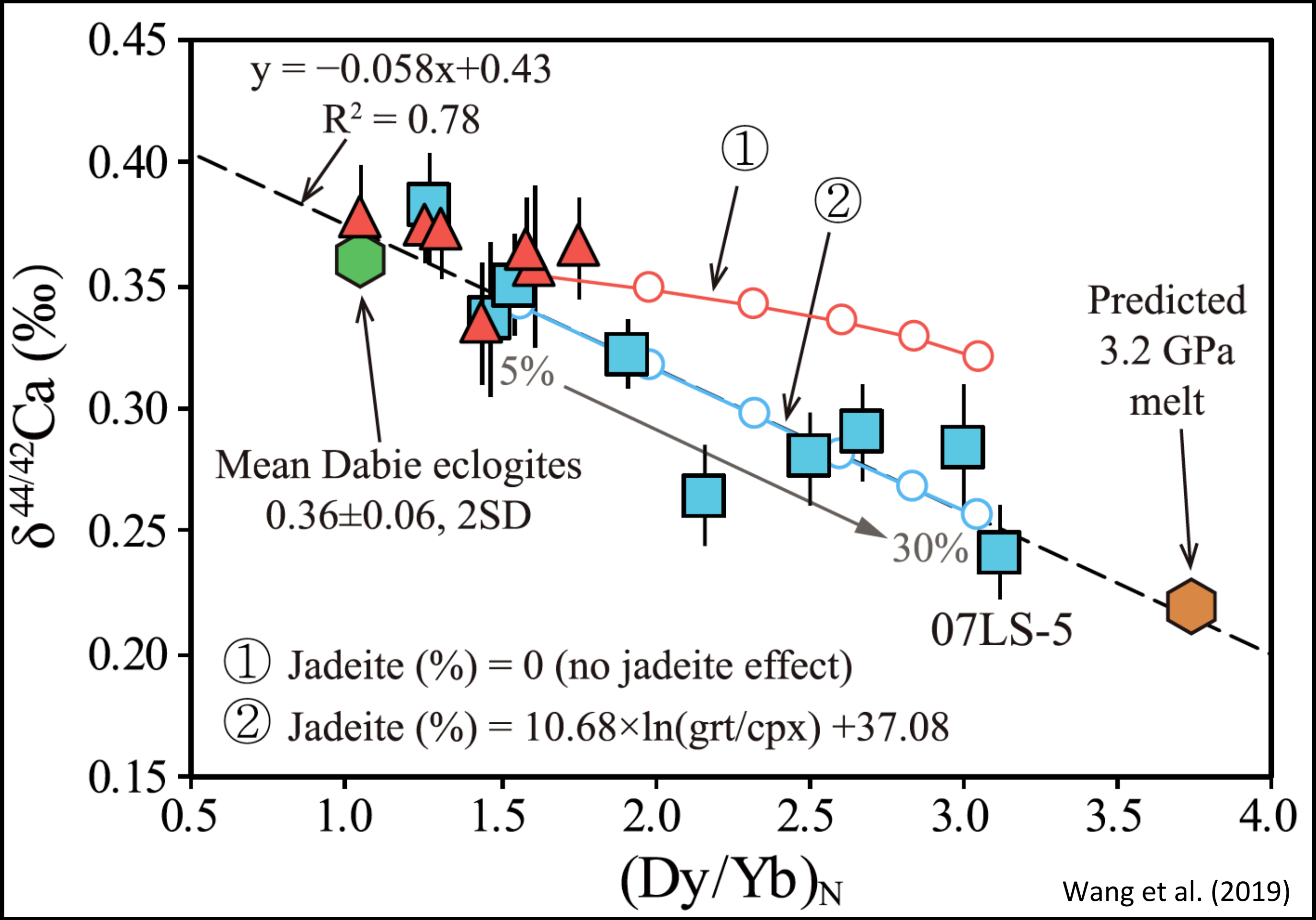
钙同位素的分馏：spinel peridotite部分熔融



Zhang et al. (2018)

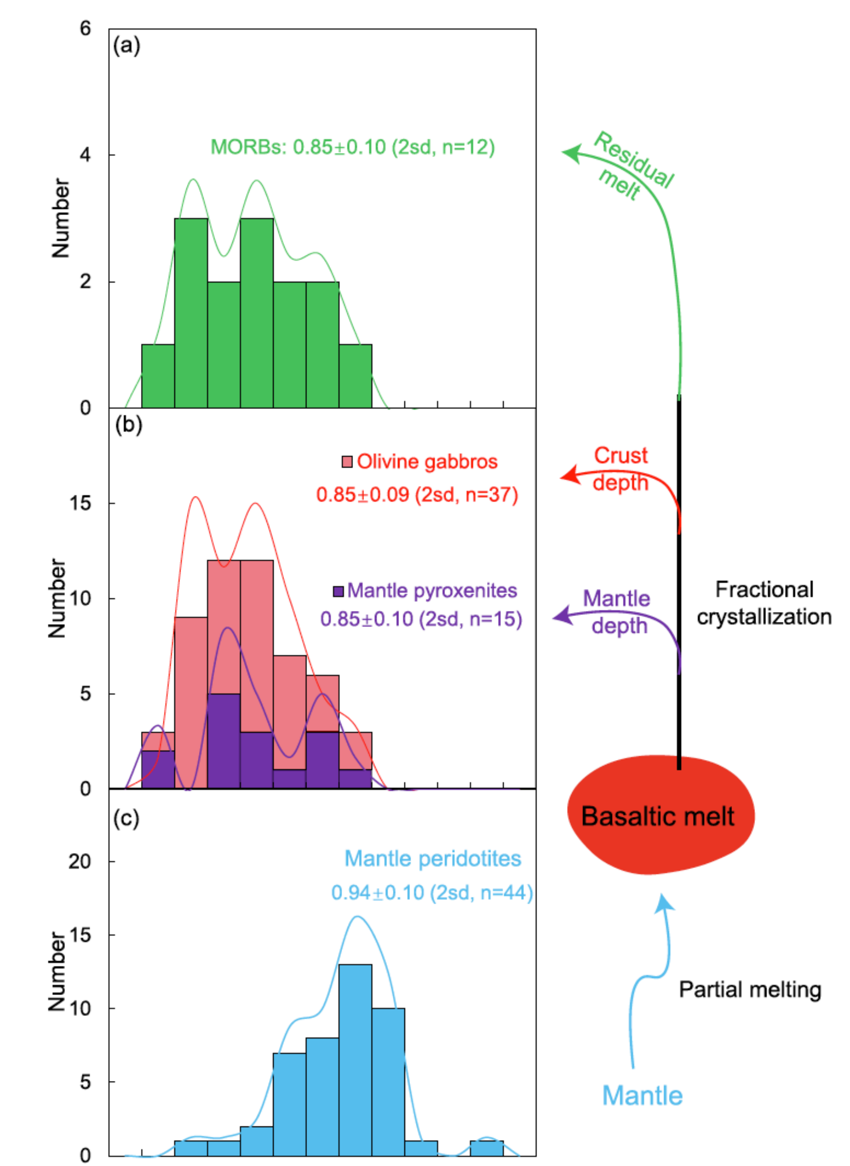
- 熔体偏轻：最大的$\delta^{44/40}$Ca效应将近0.06
- 残余偏重：最大的$\delta^{44/40}$Ca效应将近0.3

钙同位素的分馏：garnet pyroxenite部分熔融

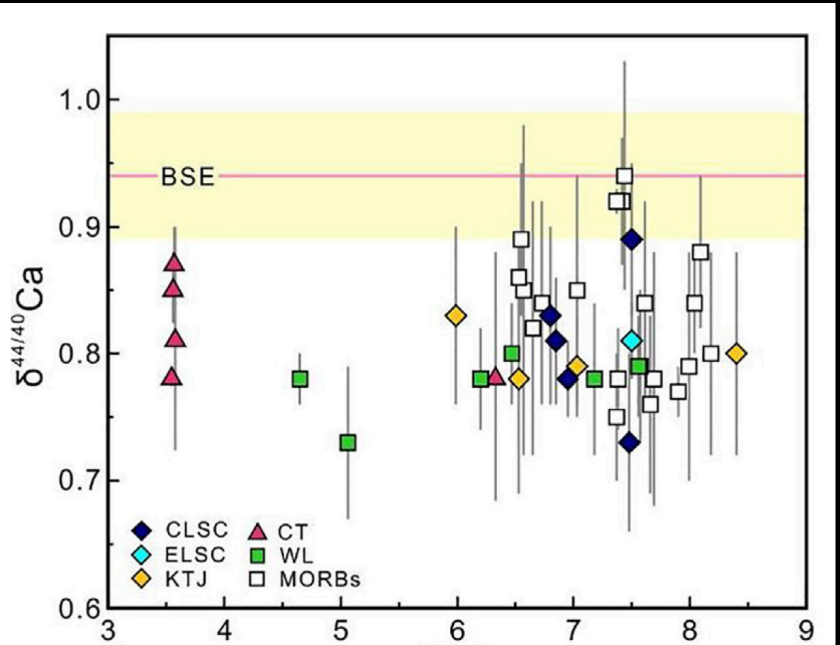


- 熔体最大的$\delta^{44/40}$Ca效应 > 0.2

钙同位素的分馏：大洋玄武岩偏轻



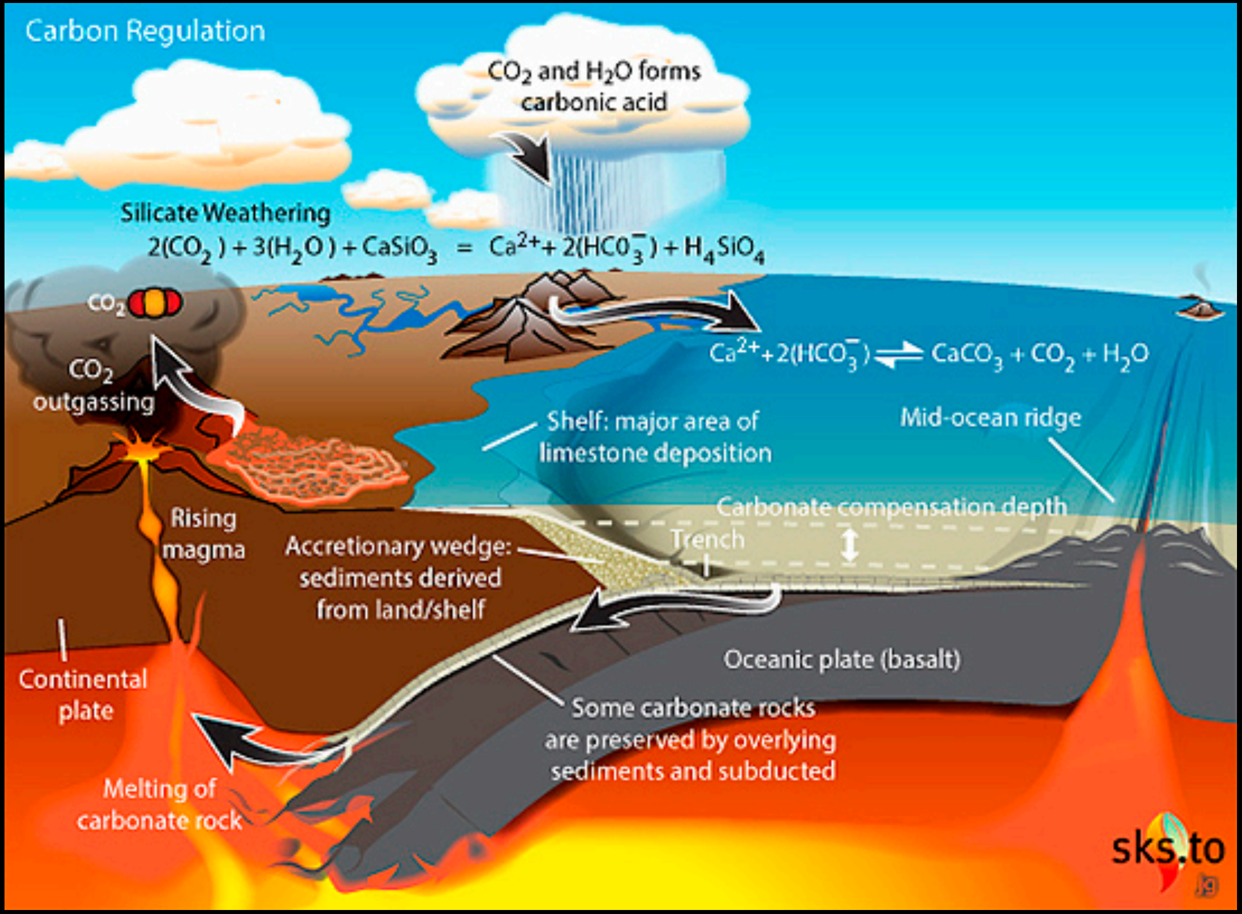
Chen et al. (2020)



Zhu et al. (2020)

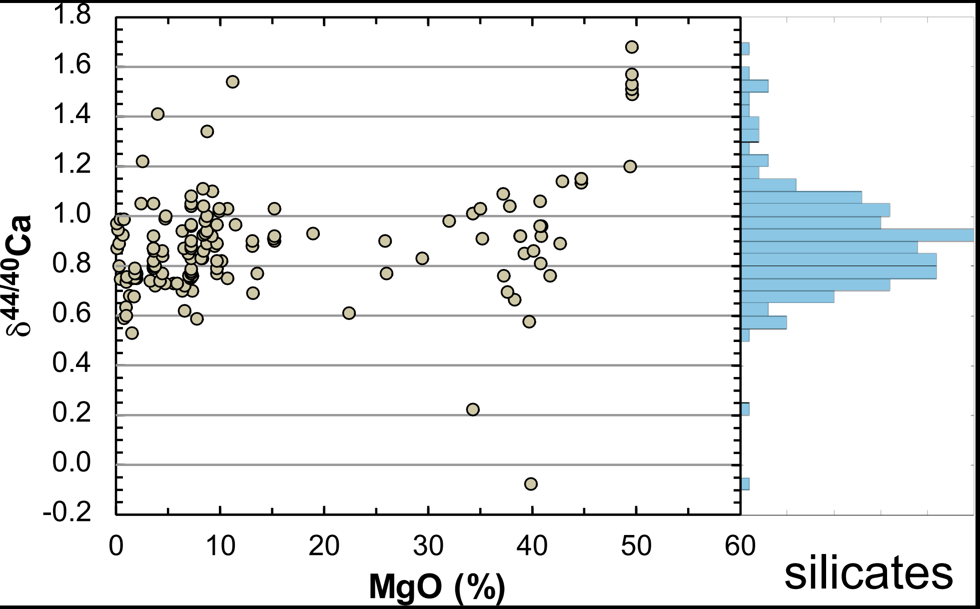
- 部分熔融效应（更多见汪在聪教授的报告）
- 再循环碳酸盐
- 残留石榴子石效应（Hirschmann and Stolper, 1996; Donnelly et al., 2004; Yang et al., 2020）

碳酸盐再循环：钙同位素的证据

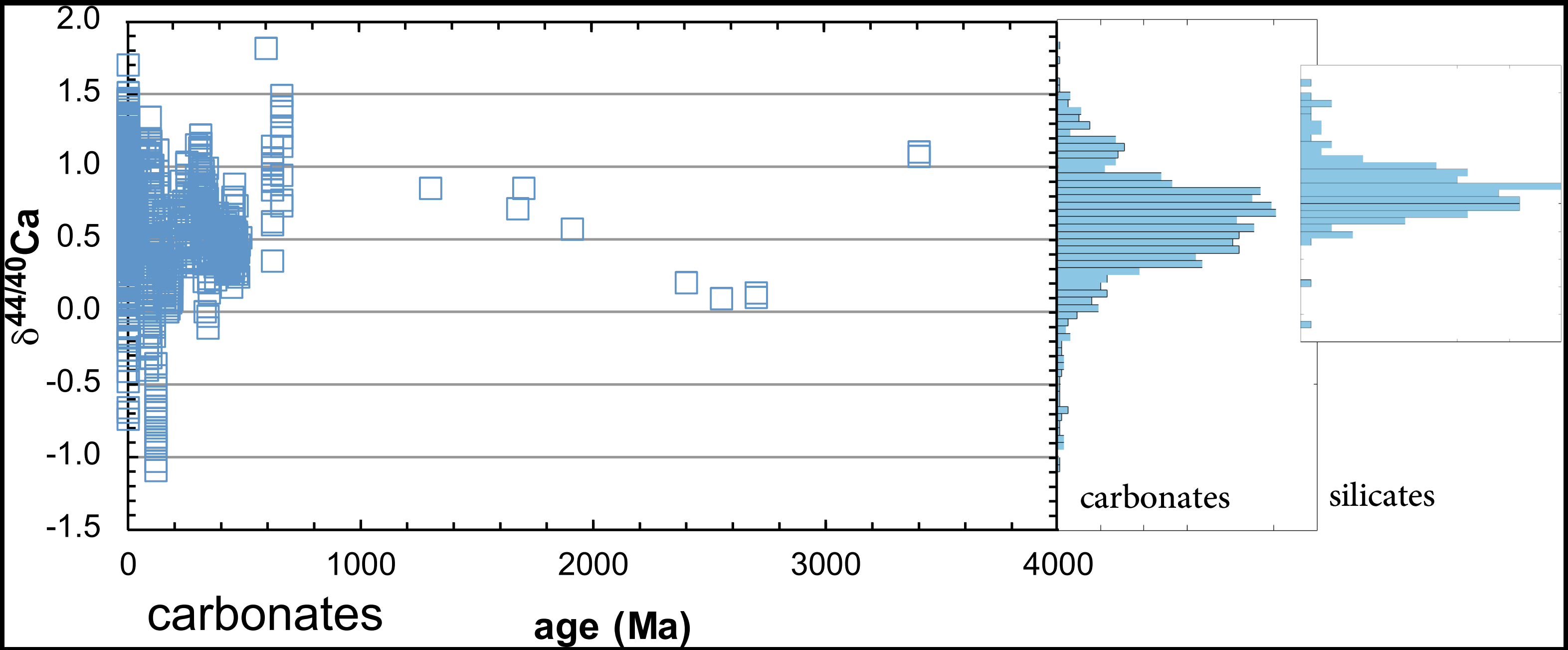


- 钙循环是碳循环的重要组成

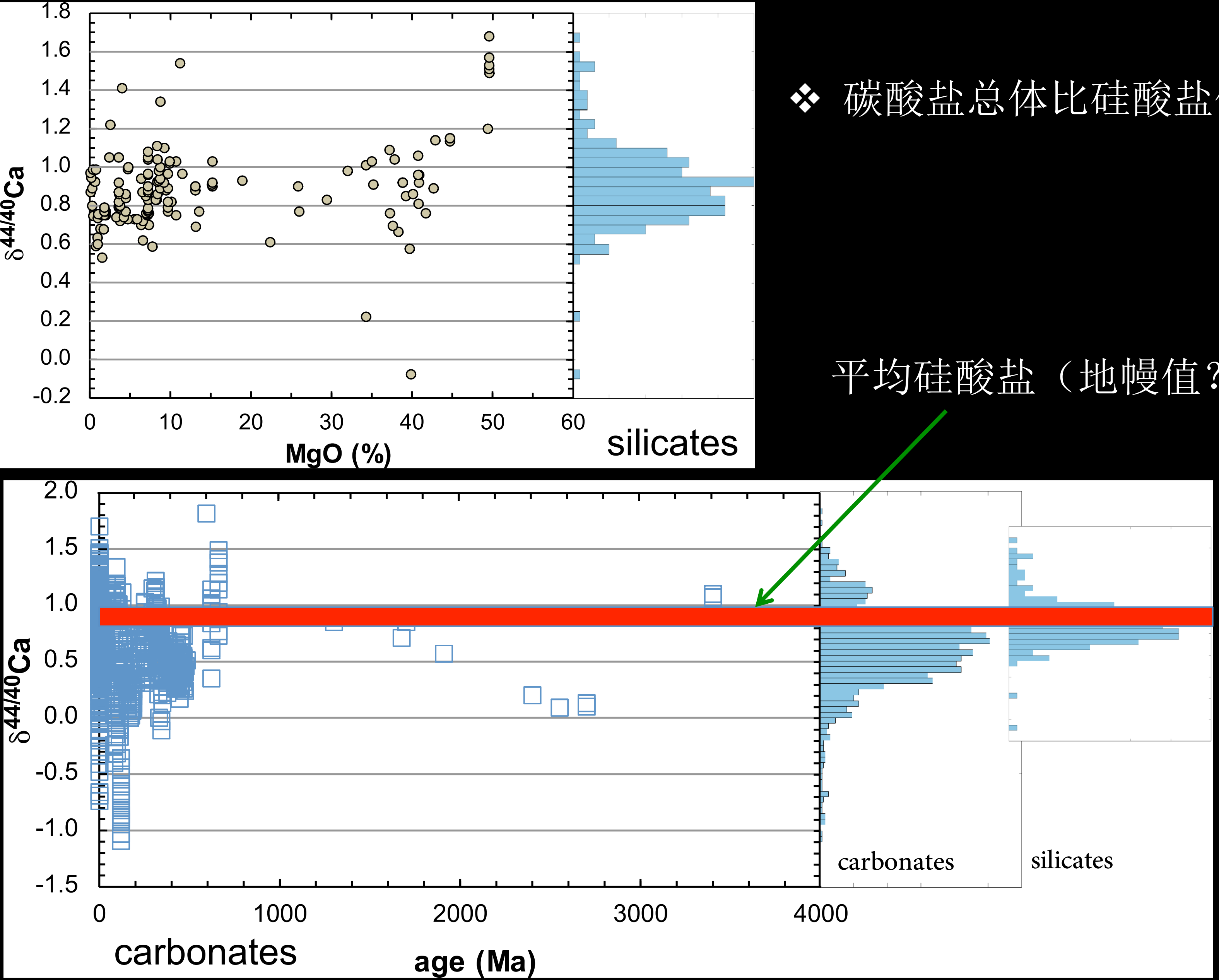
硅酸盐和碳酸盐中的钙同位素组成



❖ 碳酸盐总体比硅酸盐偏轻

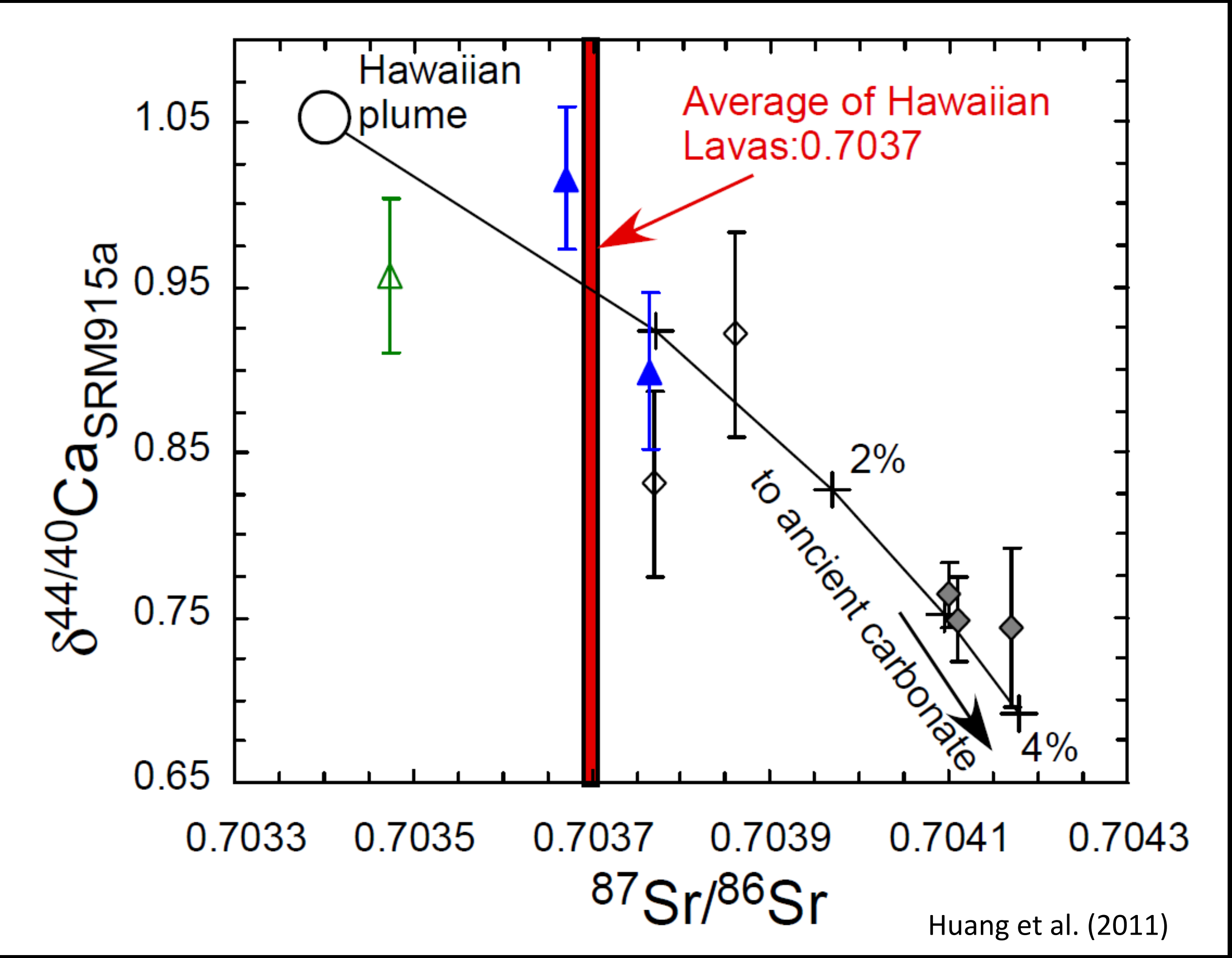


硅酸盐和碳酸盐中的钙同位素组成



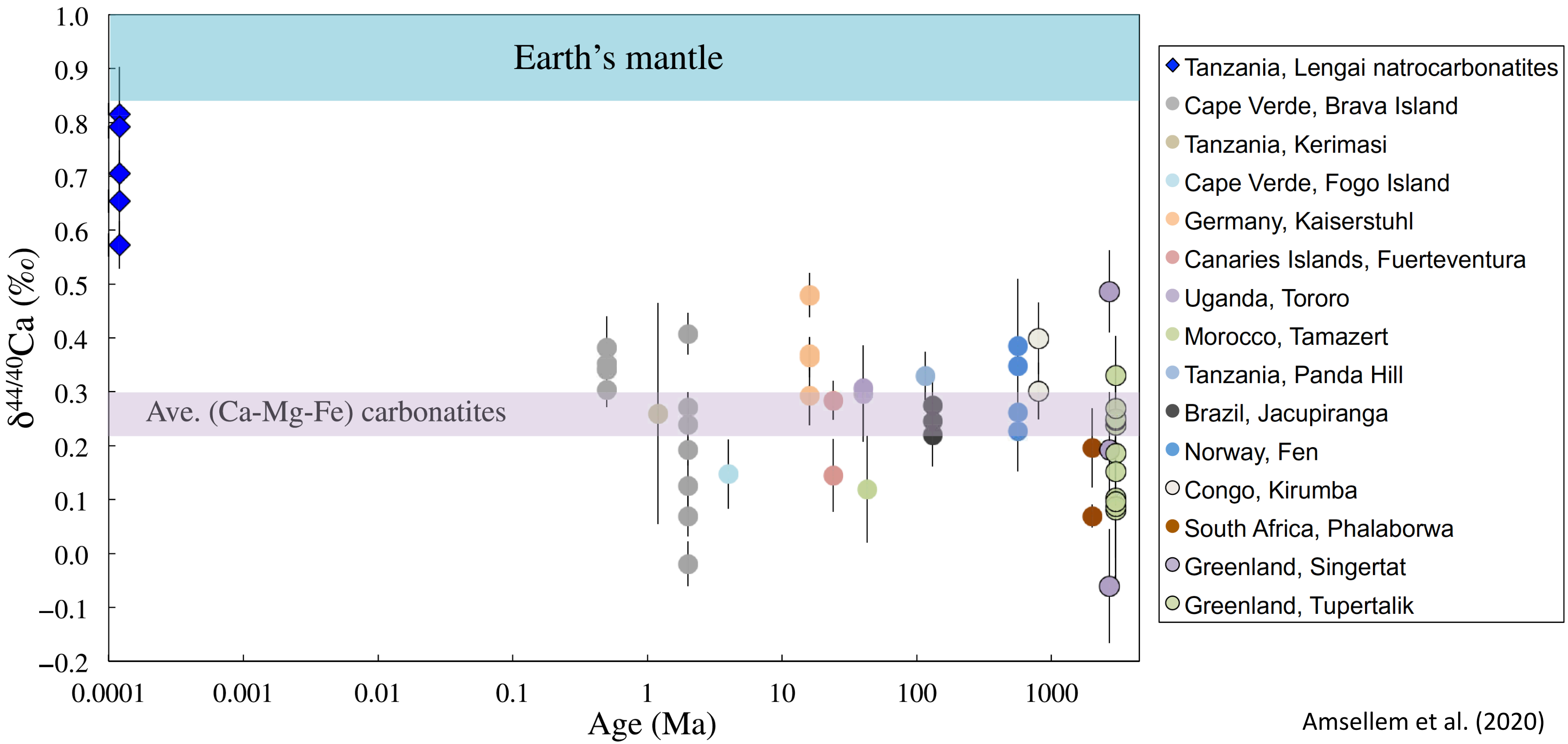
❖ 碳酸盐总体比硅酸盐偏轻

夏威夷地幔柱中再循环碳酸盐的信号



- 0.8% ancient carbonate in the Hawaiian plume
- Estimated CO_2 emission rate: **3 x 10^8 kg CO_2 per year**
- Direct measurement: **0.2 x 10^8 kg CO_2 per year** at Mauna Loa (Ryan, 2001)

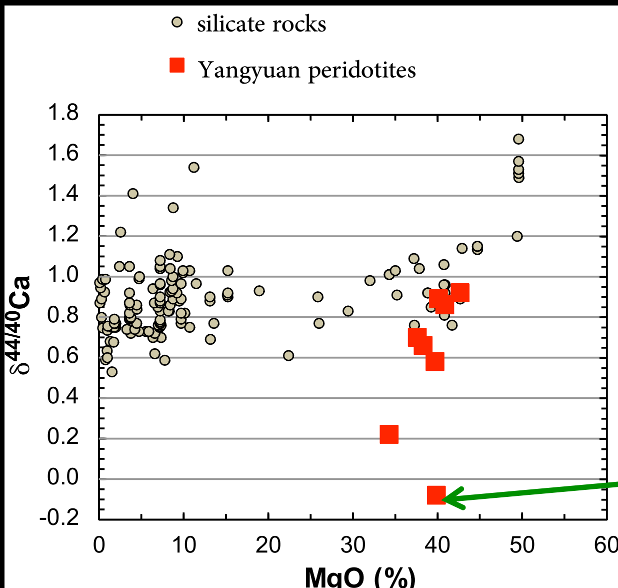
火成碳酸岩中再循环碳酸盐的信号



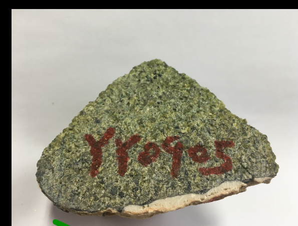
Amsellem et al. (2020)

- 古老的火成碳酸盐的钙同位素偏轻
- 其地幔源区含有大量再循环碳酸盐

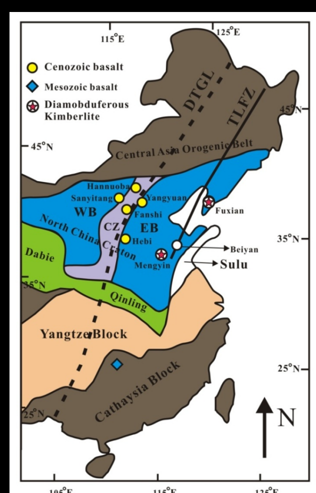
太阳系内的钙同位素变化



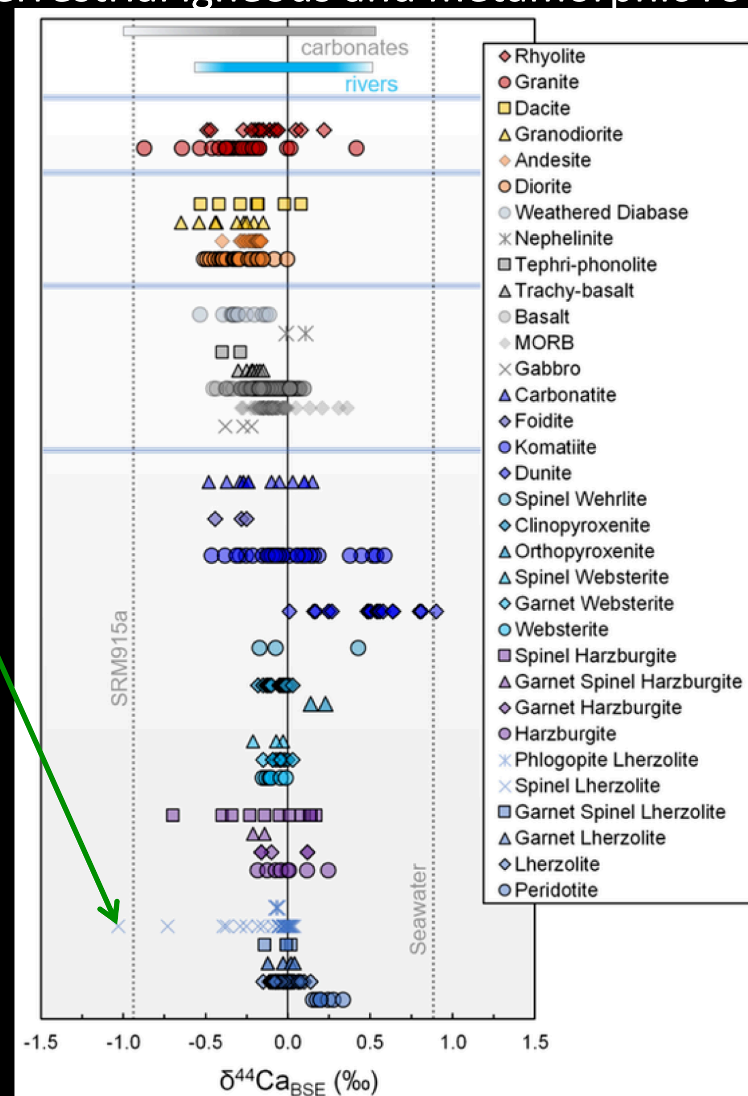
Zhao et al. (2017)



- 阳原富铁橄榄岩有硅酸盐中最低的$\delta^{44/40}$Ca

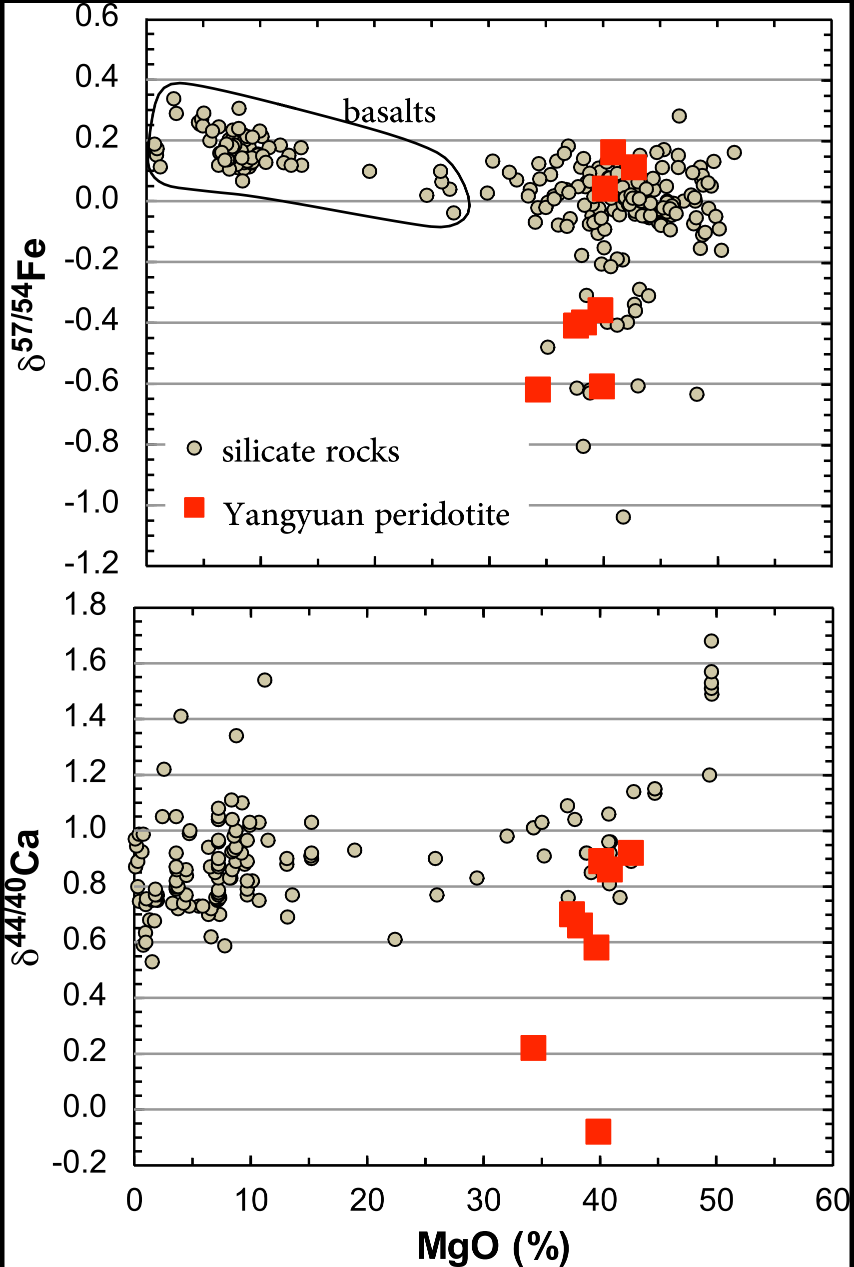


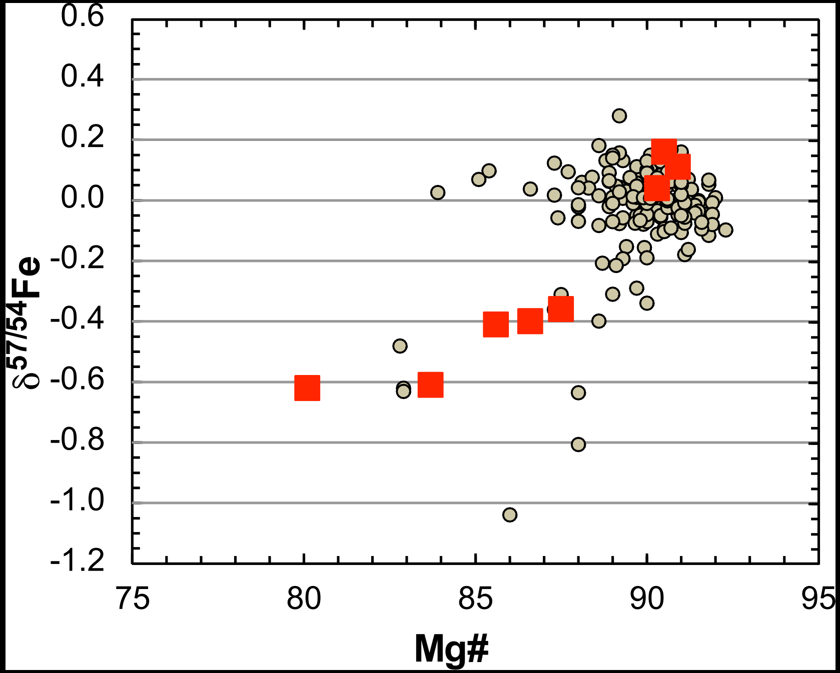
terrestrial igneous and metamorphic rocks



Antonelli and Simon (2020)

阳原富铁橄榄岩的钙铁同位素组成

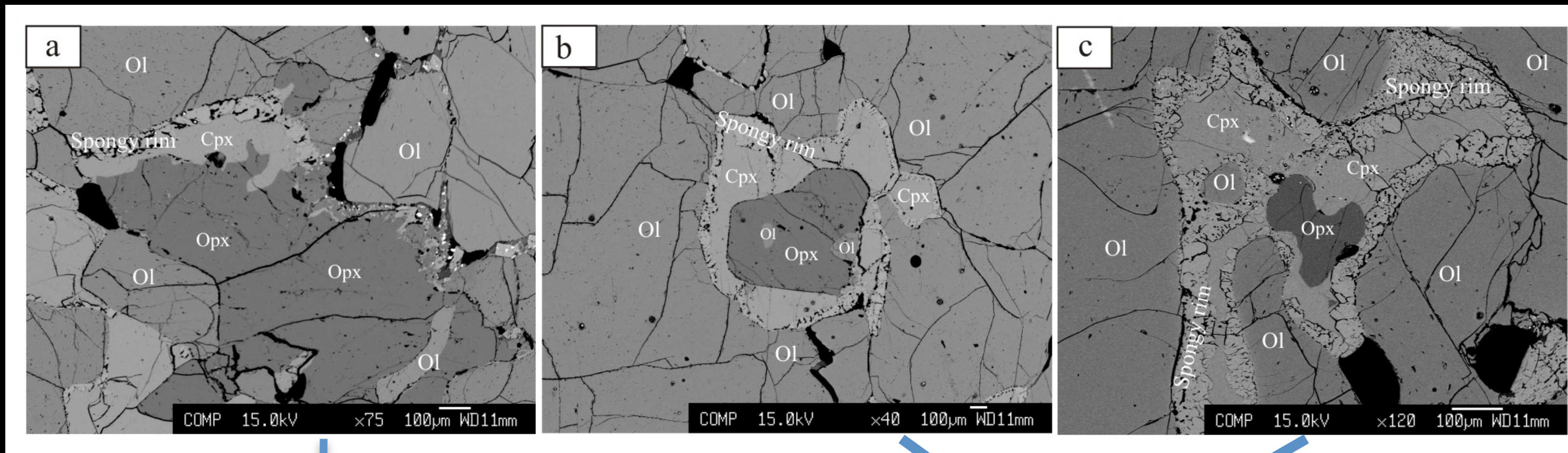




Zhao et al. (2017)

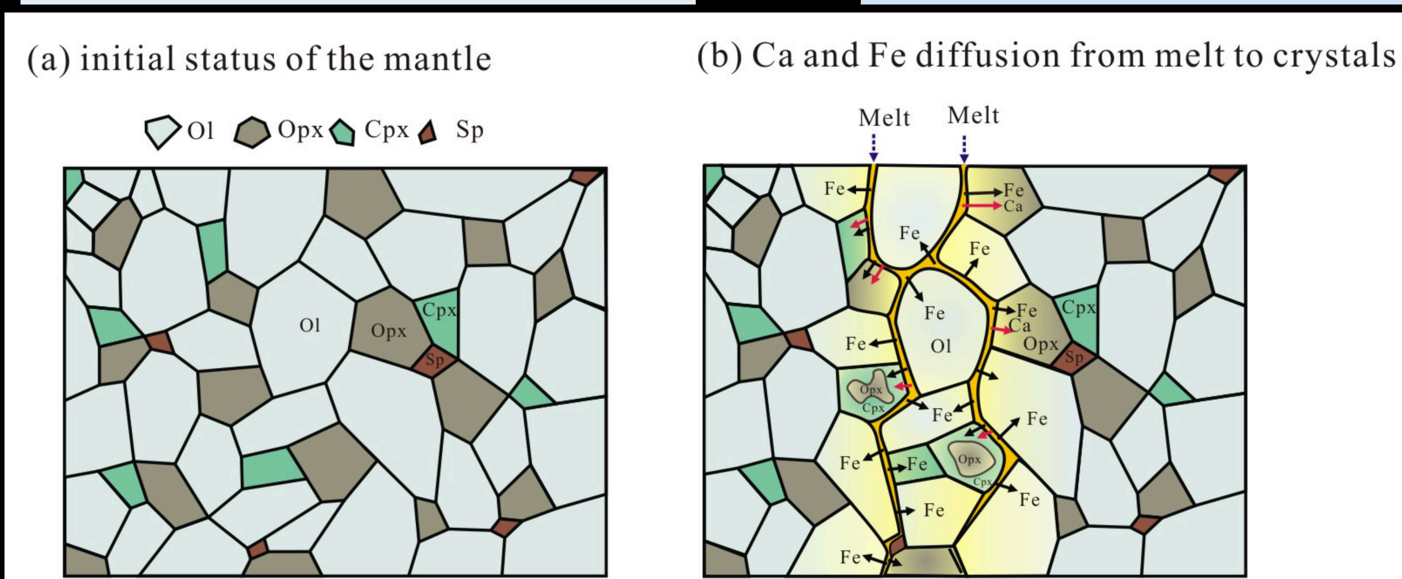
- 阳原富铁橄榄岩有硅酸盐中最低的$\delta^{44/40}Ca$，$\delta^{57/54}Fe$ 和 Mg#

阳原橄榄岩中的熔体-橄榄岩反应



nearly intact OPX grains with rare sieve-textured CPX at rims

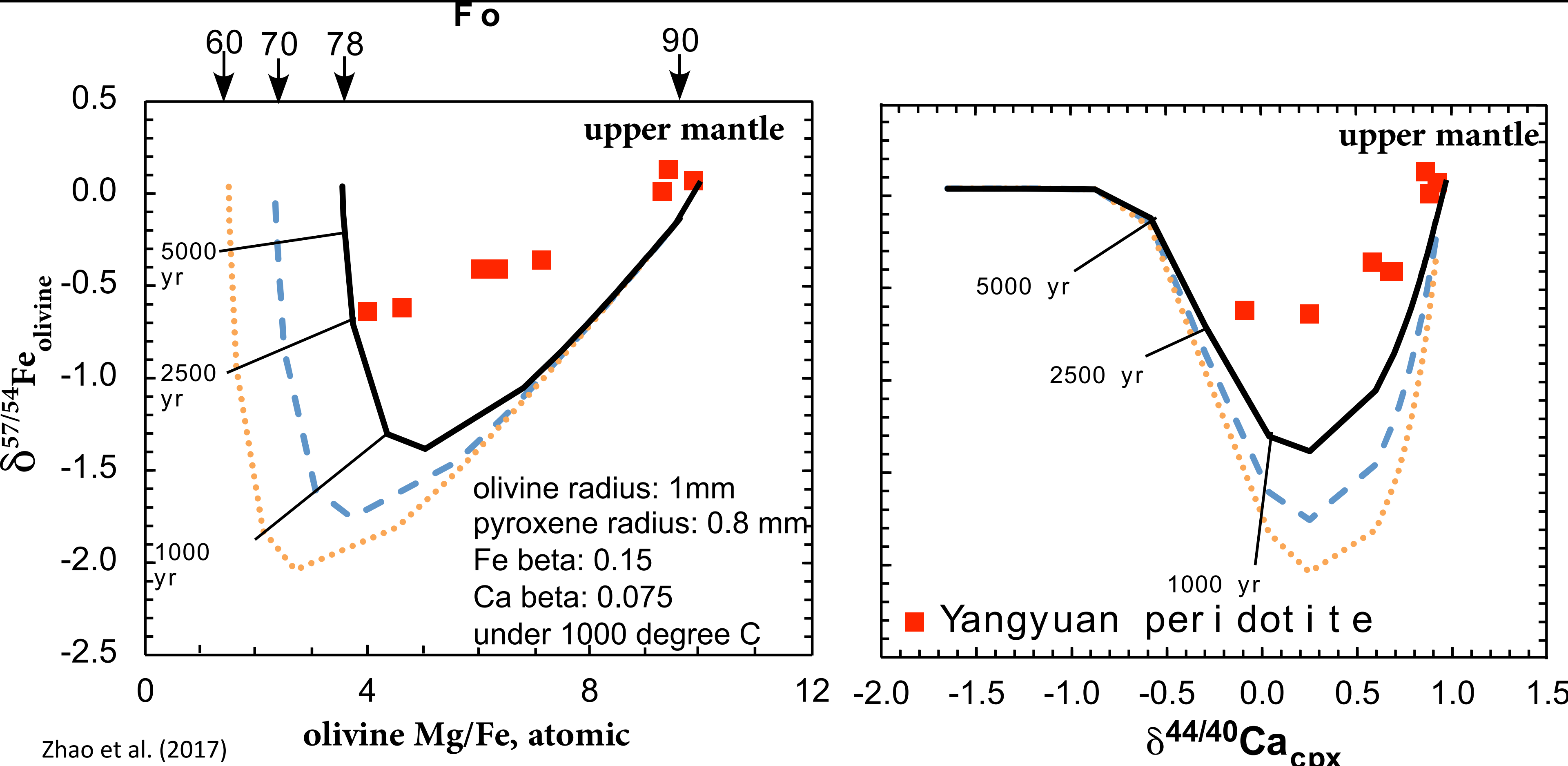
resorbed OPX relics inside newly formed sieve textured CPX



- Ca diffuses into OPX to form CPX
- Fe diffuses into OL to form low Fo OL

Zhao et al. (2017)

阳原橄榄岩中熔体-橄榄岩反应的同位素效应

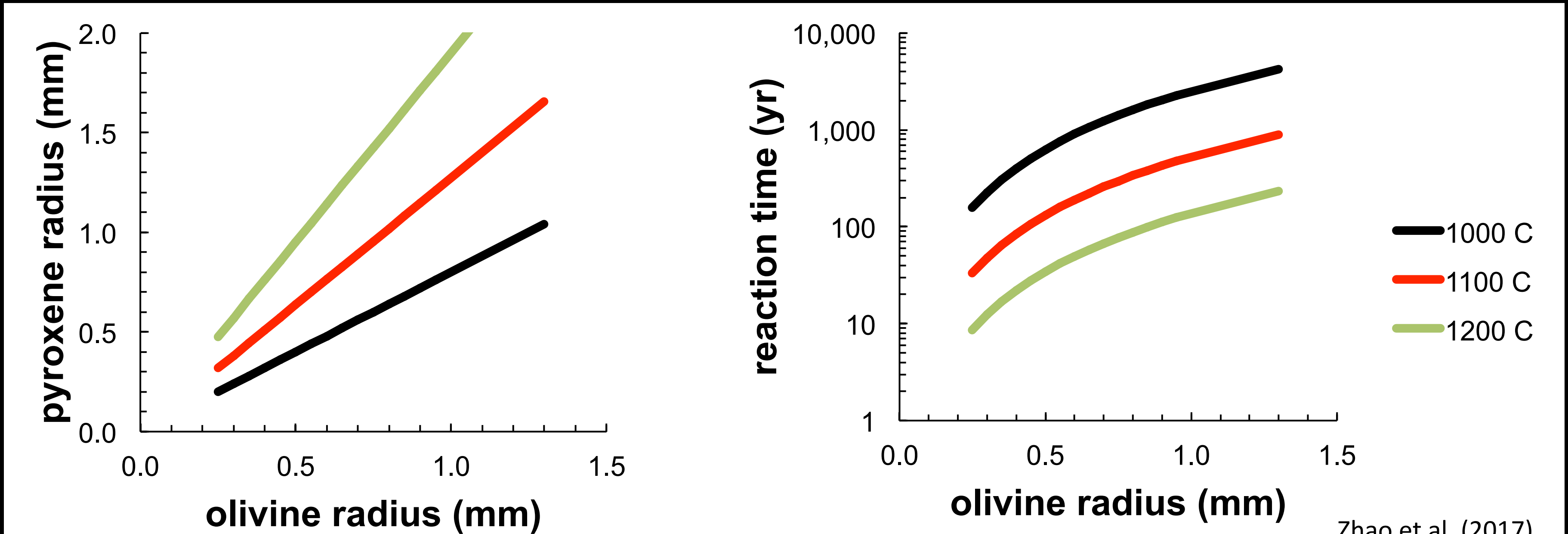


Zhao et al. (2017)

- Ca diffuses into OPX to form CPX: Lead to low $\delta^{44/40}$Ca in CPX
- Fe diffuses into OL to form low Fo OL: Lead to low $\delta^{57/54}$Fe in OL
- The coupled, light Ca-Fe isotopic endmember was produced during melts percolating through peridotites

阳原橄榄岩中熔体-橄榄岩反应的同位素效应

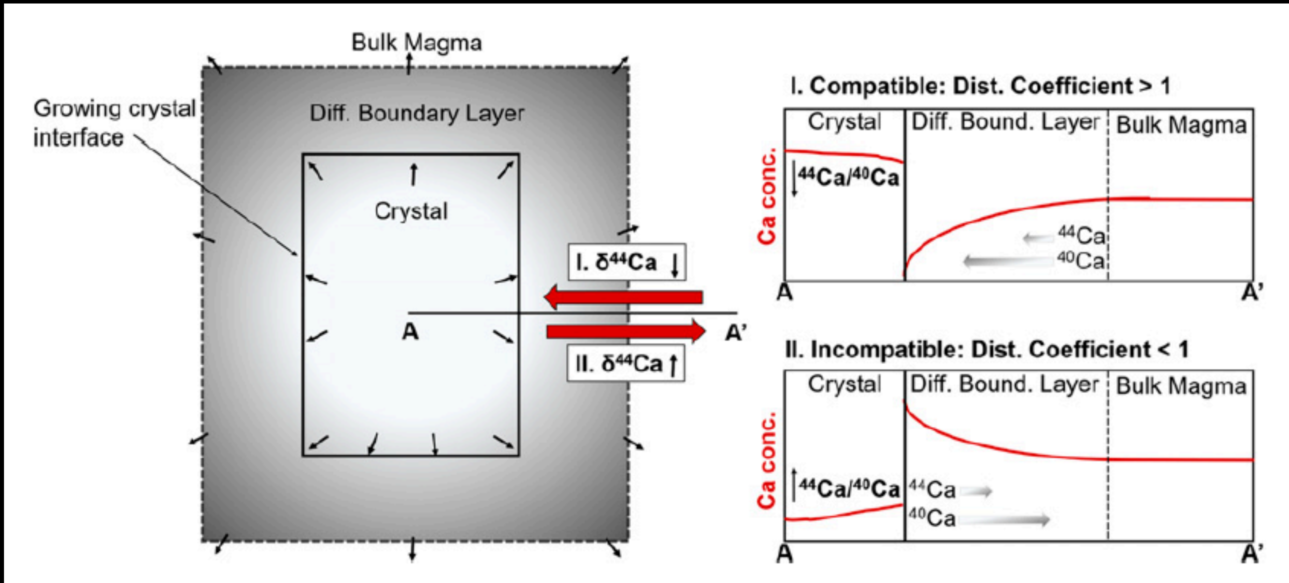
$$C(t) = Cr + \frac{6(Ci - Cr)}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(\frac{-Dtn^2\pi^2}{a^2}\right)$$



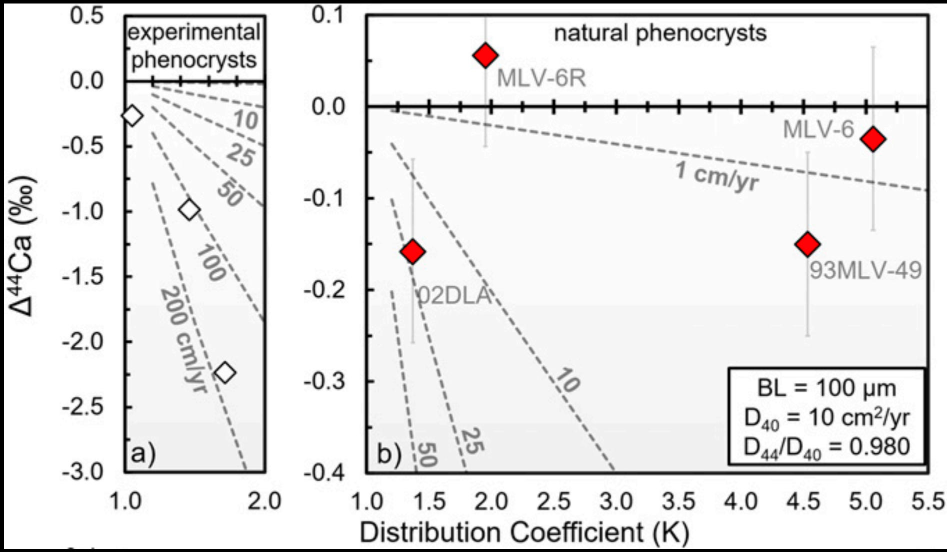
Zhao et al. (2017)

- The coupled, light Ca-Fe isotopic endmember was produced during melts percolating through peridotites at a time scale of <10 to 10,000s of years

矿物生长中的同位素效应



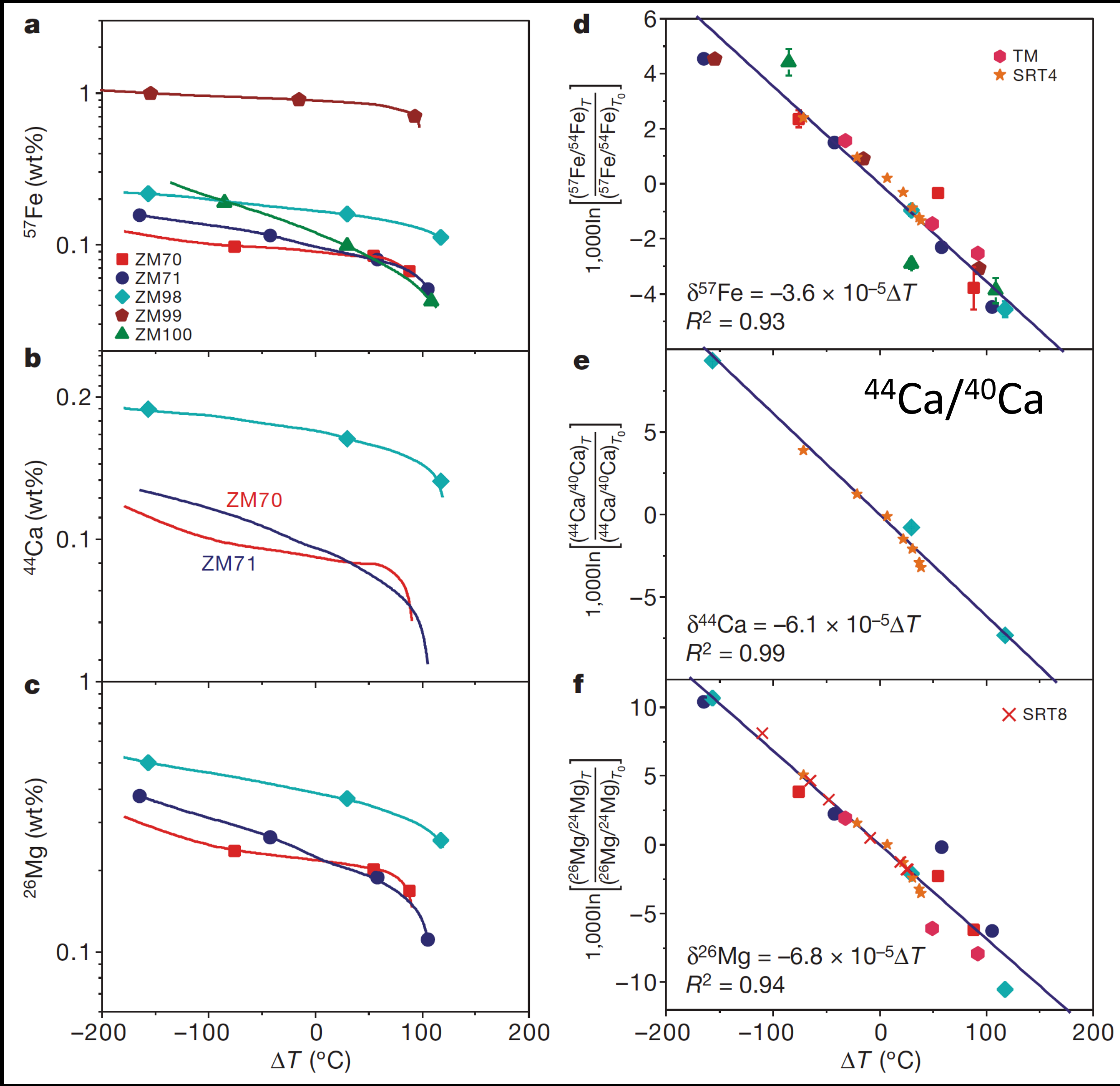
Antonelli et al. (2019)



- K>1，相容，矿物的钙同位素偏轻
- K<1，不相容，矿物的钙同位素偏重
- 矿物生长速度越快，同位素效应越大

温度效应：Soret effect

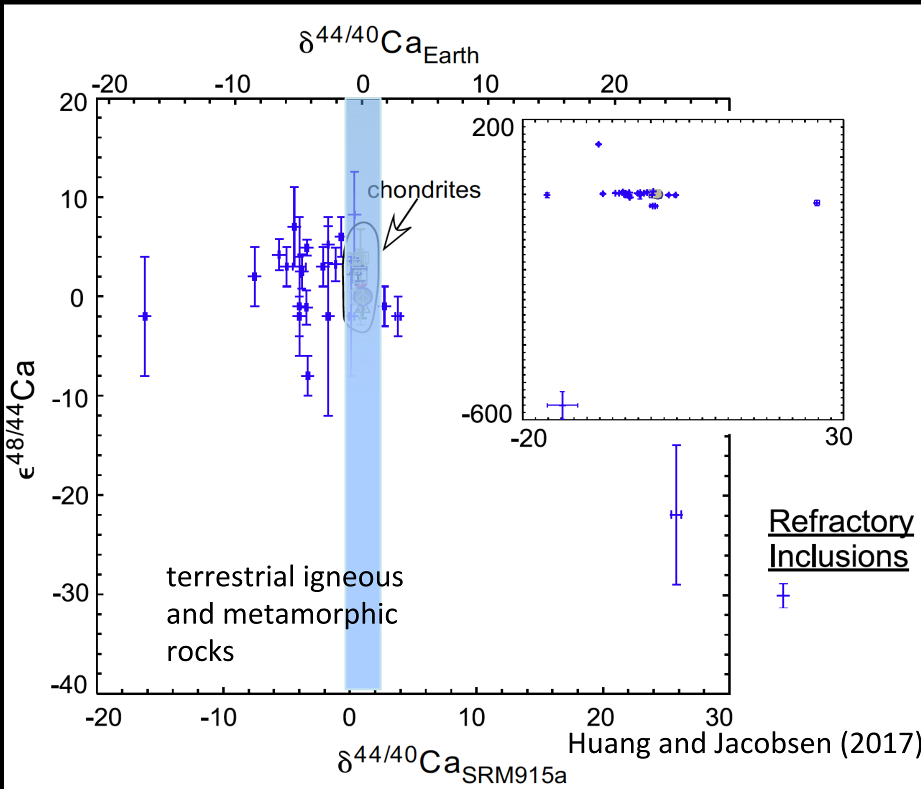
- 轻同位素富集在低温一端



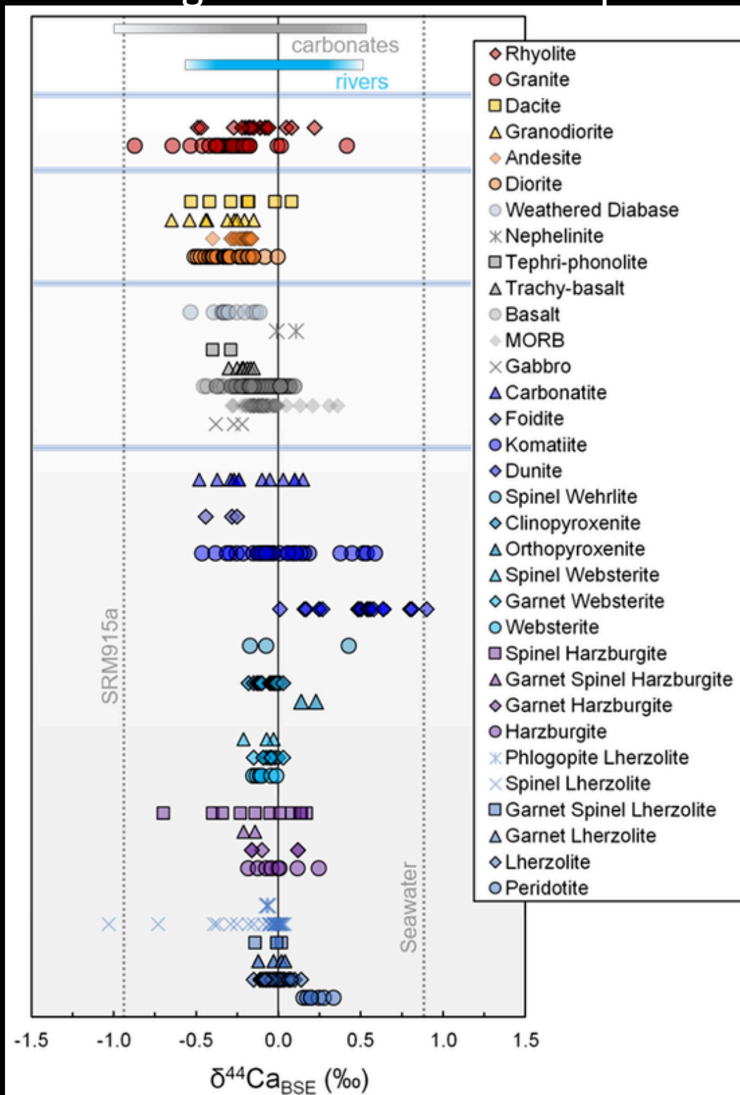
Huang et al. (2010)

太阳系内的钙同位素变化

chondrites and their components



terrestrial igneous and metamorphic rocks



Antonelli and Simon (2020)

- nucleosynthesis
- condensation/evaporation
- inter-mineral fractionation
- partial melting / crystal fractionation
- recycling of surface material
- Soret effect: thermal diffusion
- chemical diffusion