生物地球化学循环过程
铀同位素分馏

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FLORIDA STATE UNIVERSITY 1851 VIRES ARTES MORES

主要内容

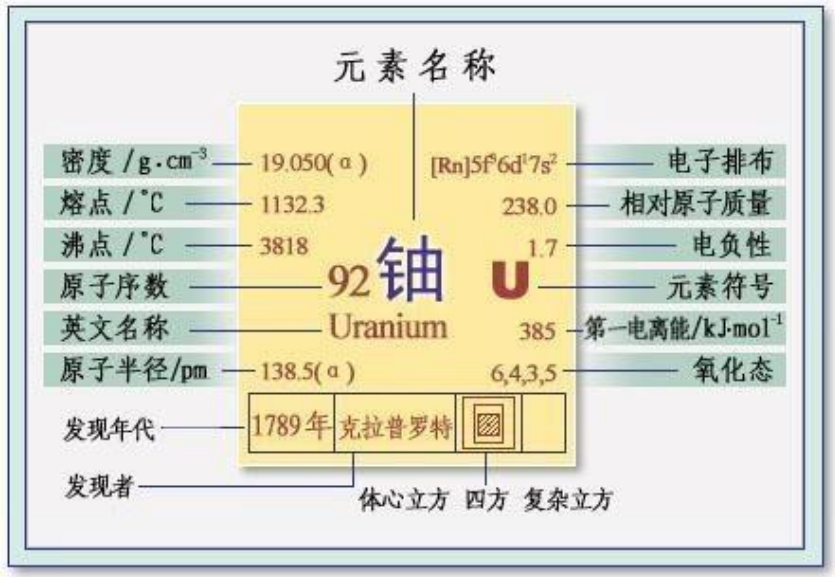
1.铀同位素地球化学循环

2.铀同位素应用

3.铀同位素分馏

4.总结

第一部分：铀同位素地球化学循环



克拉普罗特

同位素	半衰期(年)	丰度(%)
^{234}U	2.455×10^5	0.005
^{235}U	7.040×10^8	0.720
^{238}U	4.468×10^9	99.275

强不相容元素

矿物：$UO_2(s)$, $U_3O_8(s)$

主要储库：海水(3 ppb), 地壳(1.3 ppm)

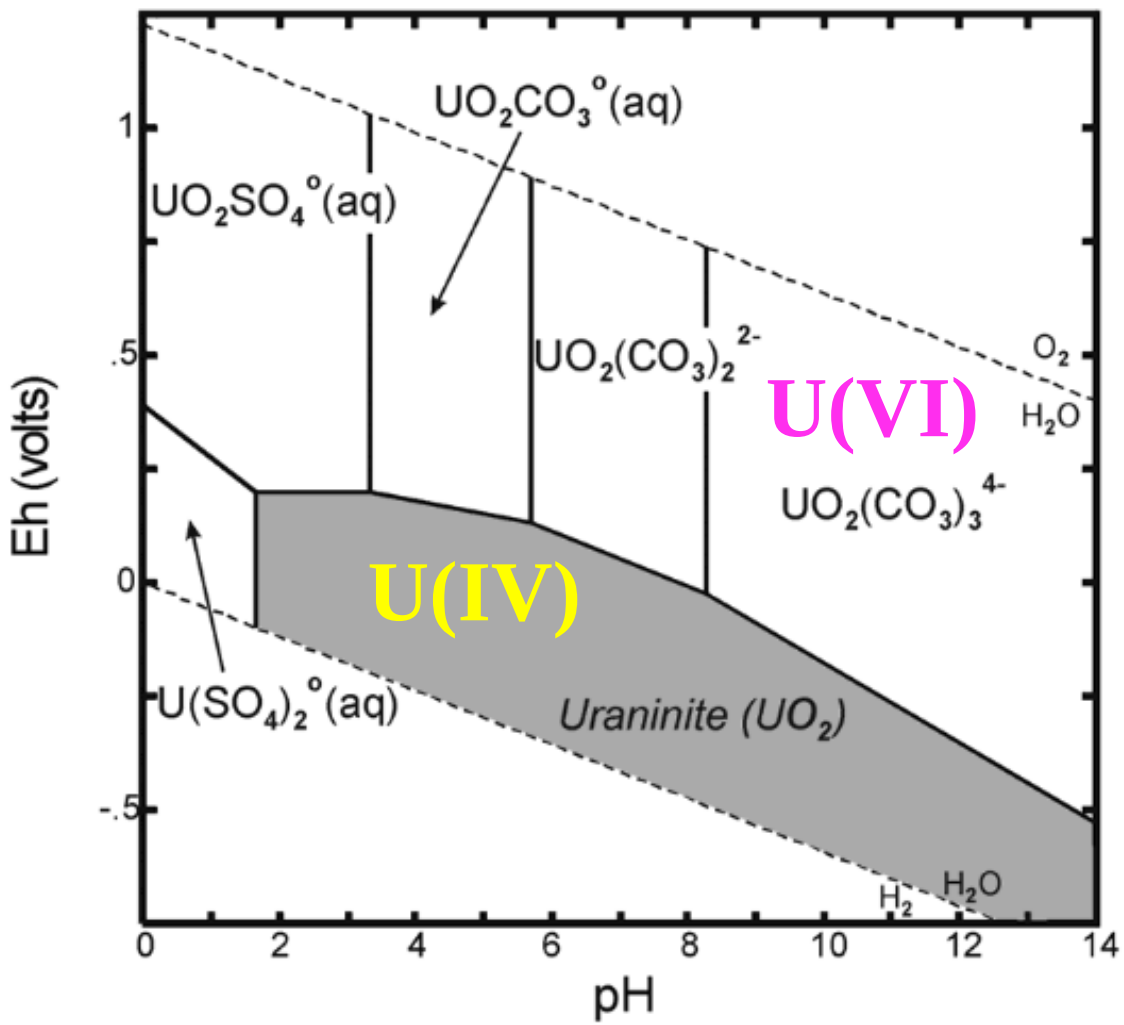
应用：核燃料, U-Pb定年

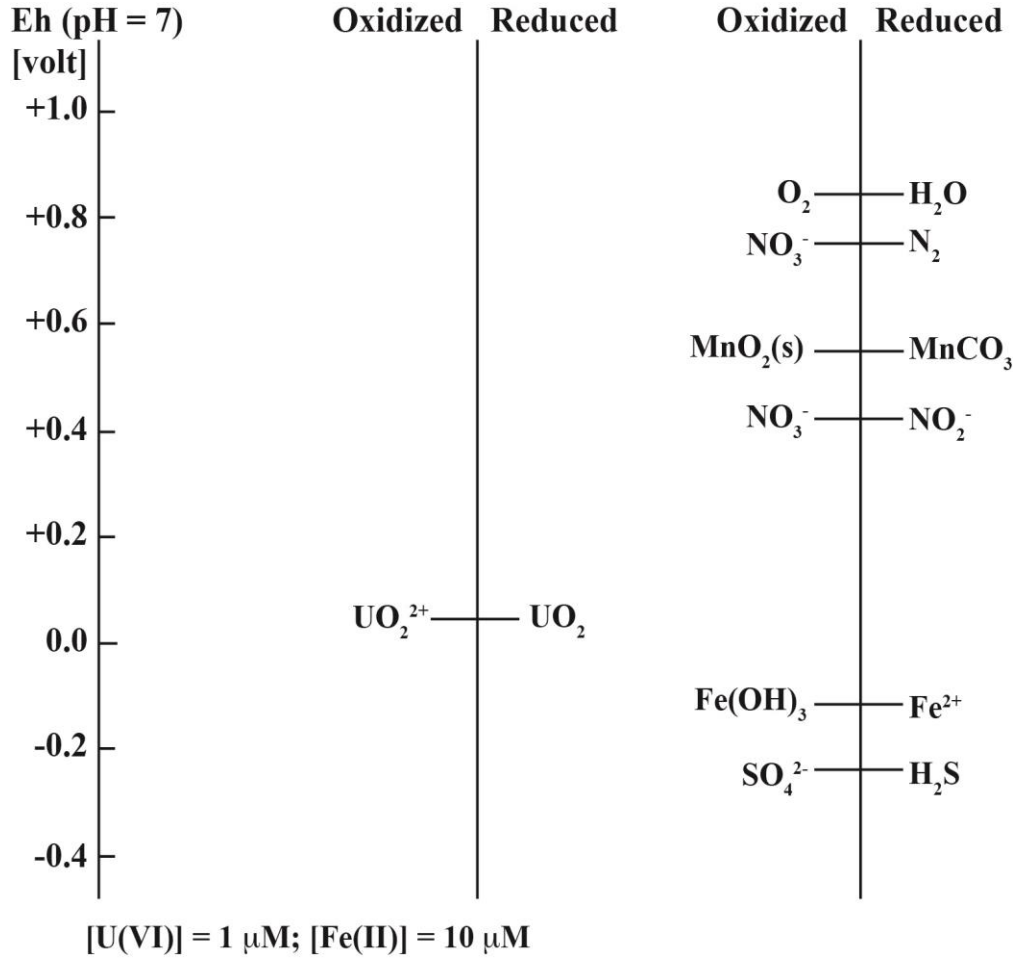
$$^{235}U \longrightarrow {}^{207}Pb$$

$$^{238}U \longrightarrow {}^{206}Pb$$

自然界铀的形态

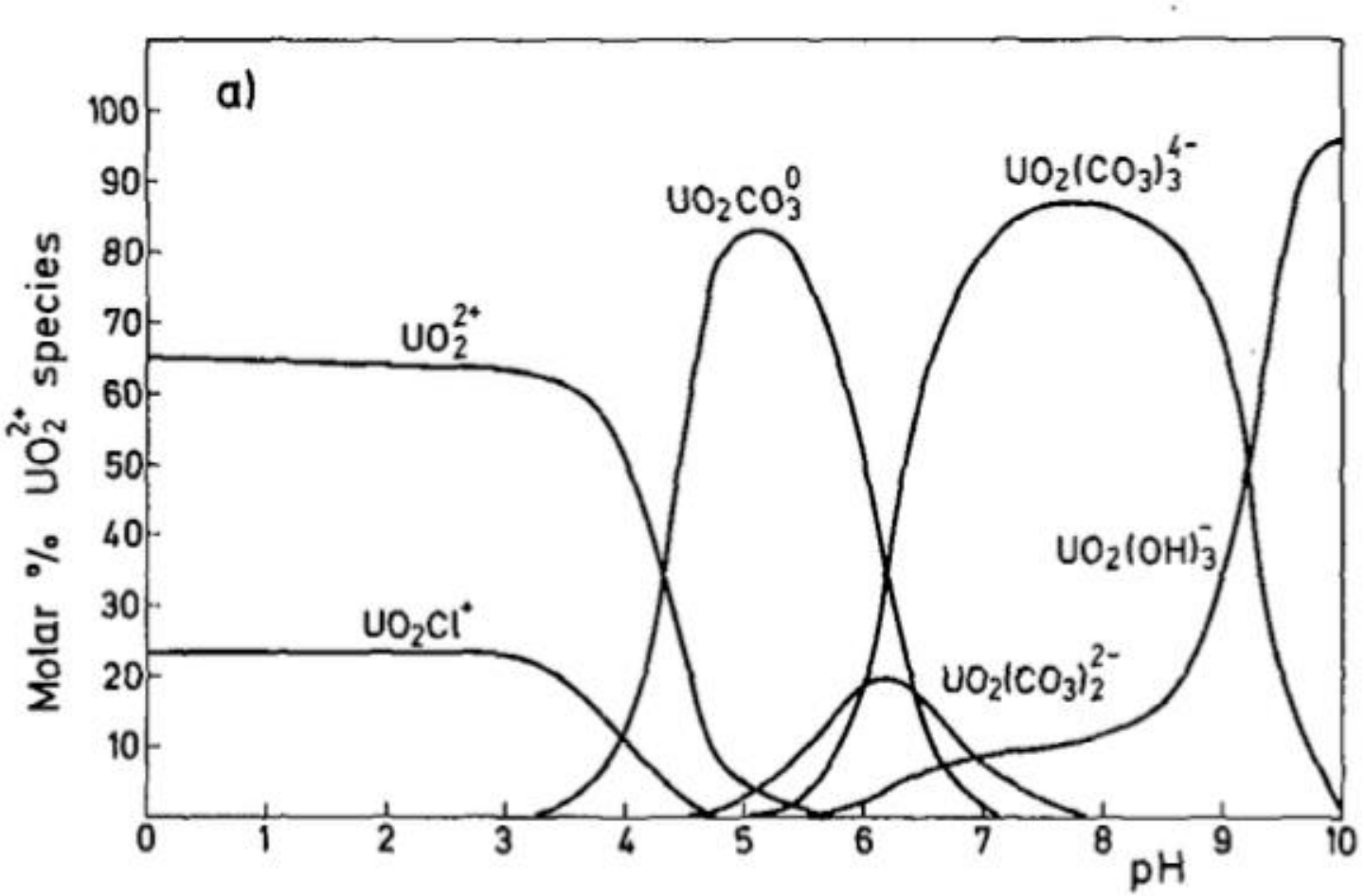
UO_2^{2+}: 铀酰根





Krupka and Serne, 2001

水溶液中铀组分分布



UO_2-CO_3 complexes

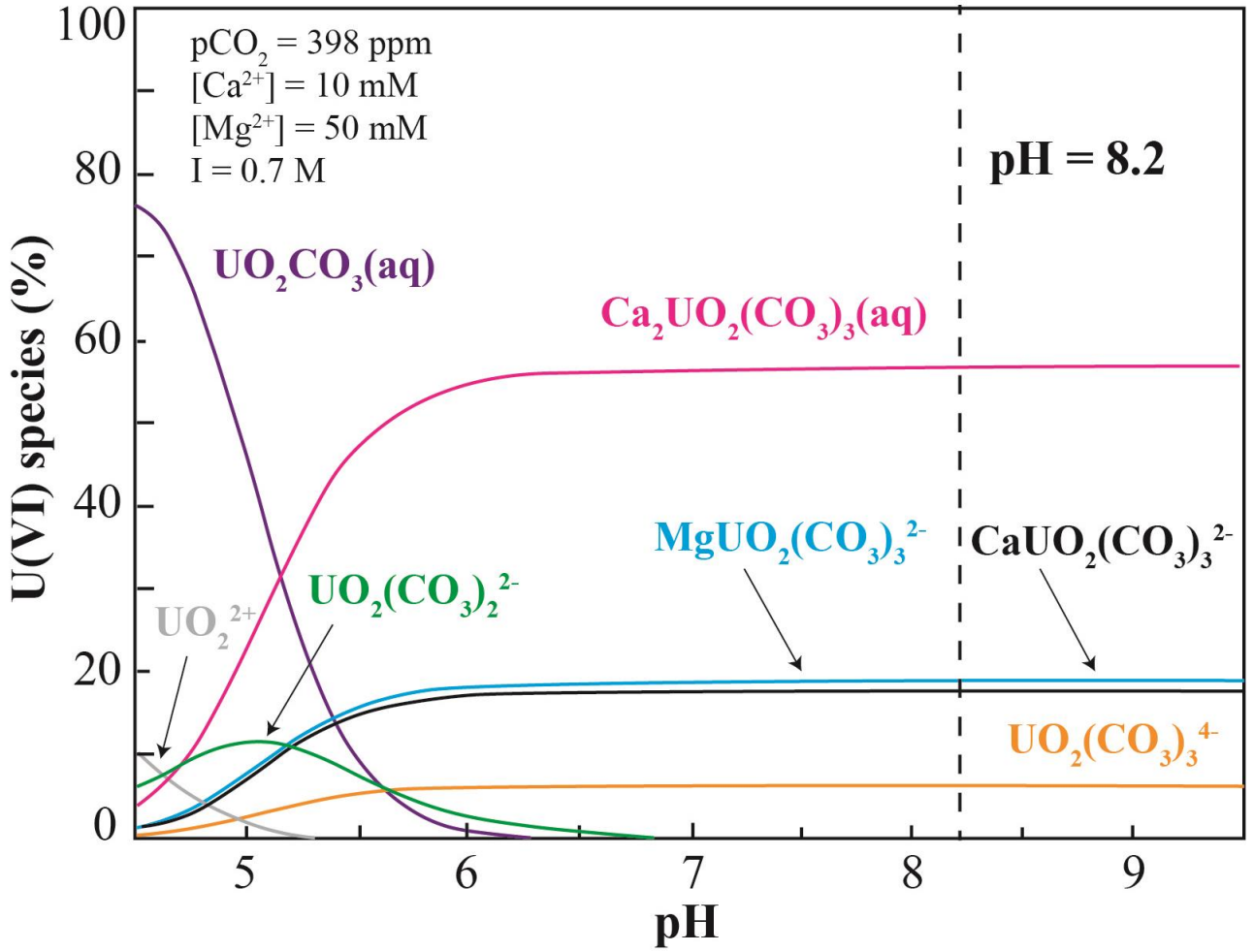
- **UO_2CO_3(aq)**
- **$UO_2(CO_3)_2^{2-}$**
- **$UO_2(CO_3)_3^{4-}$**

Djogic et al., 1986

水溶液中铀组分分布

Ca/Mg-UO_2-CO_3 complexes

- **$CaUO_2(CO_3)_3^{2-}$**
- **$MgUO_2(CO_3)_3^{2-}$**
- **$Ca_2UO_2(CO_3)_3(aq)$**



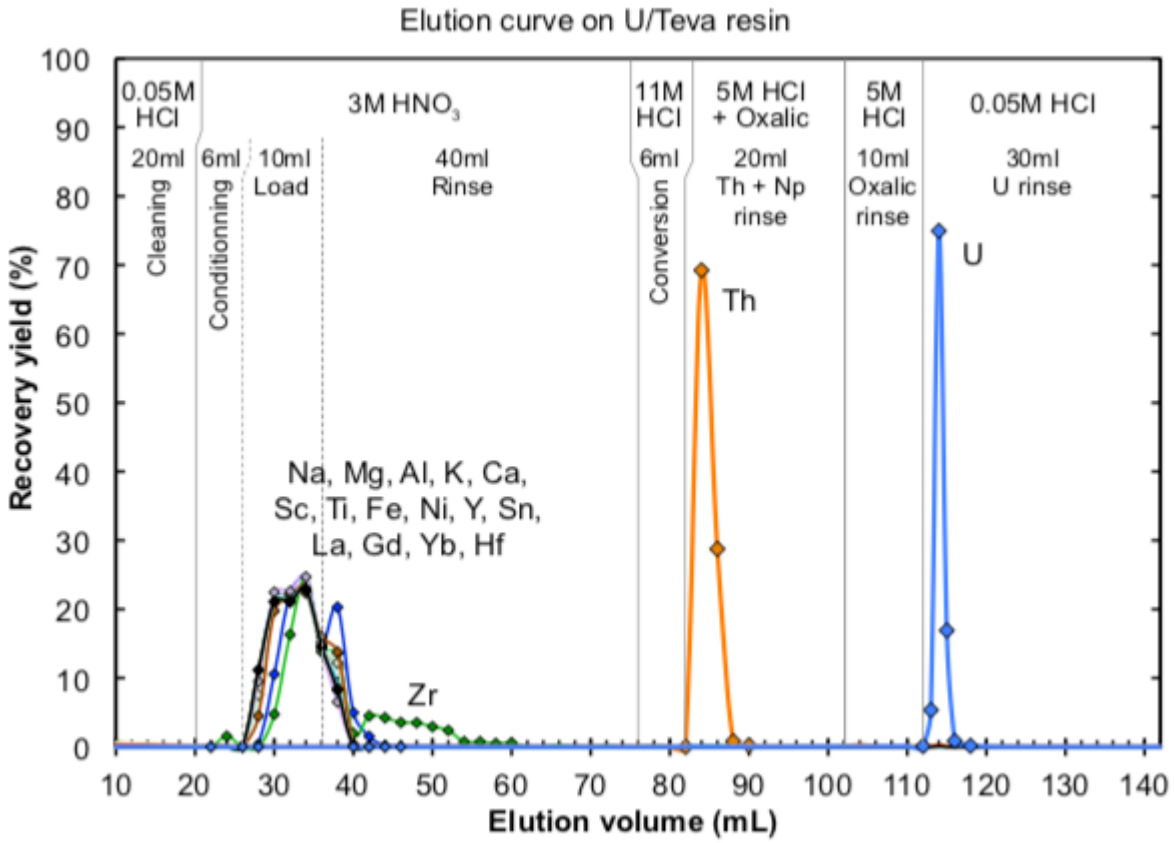
Bernhard et al., 1996; Dong and Brooks, 2006; Endrizzi et al., 2014; Lee et al., 2013

铀同位素测试方法

^{233}U-^{236}U 双稀释剂法(MC-ICP-MS)

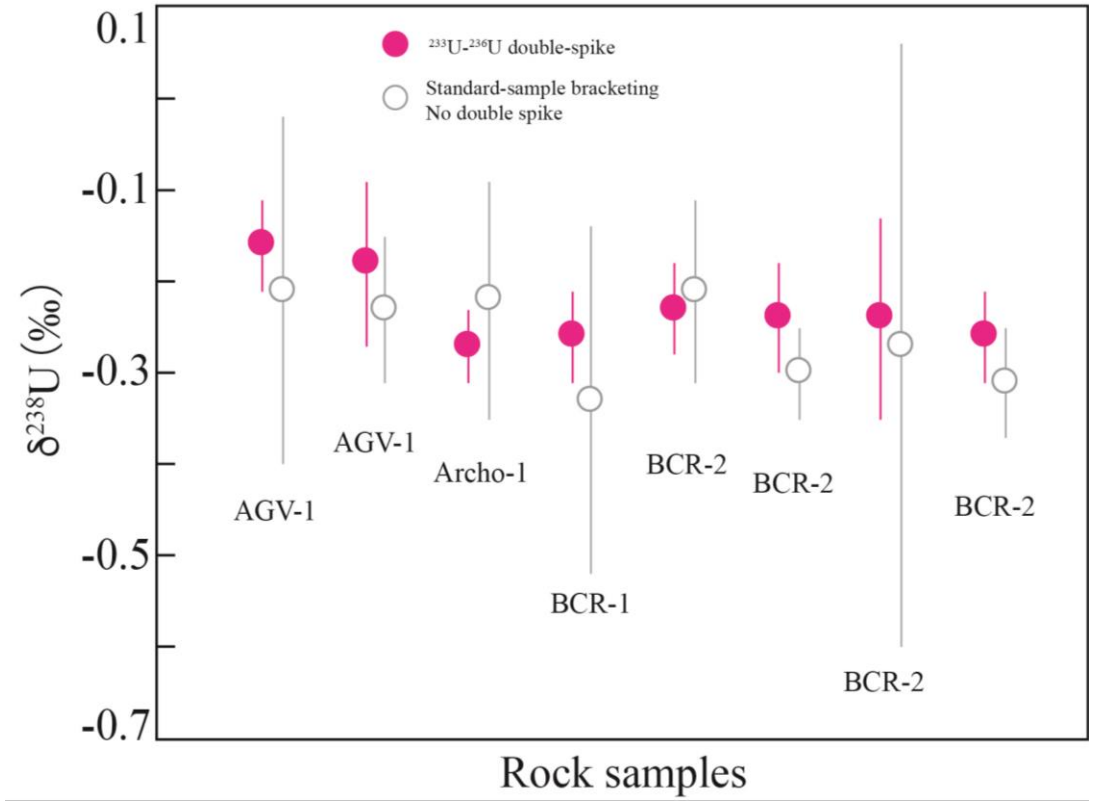
- UTEVA 特效树脂
- 测试浓度：50 ppb
- 测试精度：< ±0.10 ‰

$$\delta^{238}U = \left[\frac{\left({}^{238}U / {}^{235}U \right)_{sample}}{\left({}^{238}U / {}^{235}U \right)_{CRM-145a}} - 1 \right] \times 1000$$

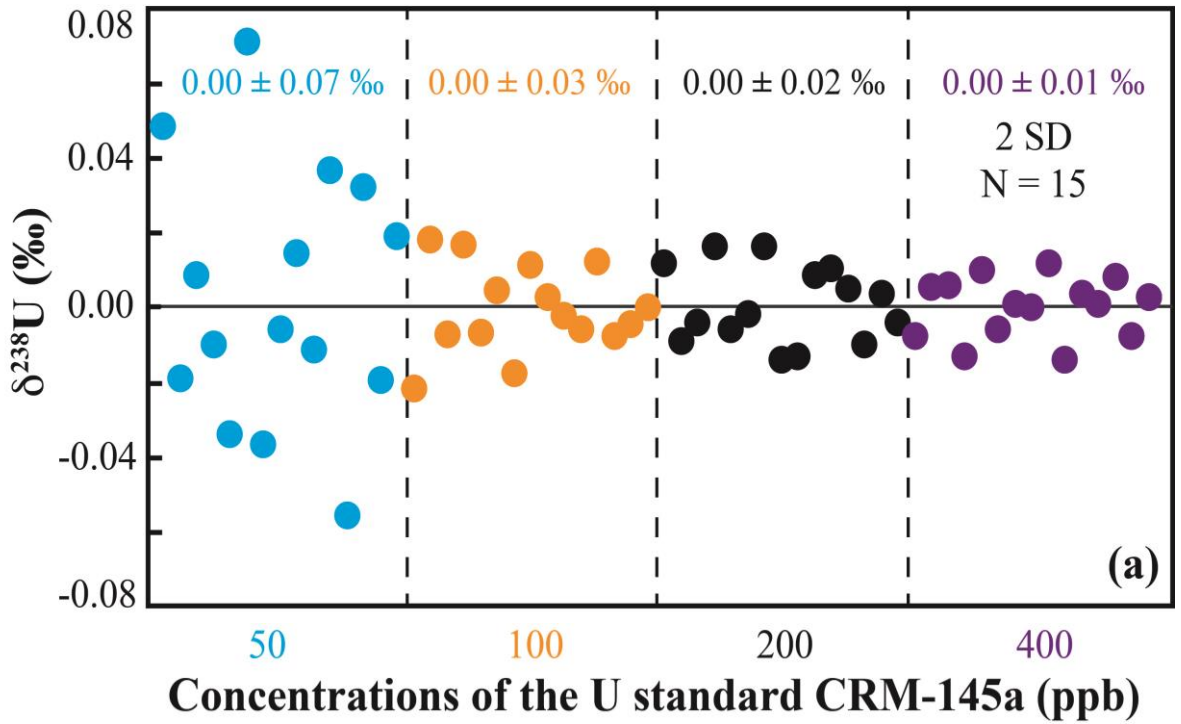


Stirling et al., 2005; Rademaher et al., 2006; Weyer et al., 2008; Chen et al., 2018a

铀同位素测试方法



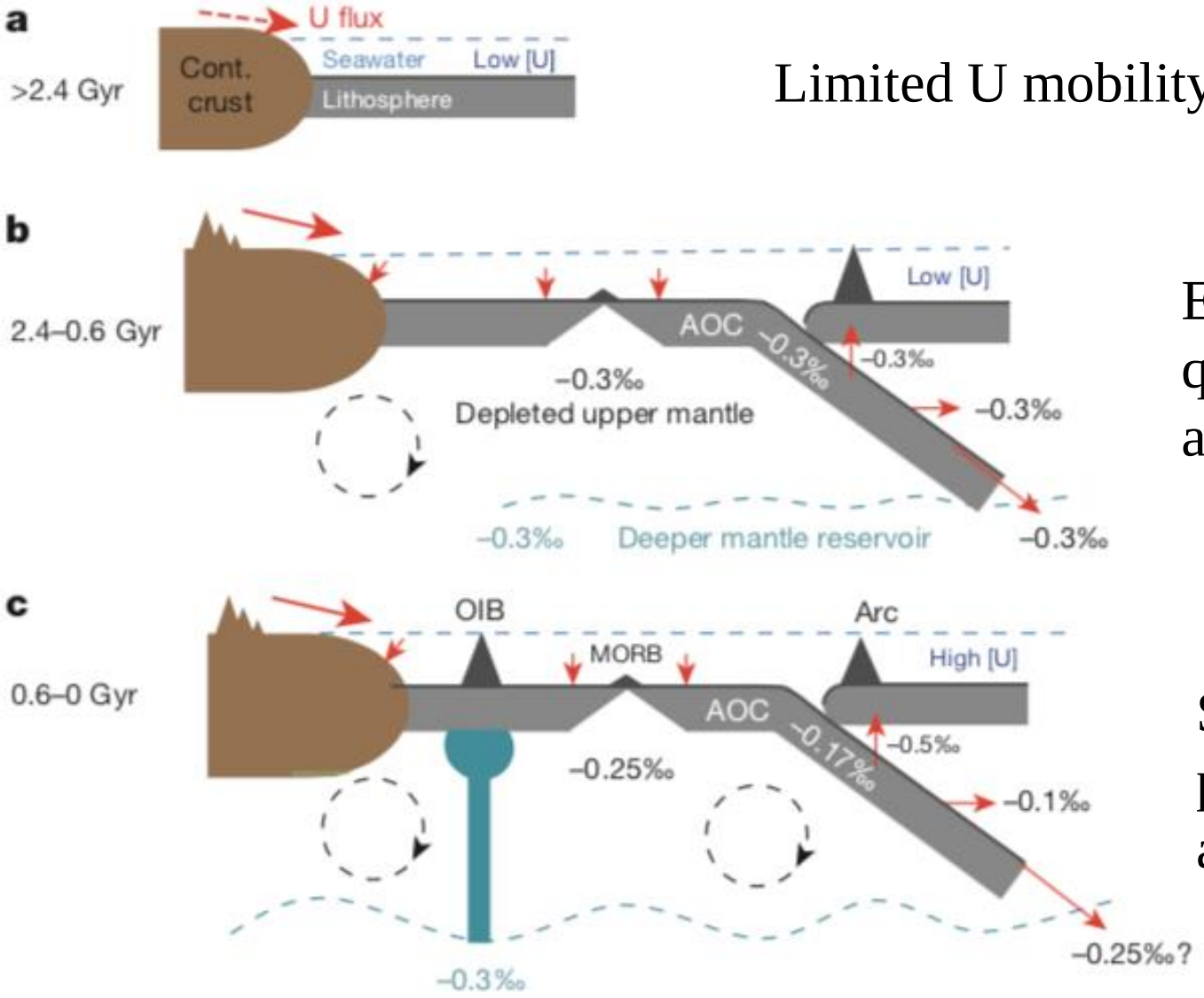
双稀释剂vs.标准样品间插法



高精度测试方法 ± 0.03 ‰

Tissot et al., 2015; Chen et al., 2018a

全球铀元素循环



Limited U mobility due to low atmospheric oxygen

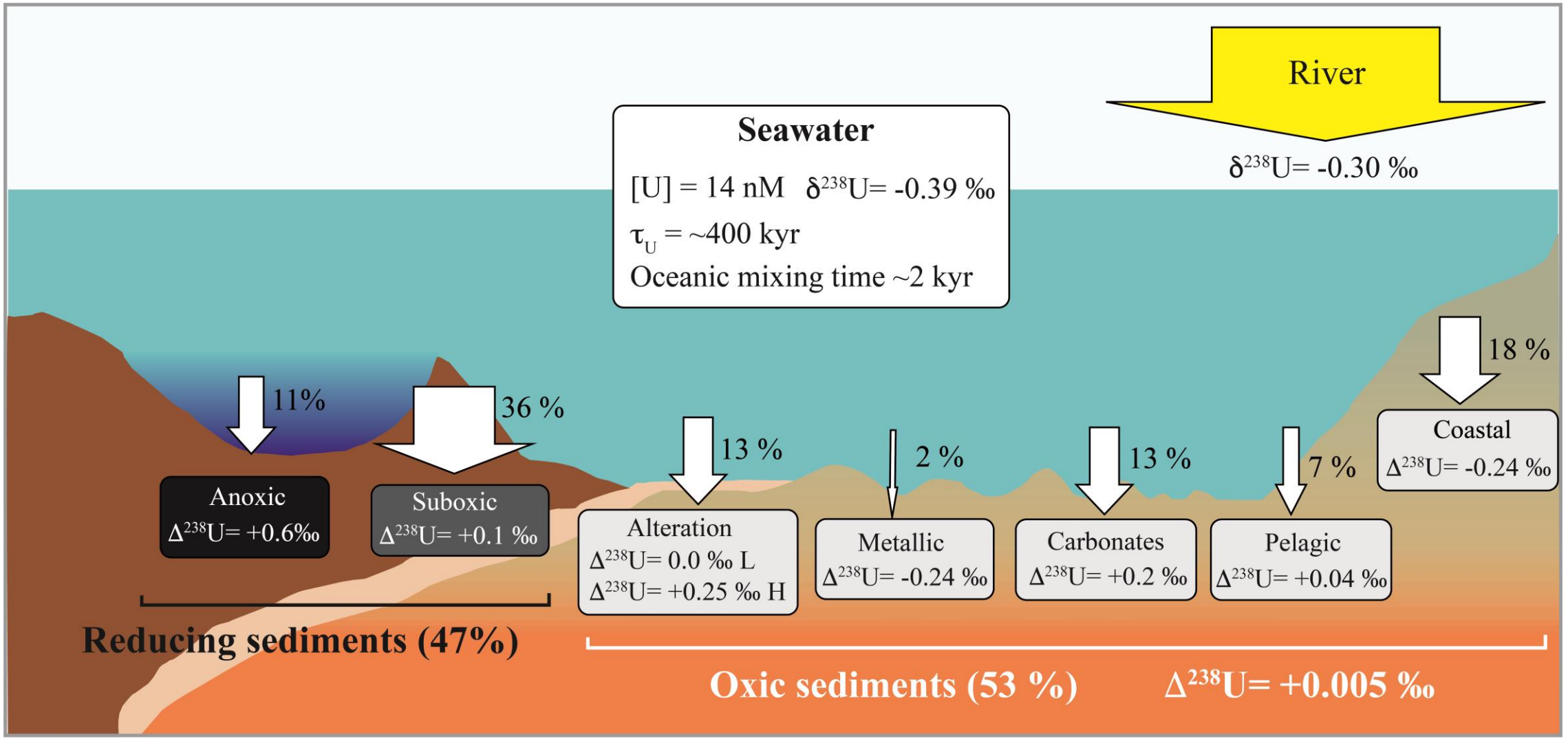
Enhanced oxidative weathering but quantitative removal of oceanic U and subducted to deep mantle

Strong oxidative weathering and partial U reduction and uptake by altered oceanic crust

Figure 2 | Cartoon of the terrestrial U isotope cycle over the history of Earth.

Andersen et al., 2015

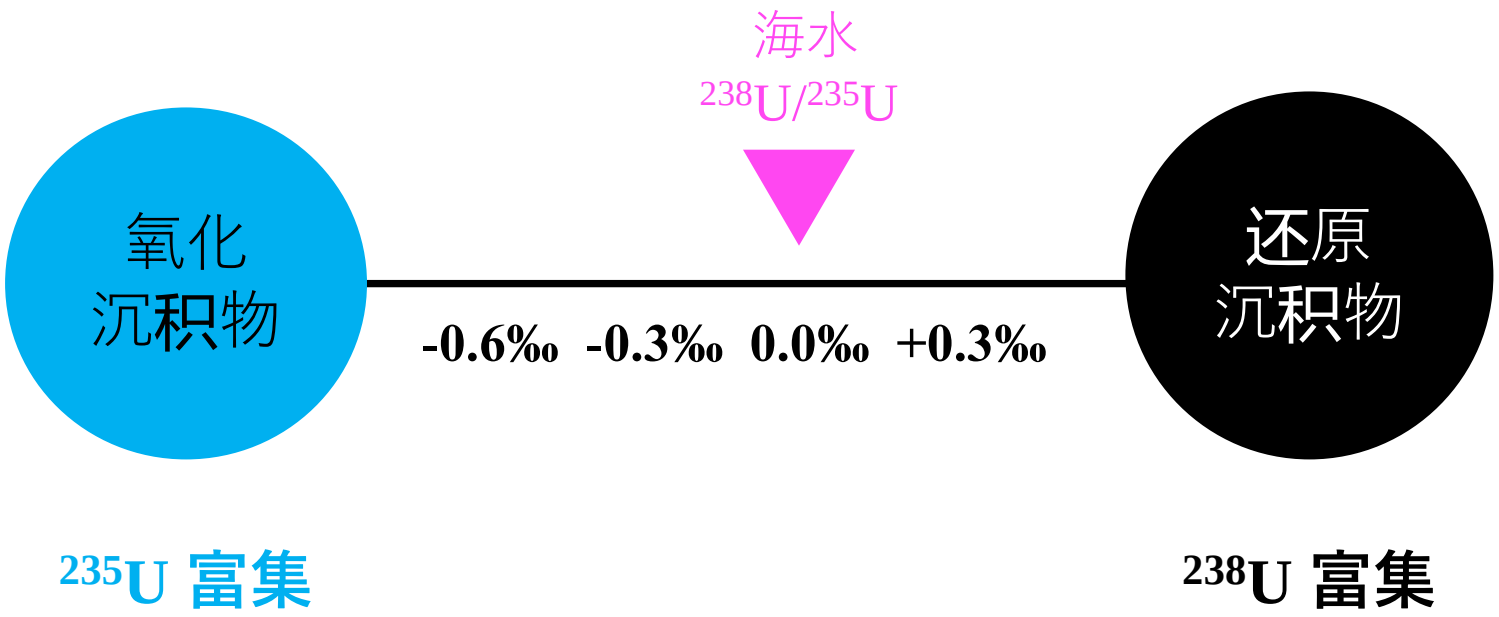
现代海洋铀同位素循环



Data from Tissot et al., 2015

海水$^{238}U/^{235}U$反应海洋氧化还原环境变化

$$\delta^{238}U_{sw} = \delta^{238}U_{in} - \frac{A_{an}k_{an}\Delta^{238}U_{an} + A_{sub}k_{sub}\Delta^{238}U_{sub} + A_{ox}k_{ox}\Delta^{238}U_{ox}}{A_{an}k_{an} + A_{sub}k_{sub} + A_{ox}k_{ox}}$$



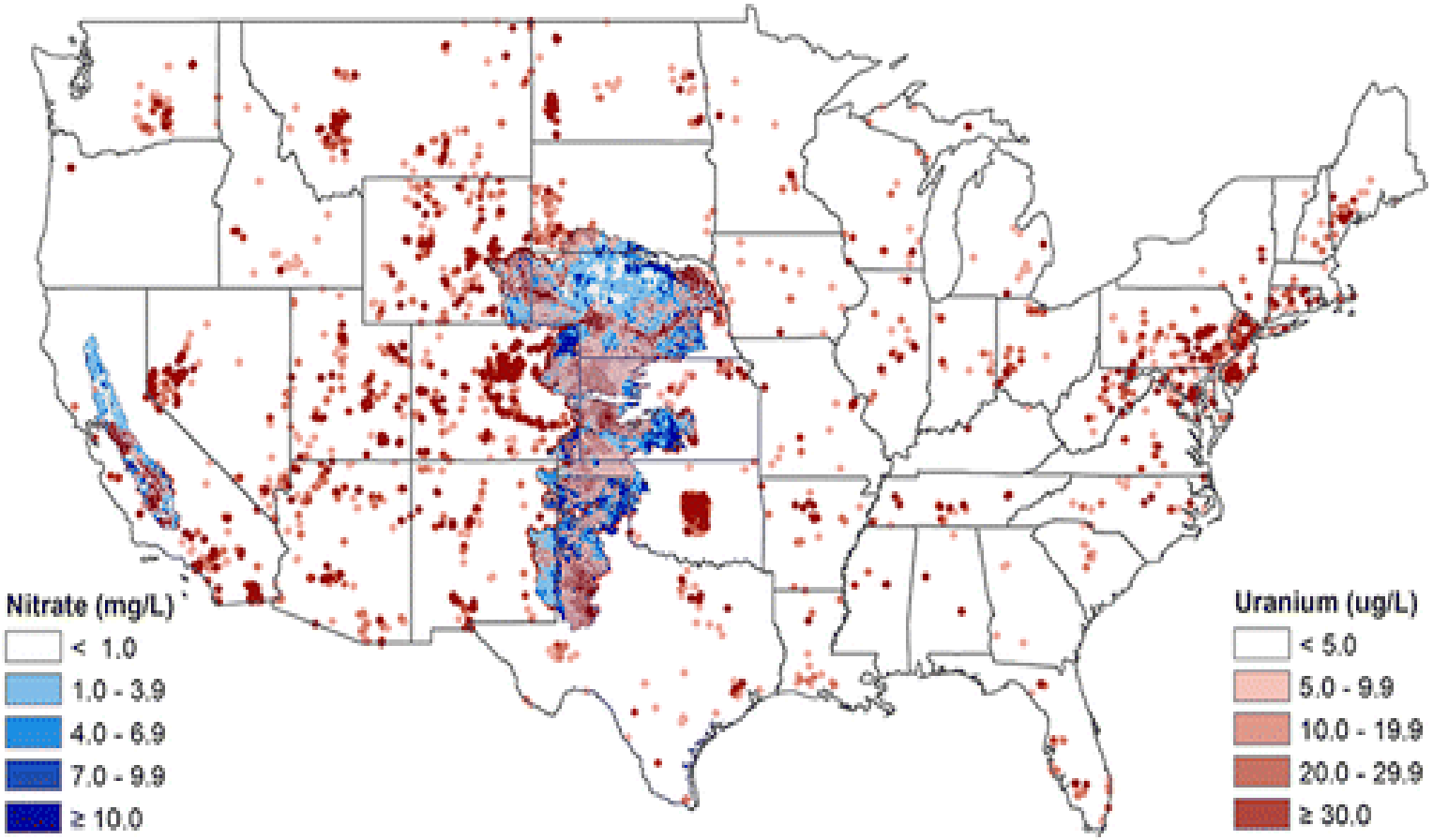
海水$\delta^{238}U$随海洋还原环境增强而减小

第二部分：铀同位素应用

现代环境：示踪地下水铀污染与修复

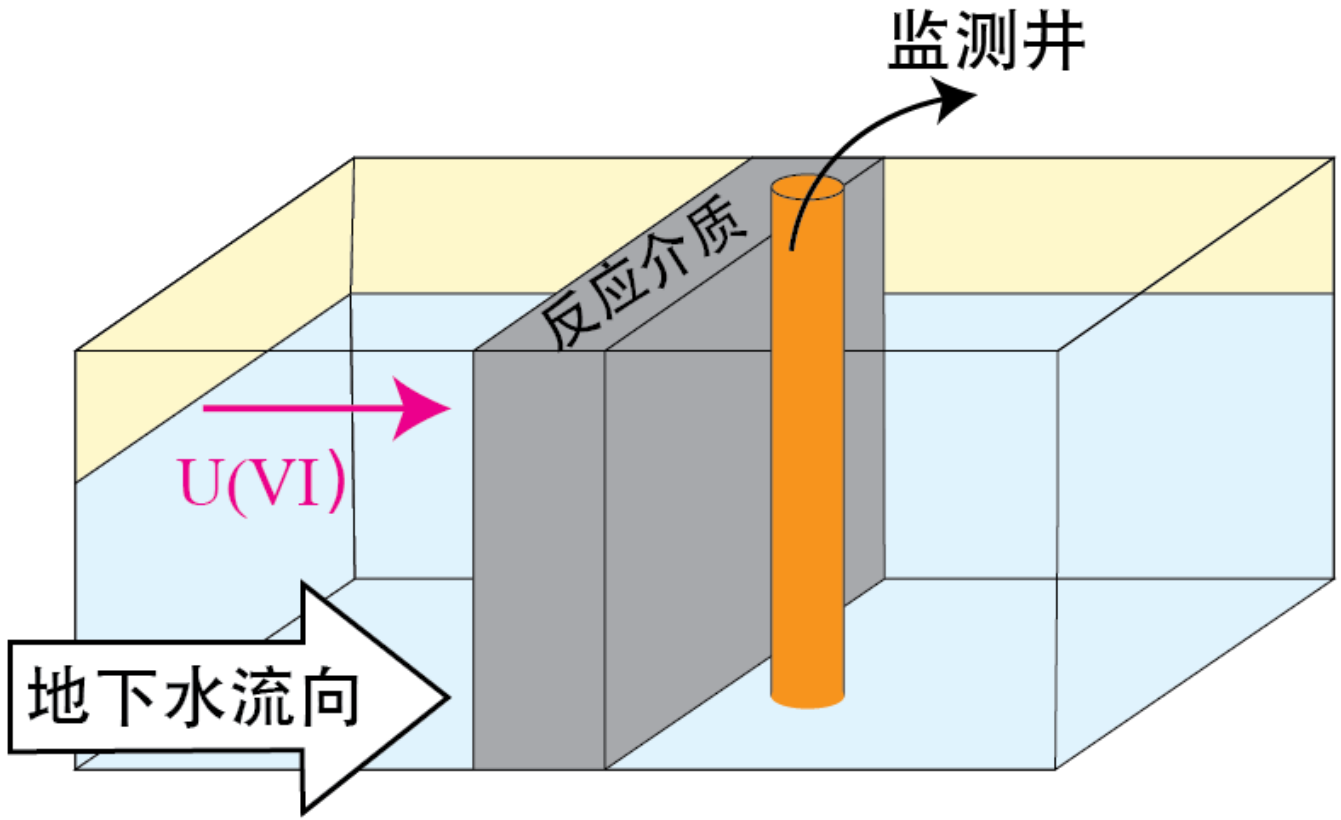
古环境：重建古海洋氧化还原环境变化

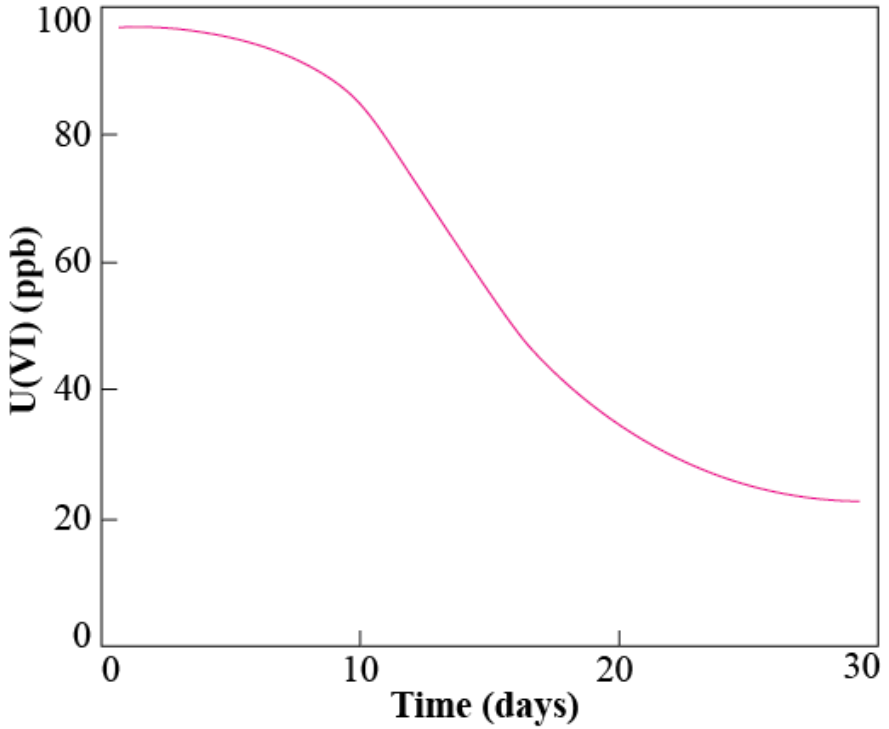
为什么研究铀同位素($^{238}U/^{235}U$)？



Nolan and Weber, 2015

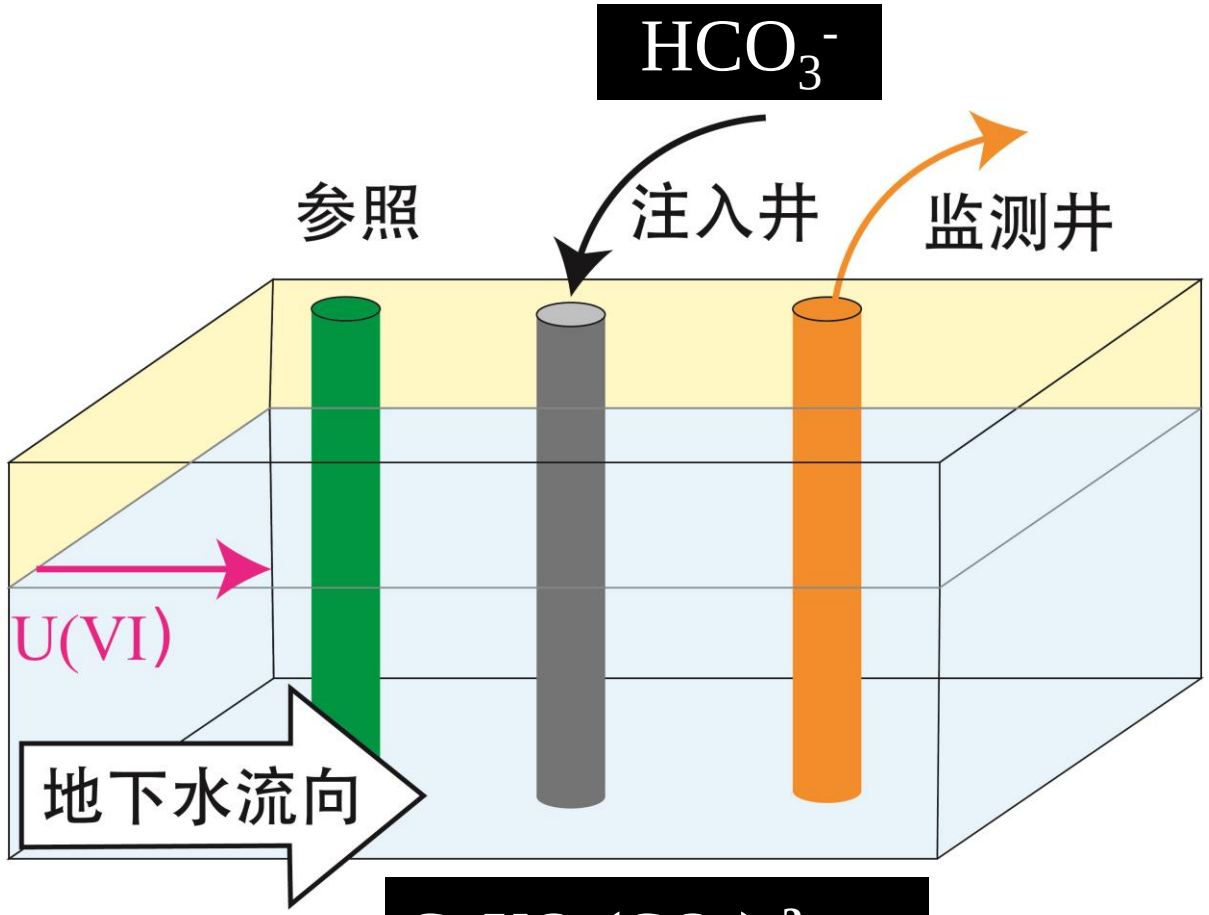
$^{238}U/^{235}U$示踪地下水铀迁移与转化





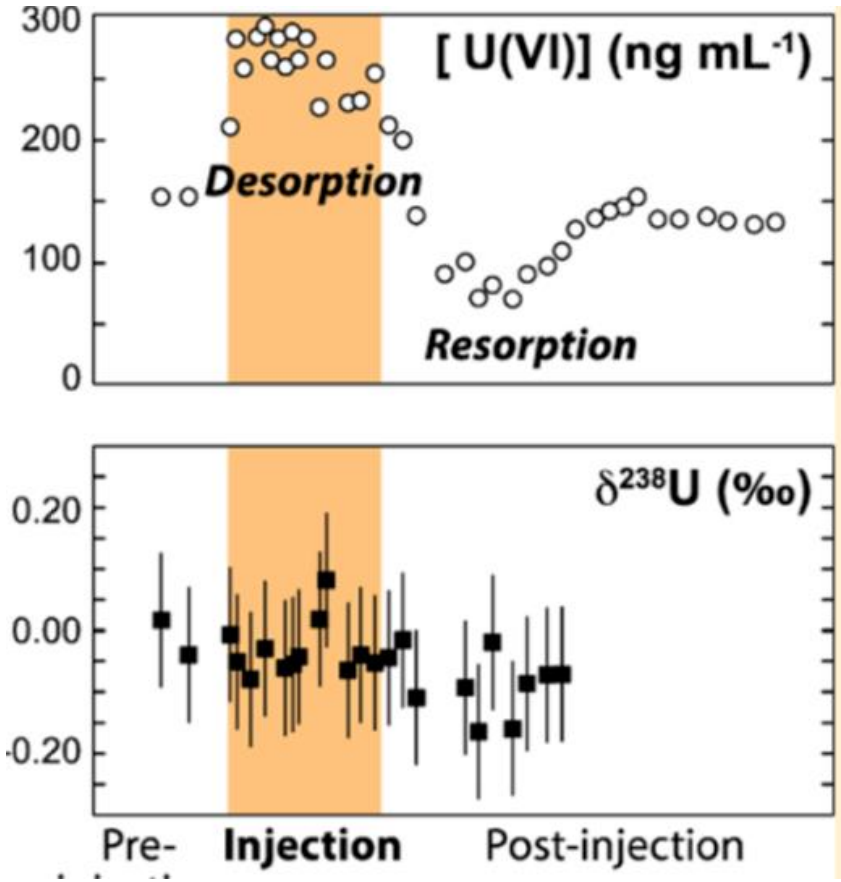
哪些过程降低地下水U(VI)浓度降低: 吸附，还原，扩散，混合？

吸附与解吸过程地下水$^{238}U/^{235}U$变化



$CaUO_2(CO_3)_3^{2-}$

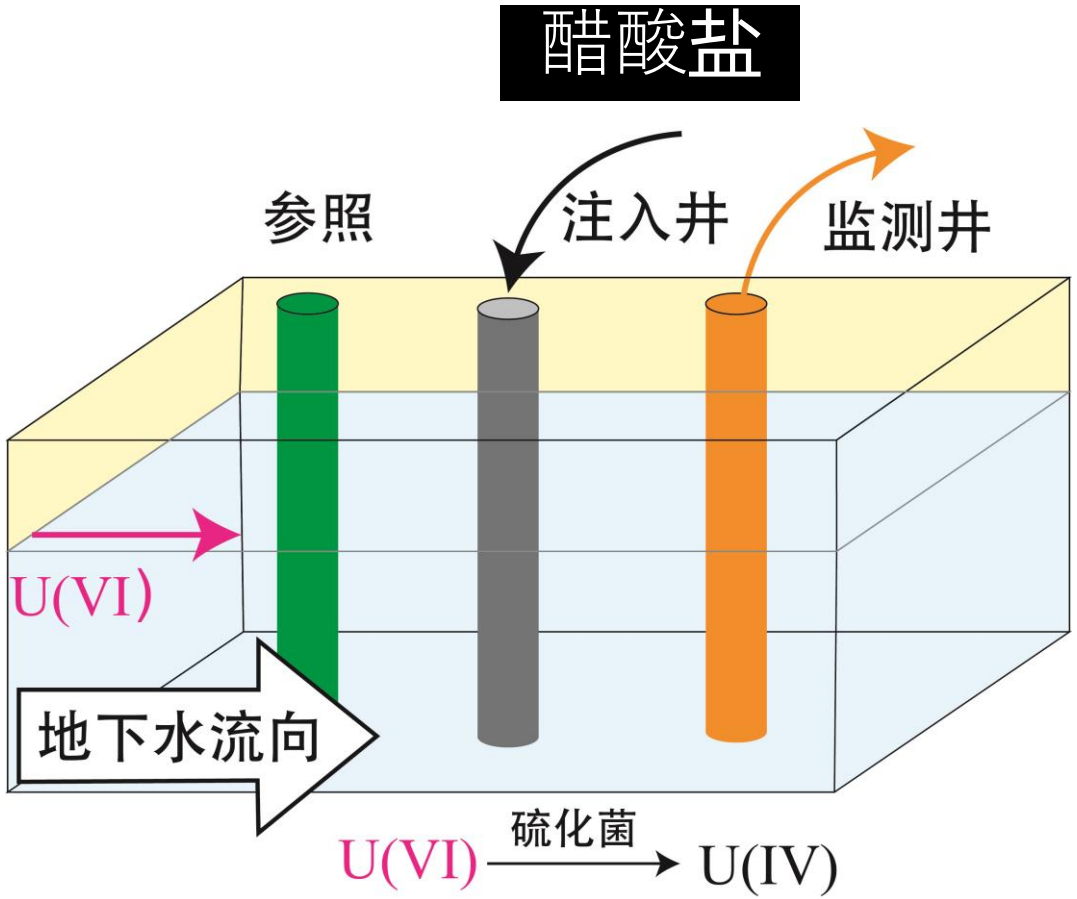
$Ca_2UO_2(CO_3)_3(aq)$

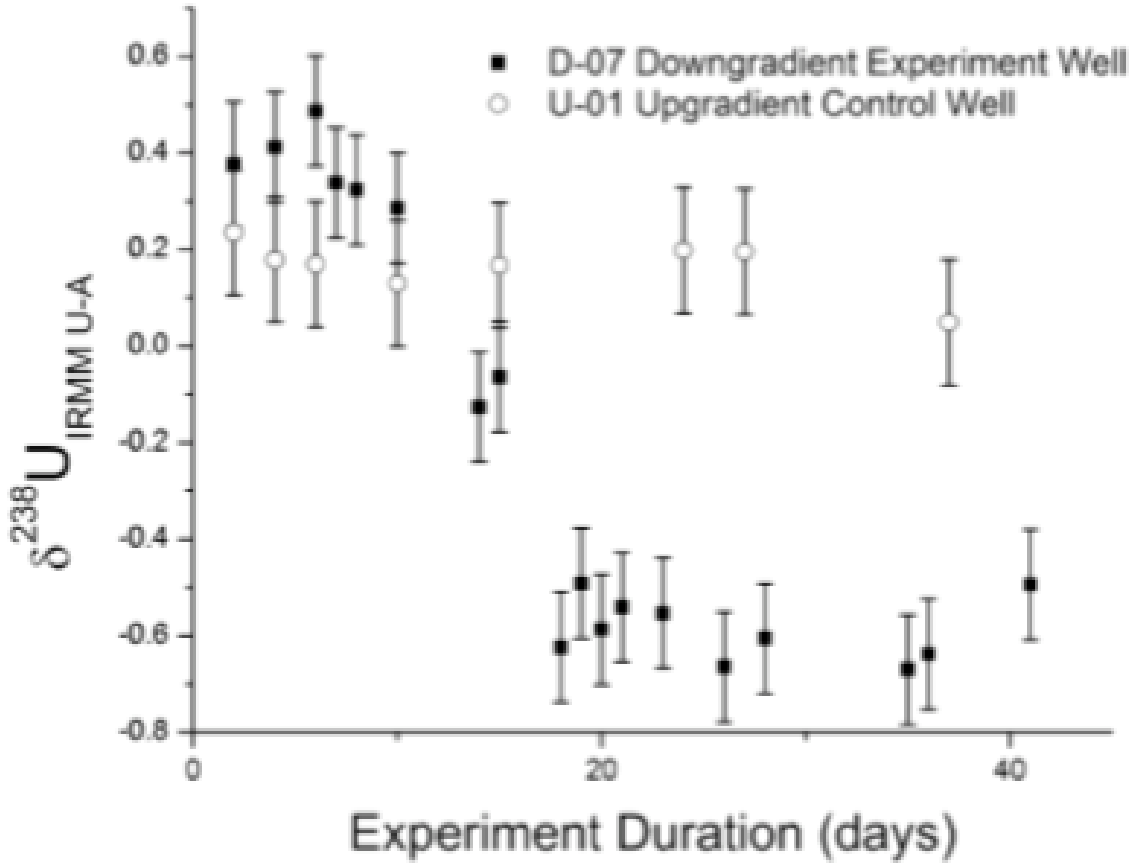


地下水吸附与解吸过程$^{238}U/^{235}U$比值不变

Shiel et al., 2013

$^{238}U/^{235}U$示踪地下水铀还原

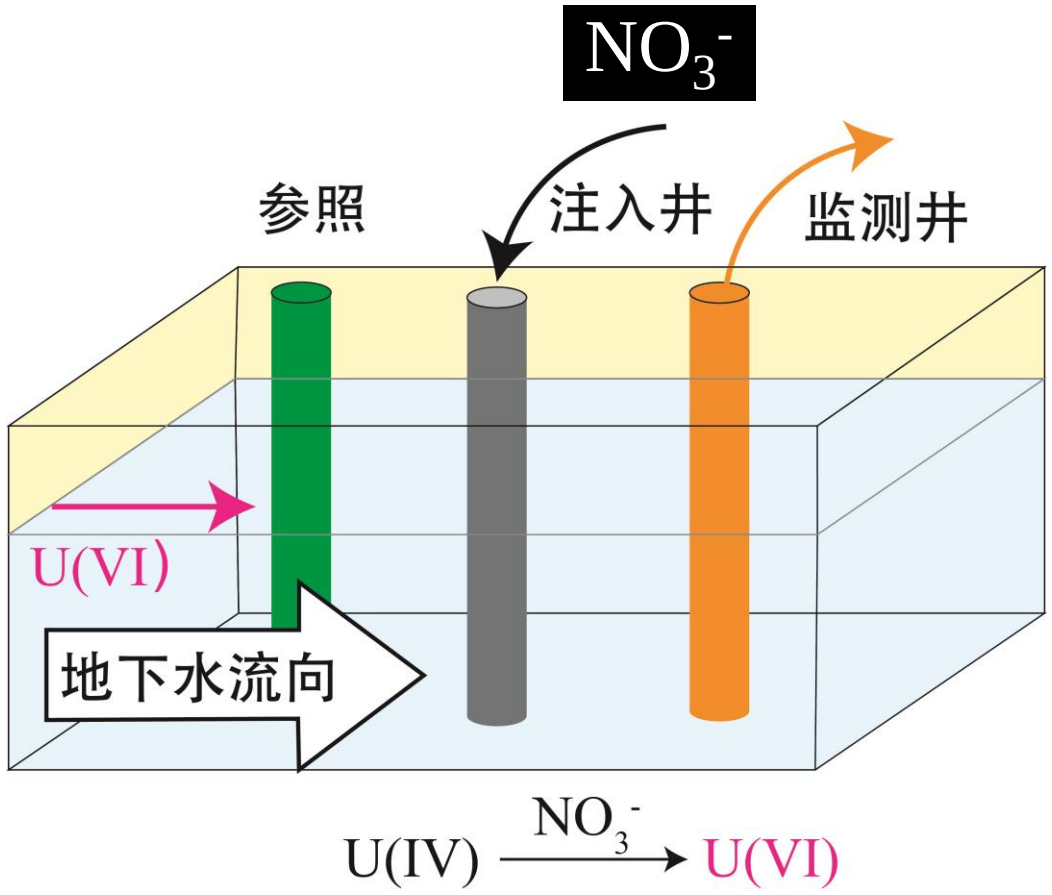


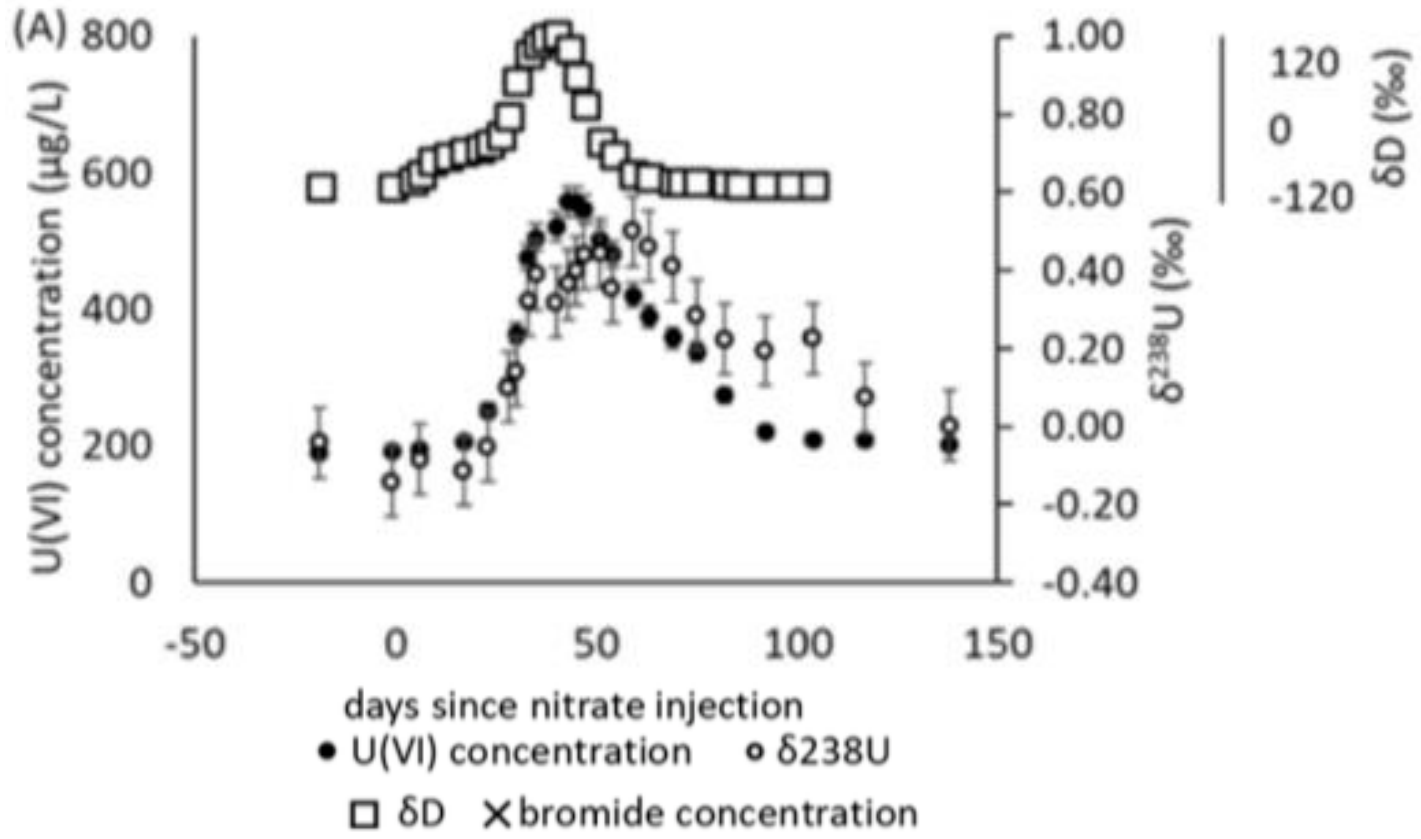


地下水铀被还原导致$^{238}U/^{235}U$比值降低

Bopp et al., 2010

$^{238}U/^{235}U$示踪地下水铀氧化

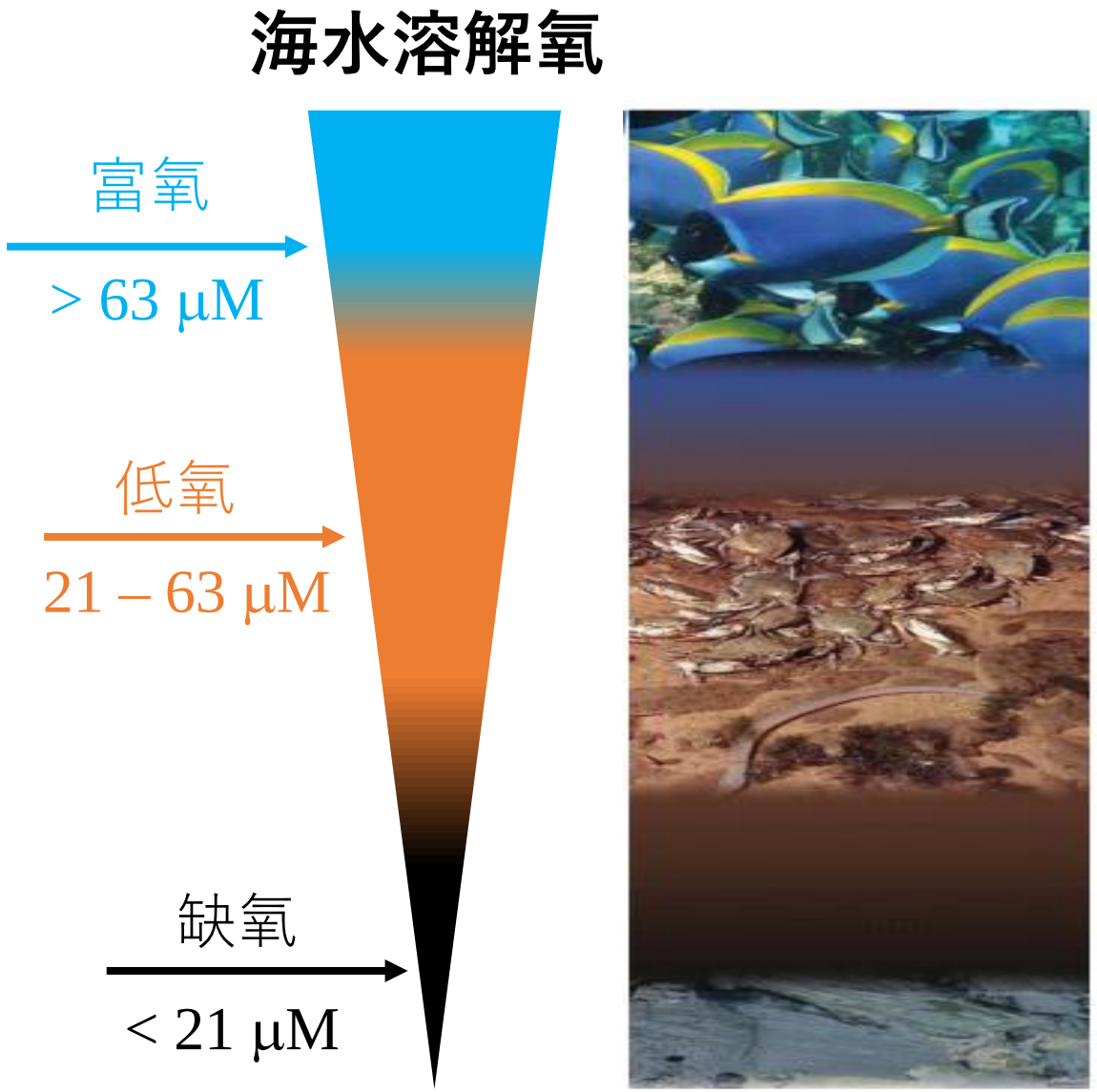




地下水U(IV)被NO_3^-氧化导致地下水$^{238}U/^{235}U$比值升高

Jemison et al., 2018

$^{238}U/^{235}U$重建古海洋氧化还原环境变化



海洋氧化还原

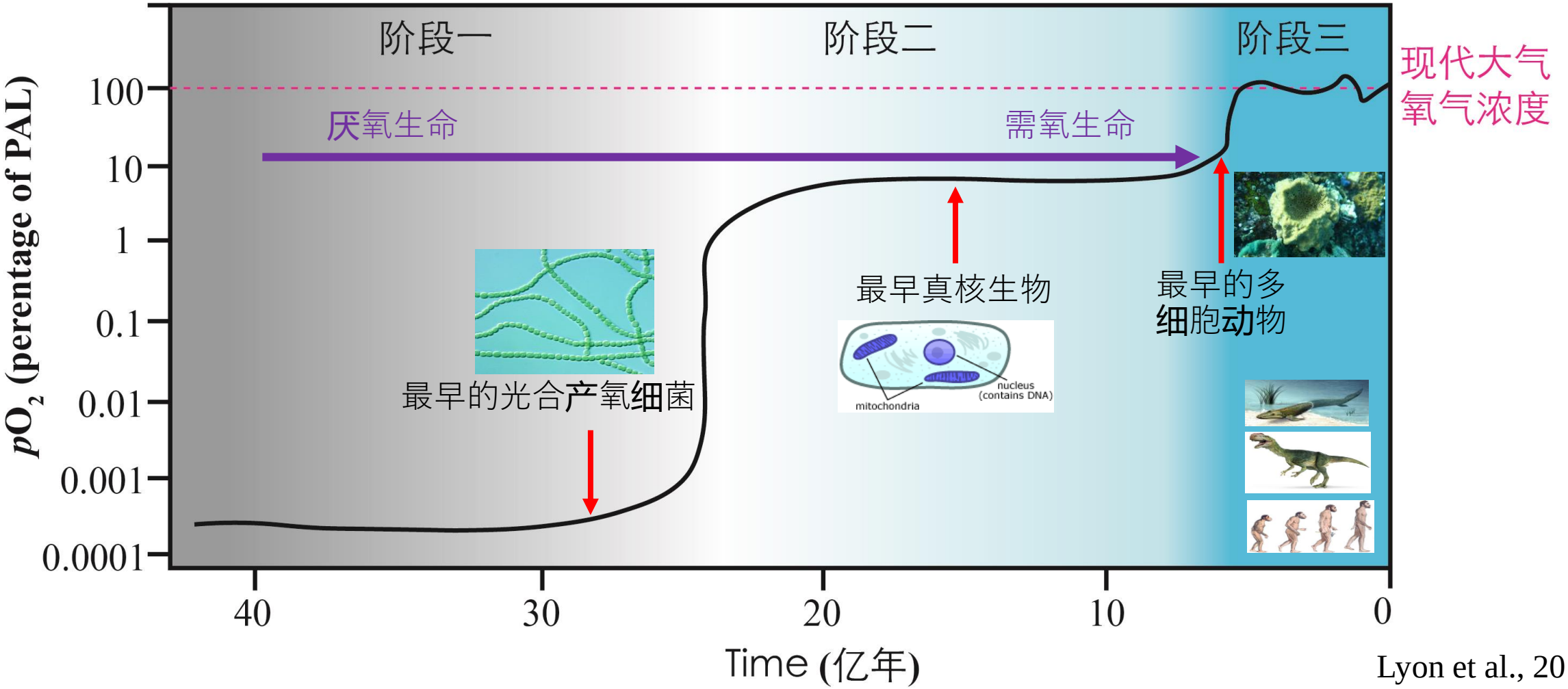
氧化环境：富氧

还原环境：缺氧甚至硫化(H_2S)

- 海洋溶解氧浓度极大影响控制海洋生产力、生物分布及其多样性
- 海洋溶解氧浓度也影响元素循环

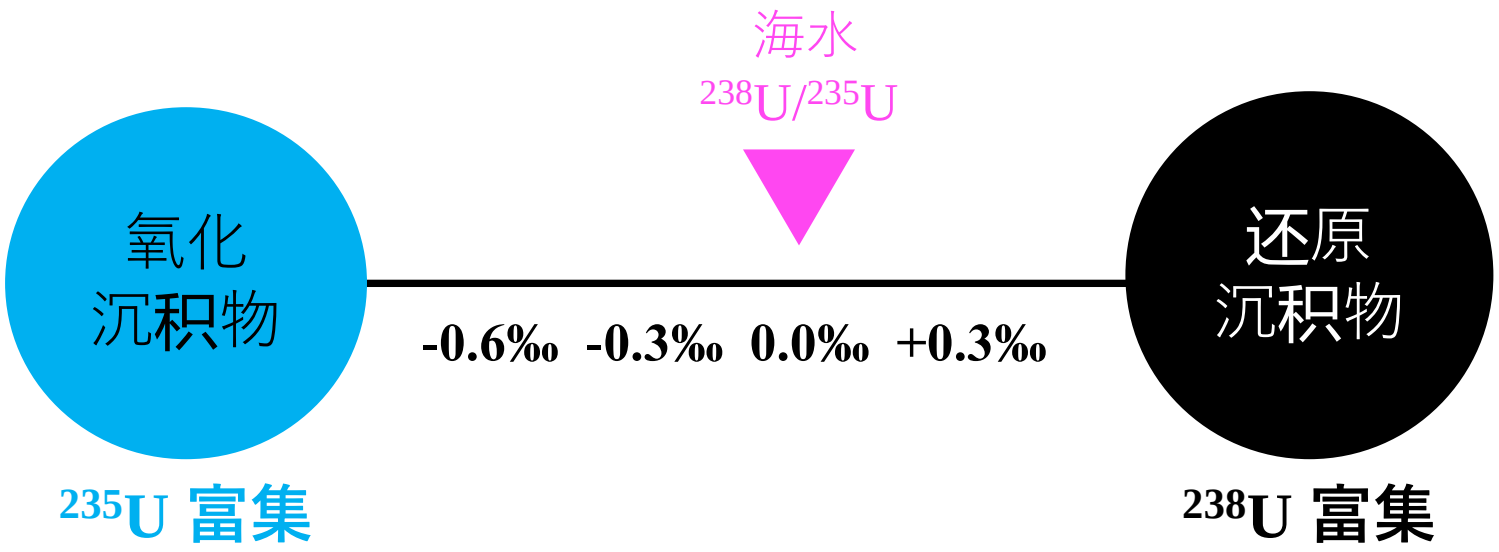
$^{238}U/^{235}U$重建古海洋氧化还原环境变化

古海洋的氧化还原对理解与认知地球氧气与生命的协同演化至关重要



Lyon et al., 2014

沉积岩$^{238}U/^{235}U$指示古海洋氧化还原变化



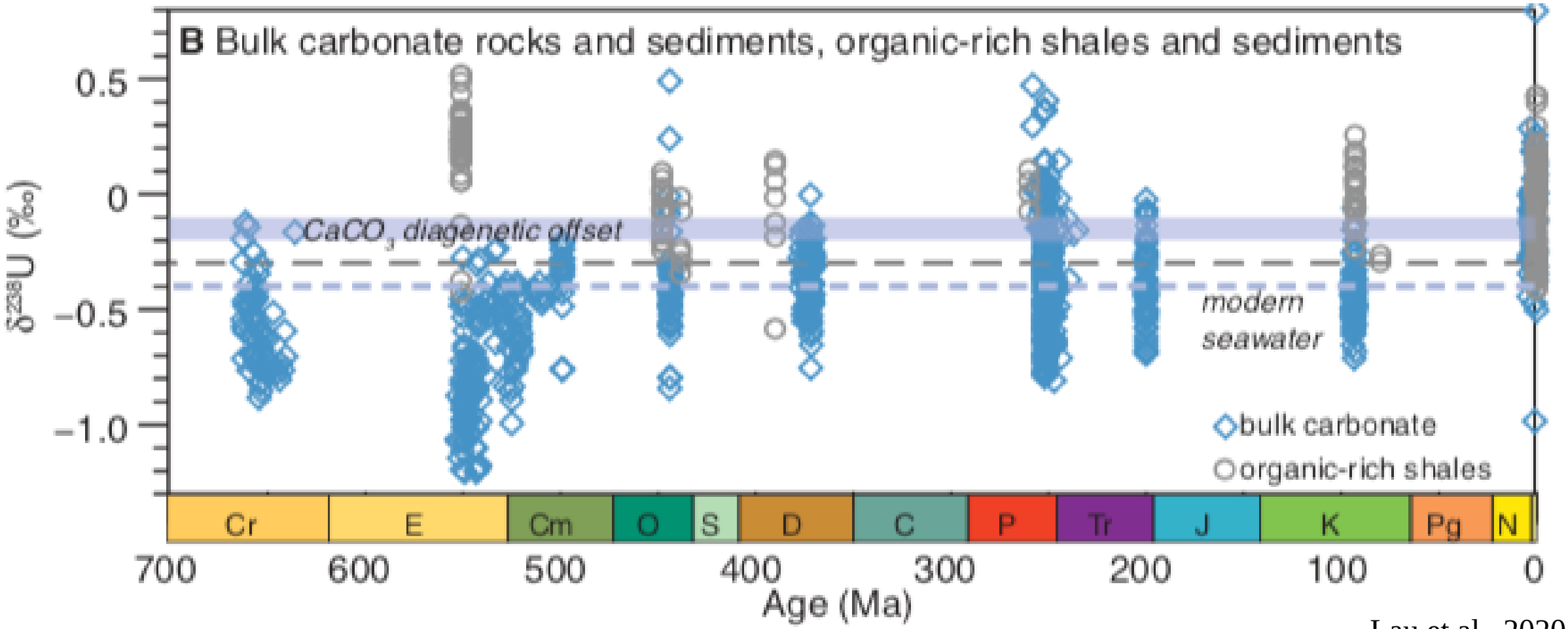
海水$\delta^{238}U$随海洋还原环境增强而减小

假设：$\Delta^{238}U = \delta^{238}U_{黑色页岩} - \delta^{238}U_{海水} = +0.60$ ‰

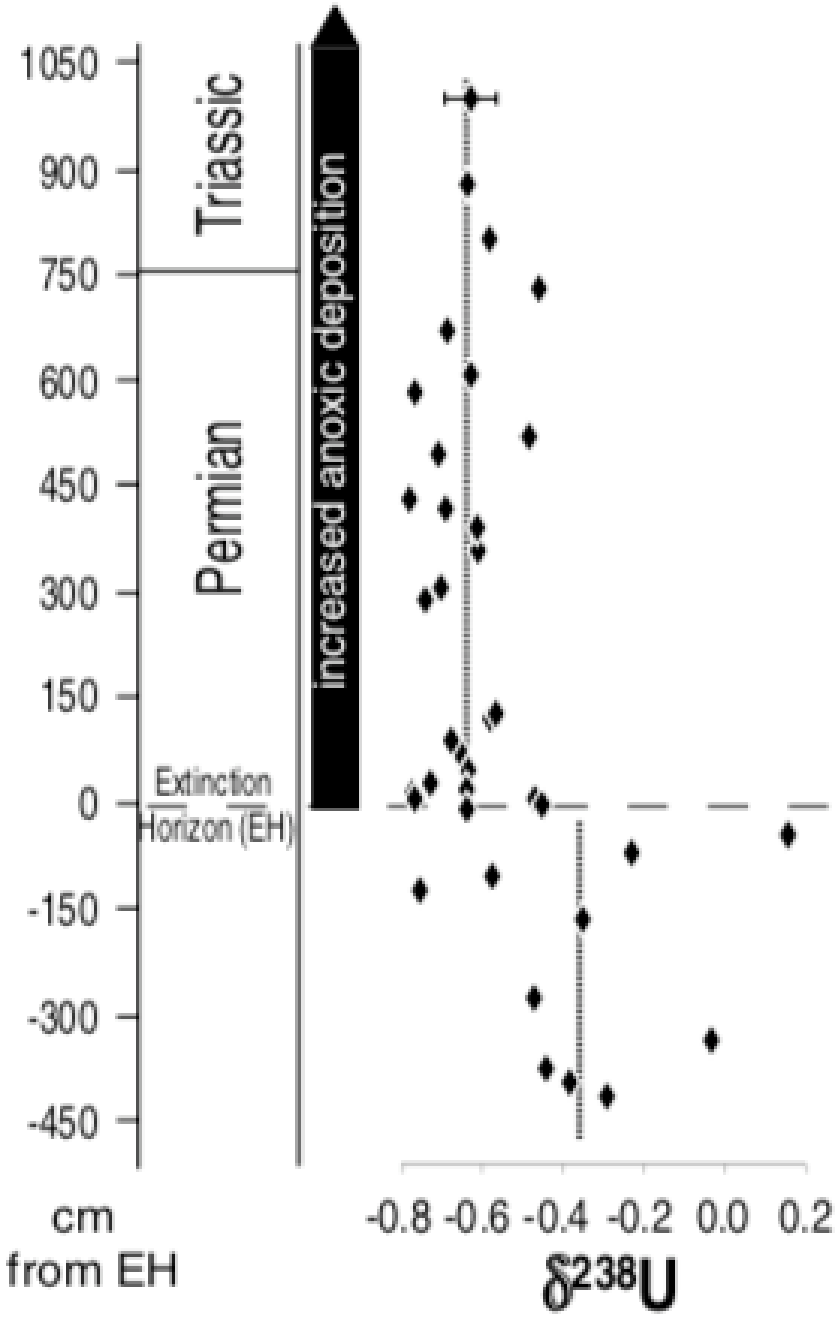
假设：$\Delta^{238}U = \delta^{238}U_{碳酸岩} - \delta^{238}U_{海水} = 0.0$ ‰

碳酸岩$\delta^{238}U$

假设：$\delta^{238}U_{碳酸岩} = \delta^{238}U_{海水}$



Lau et al., 2020



PNAS

Rapid expansion of oceanic anoxia immediately before the end-Permian mass extinction

Gregory A. Brennecka[a,1], Achim D. Herrmann[a,b], Thomas J. Algeo[c], and Ariel D. Anbar[a,d]

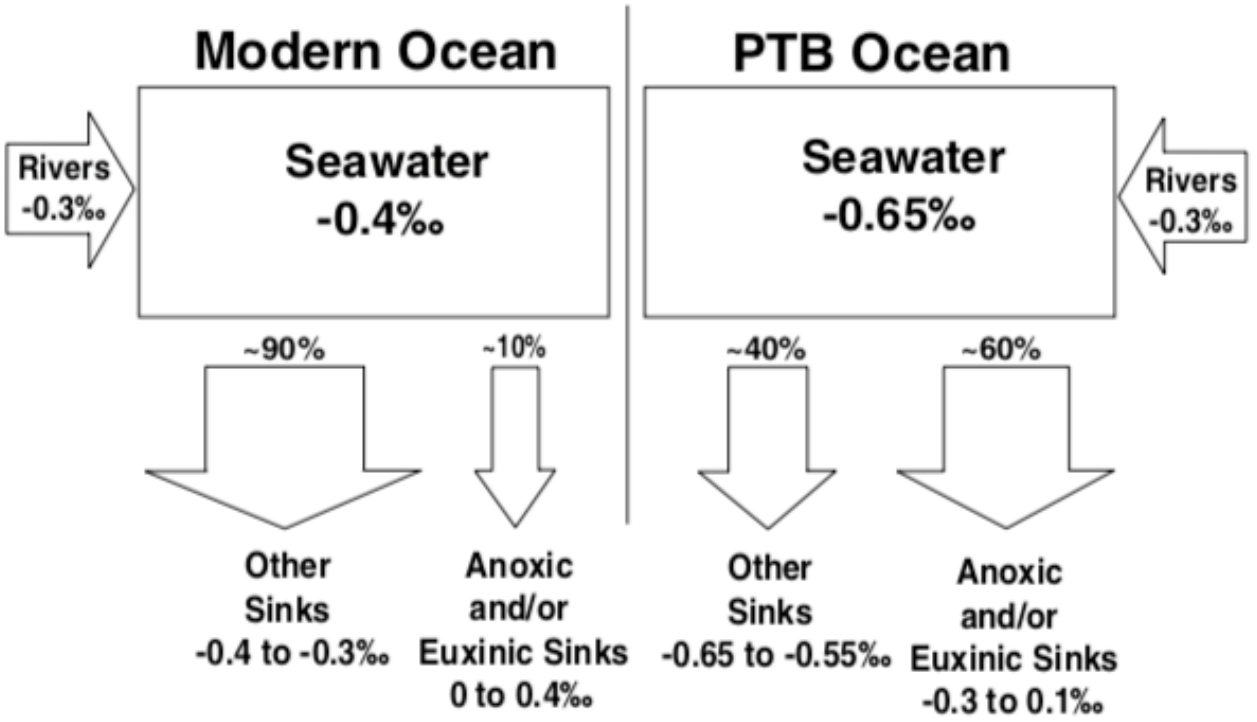
[a]School of Earth and Space Exploration, Arizona State University, P.O. Box 871404, Tempe, AZ 85287-1404; [b]Barrett, the Honors College, Arizona State University, Tempe, AZ 85287-1612; [c]Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013; and [d]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1404

Edited by Donald E. Canfield, University of Southern Denmark, Odense M., Denmark, and approved September 11, 2011 (received for review April 18, 2011)

Periods of oceanic anoxia have had a major influence on the evolutionary history of Earth and are often contemporaneous with mass extinction events. Changes in global (as opposed to local) redox conditions can be potentially evaluated using U system

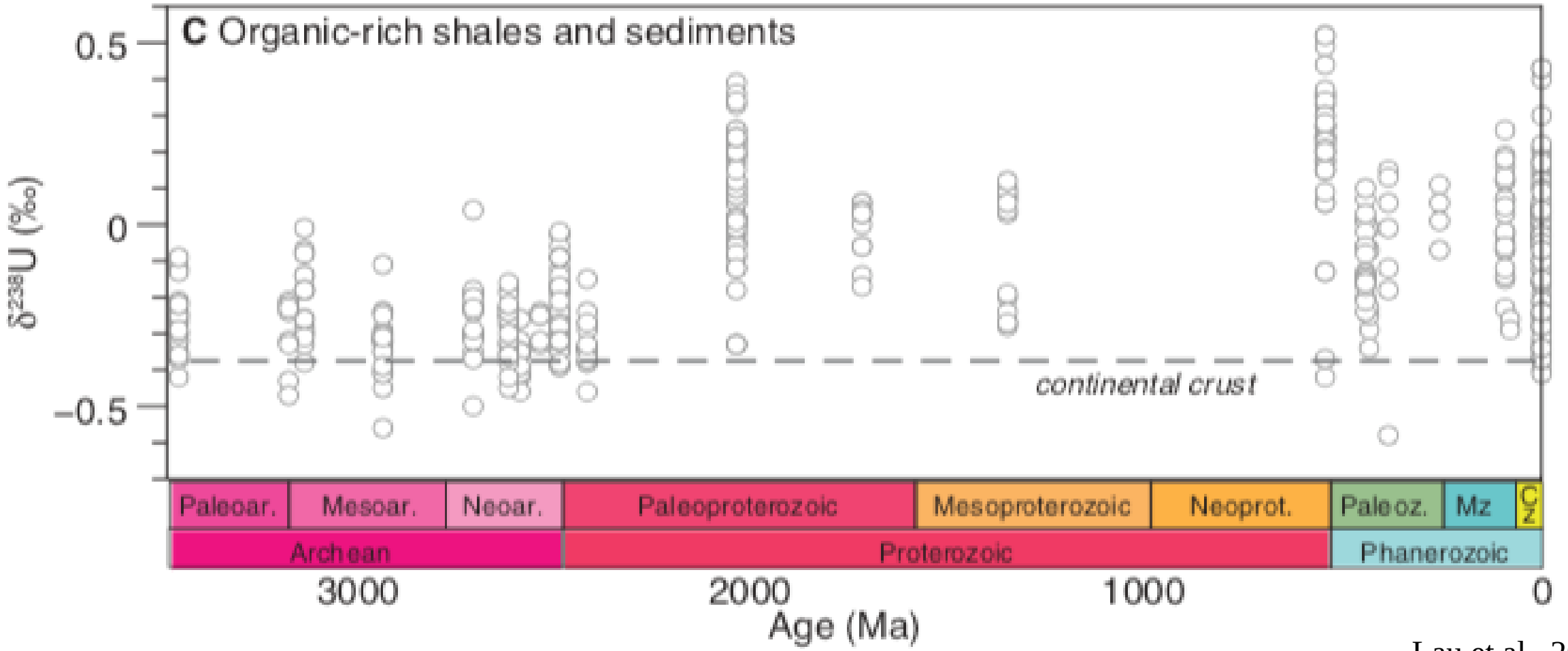
anoxia, the flux of reduced U to anoxic facies (such as black shales) increases, preferentially removing ^{238}U from seawater. The loss of isotopically heavy U drives seawater to lighter isotopic compositions (23). Changes in the U isotope ratios of organic-

$$\delta^{238}U_{input} = ((1 - f_{anoxic}) \times \delta^{238}U_{other}) + (f_{anoxic} \times \delta^{238}U_{anoxic}).$$



富有机质沉积物$\delta^{238}U$

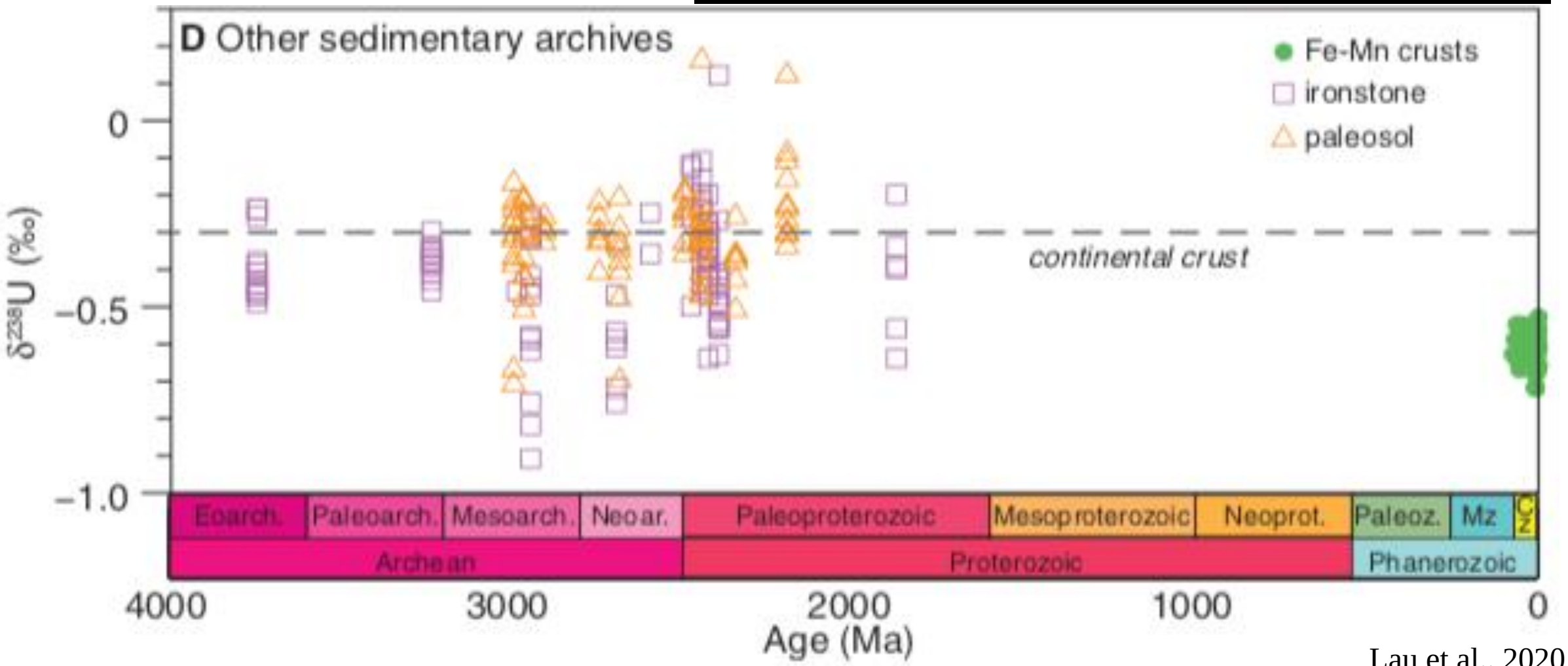
假设：$\Delta^{238}U = \delta^{238}U_{黑色页岩} - \delta^{238}U_{海水} = +0.60$ ‰



Lau et al., 2020

其它沉积物$\delta^{238}U$

假设：$\Delta^{238}U = \delta^{238}U_{Fe\text{-}Mn} - \delta^{238}U_{海水} = -0.20$ ‰



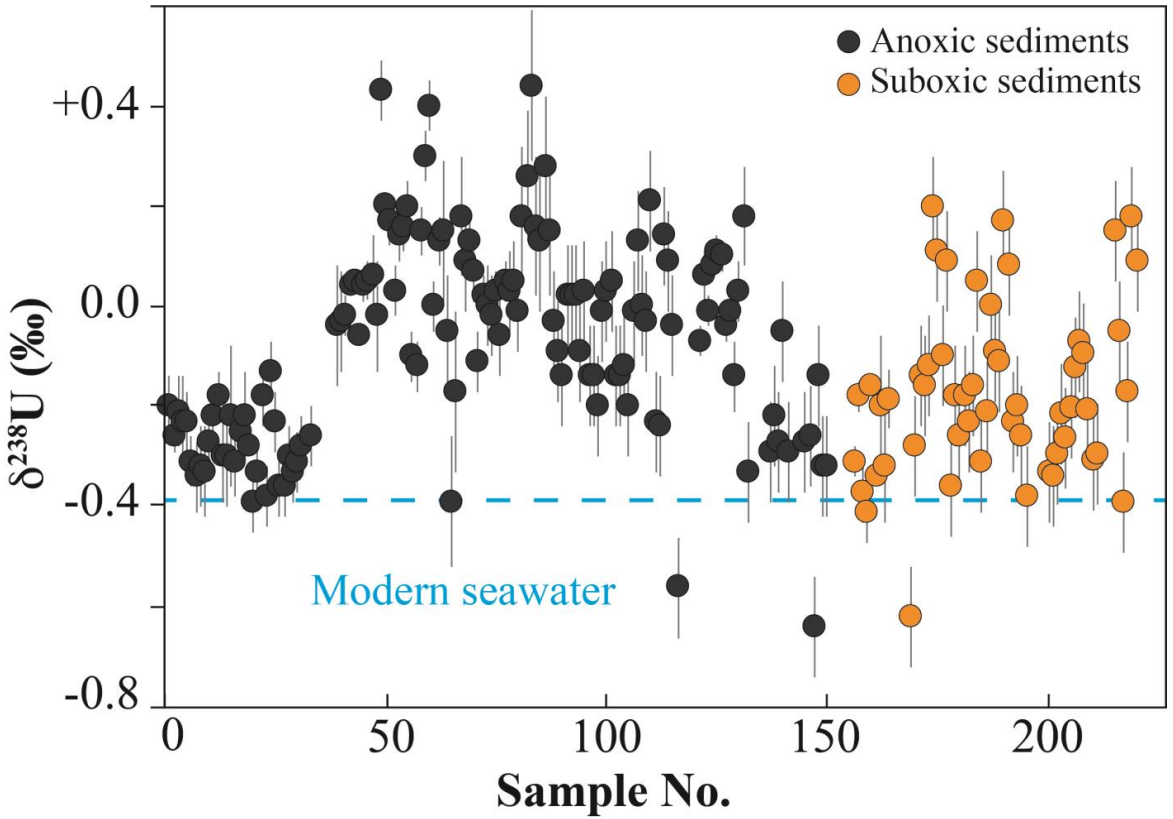
Lau et al., 2020

第三部分：生物地球化学循环过程铀同位素分馏

1. 氧化还原：生物与非生物
2. 吸附：铁锰氧化物、矿物、藻类
3. 碳酸岩共沉淀与成岩过程

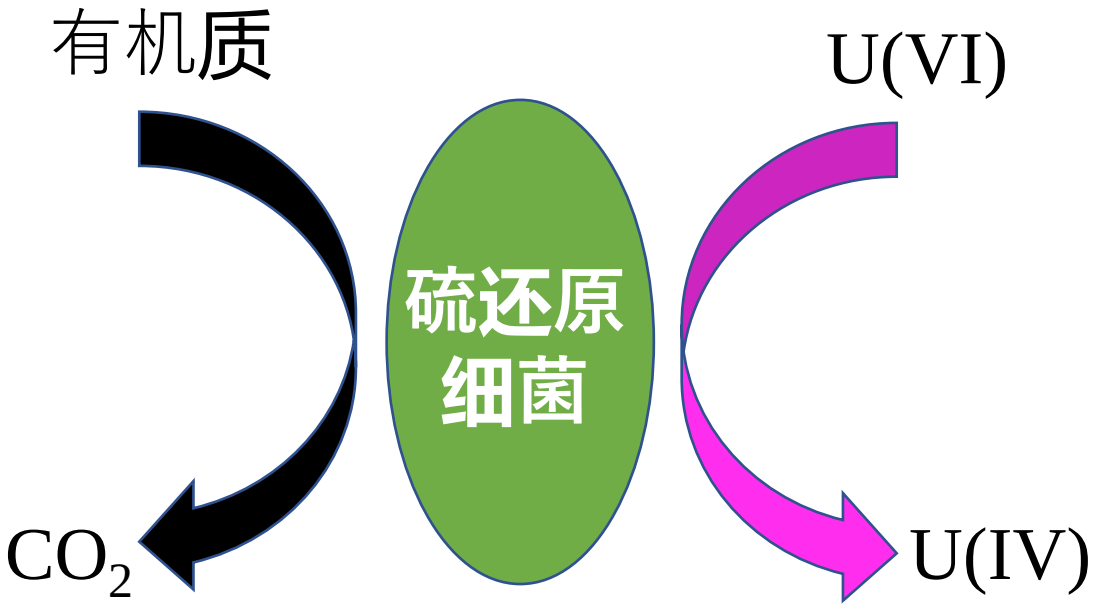
为什么测定不同过程中同位素分馏？

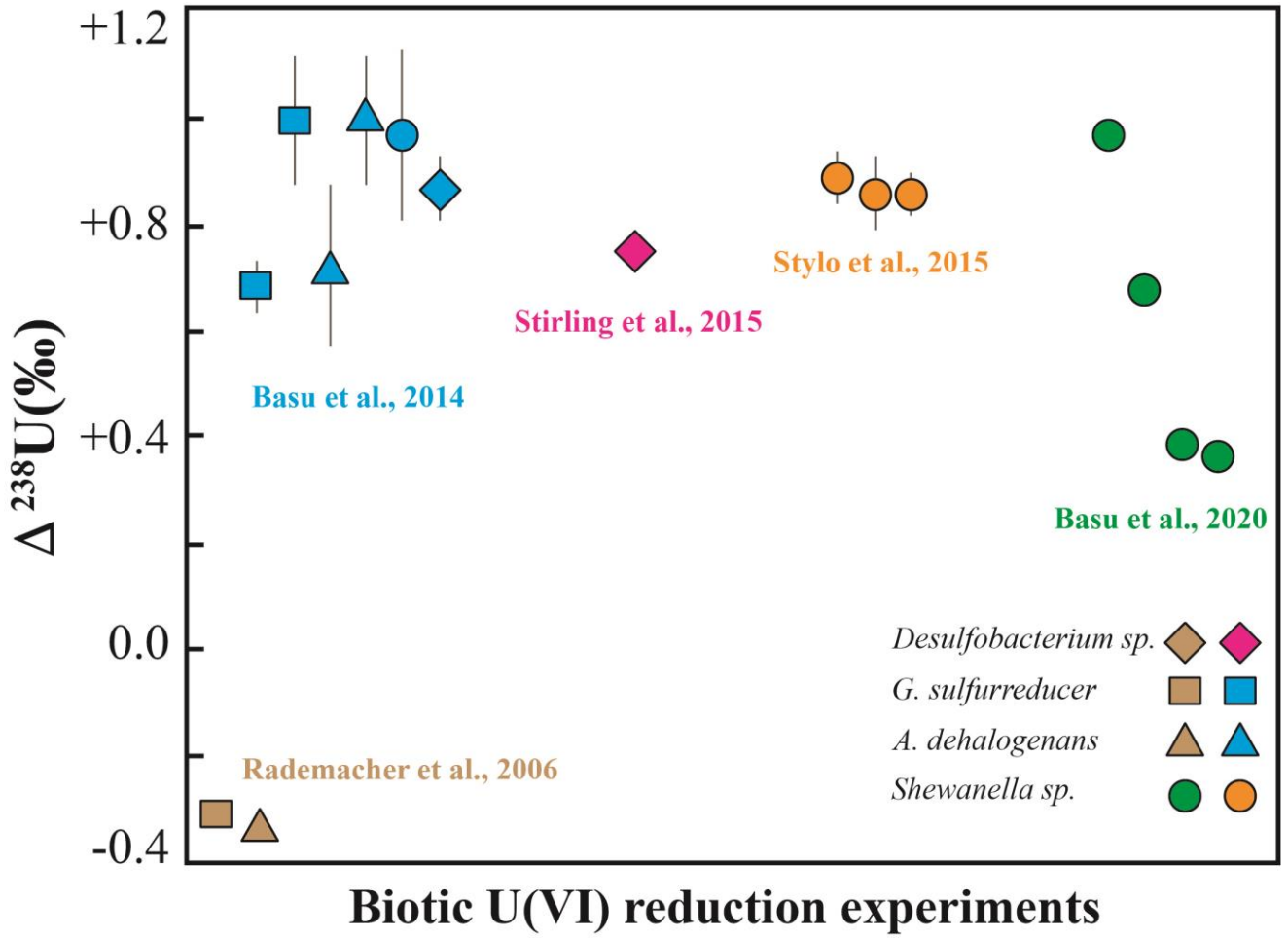
$$\delta^{238}U_{sw} = \delta^{238}U_{in} - \frac{A_{an}k_{an}\Delta^{238}U_{an} + A_{sub}k_{sub}\Delta^{238}U_{sub} + A_{ox}k_{ox}\Delta^{238}U_{ox}}{A_{an}k_{an} + A_{sub}k_{sub} + A_{ox}k_{ox}}$$



哪些过程控制还原沉积物中$\delta^{238}U$的变化？

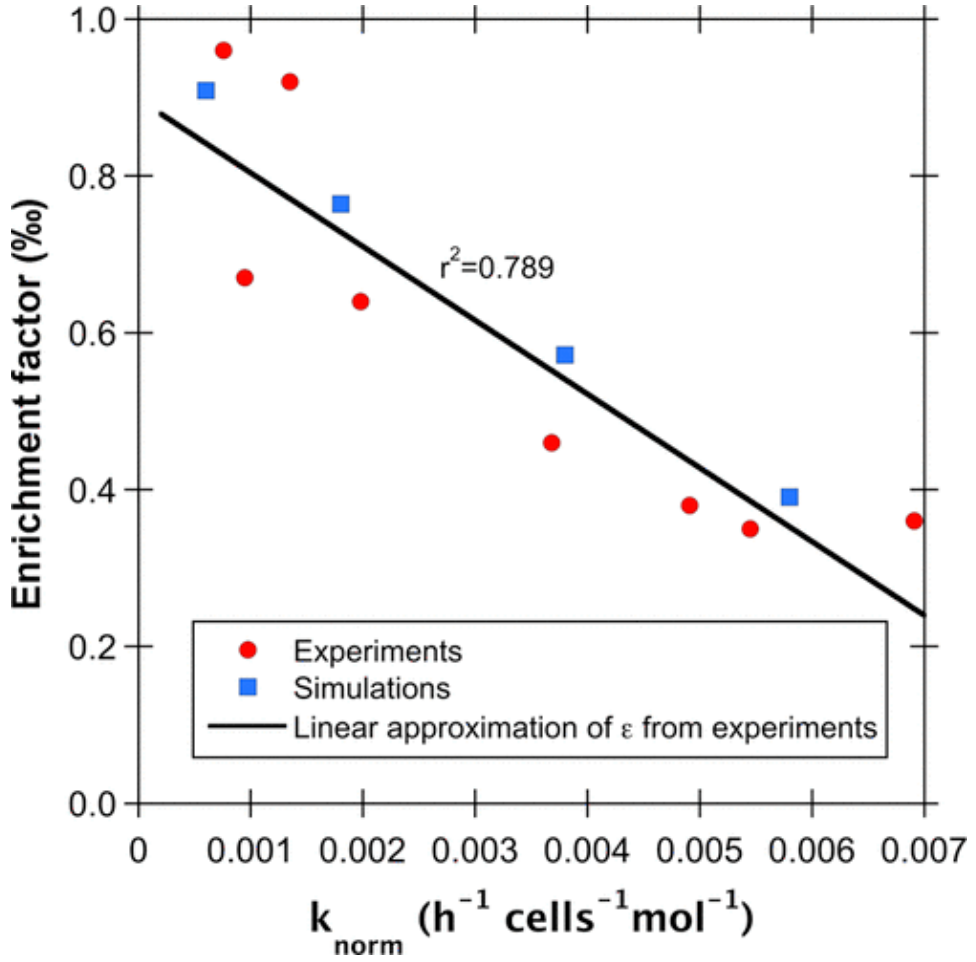
生物还原铀同位素分馏

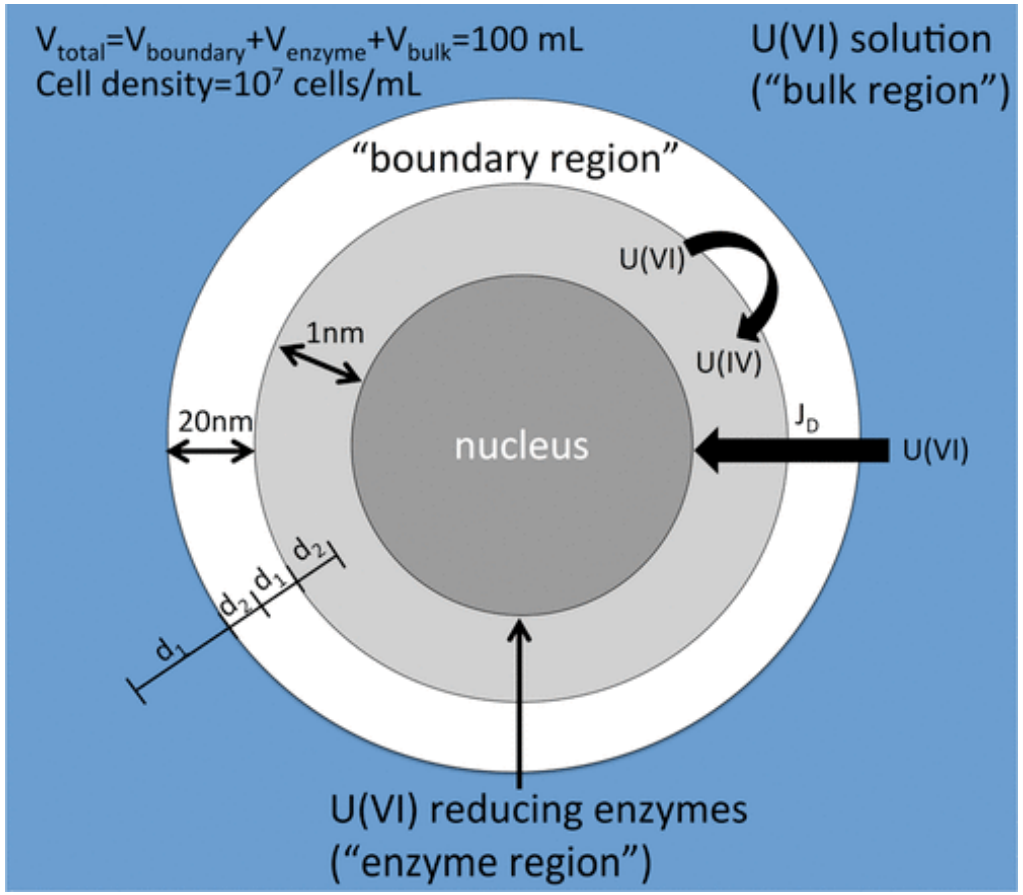




生物还原产物U(IV)富集^{238}U

生物还原铀同位素分馏—动力学

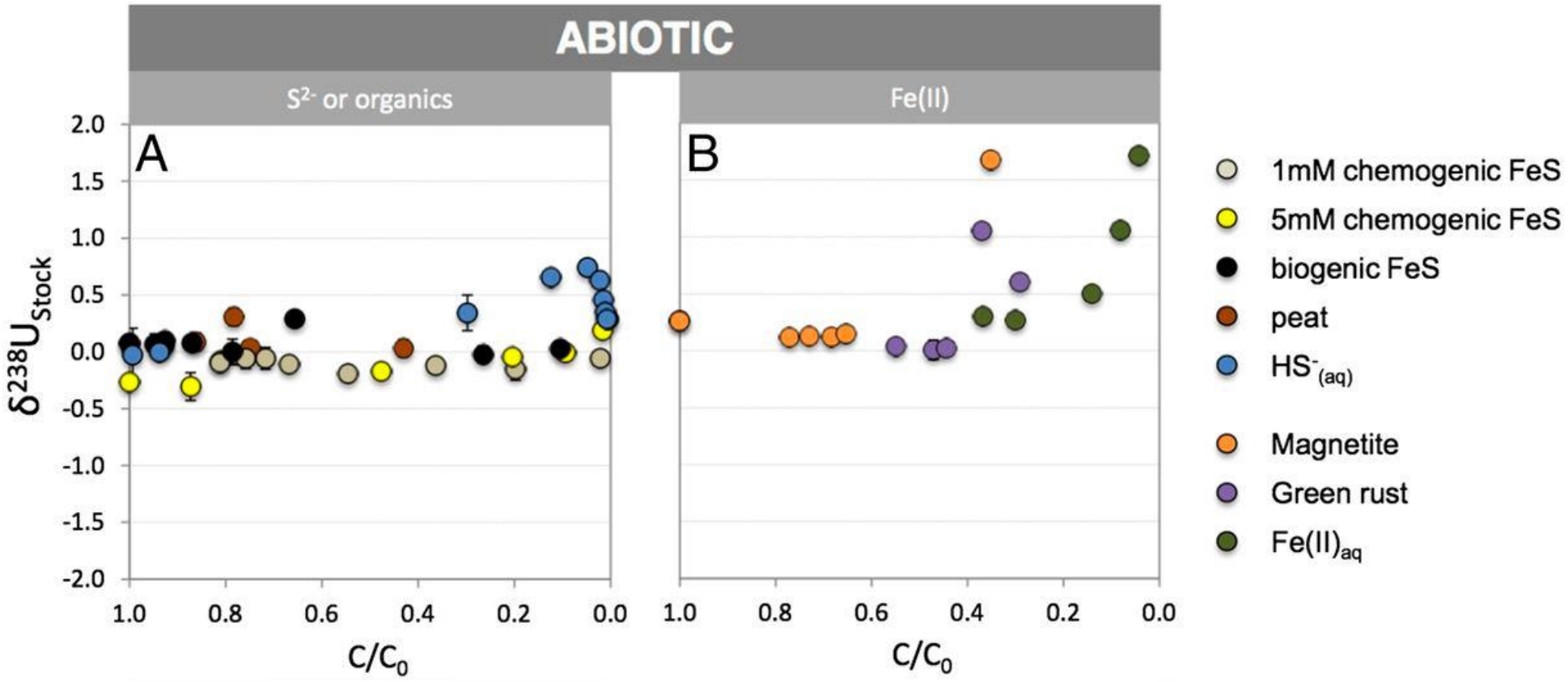




铀同位素分馏大小随铀还原速率增大而减小

Basu et al., 2020

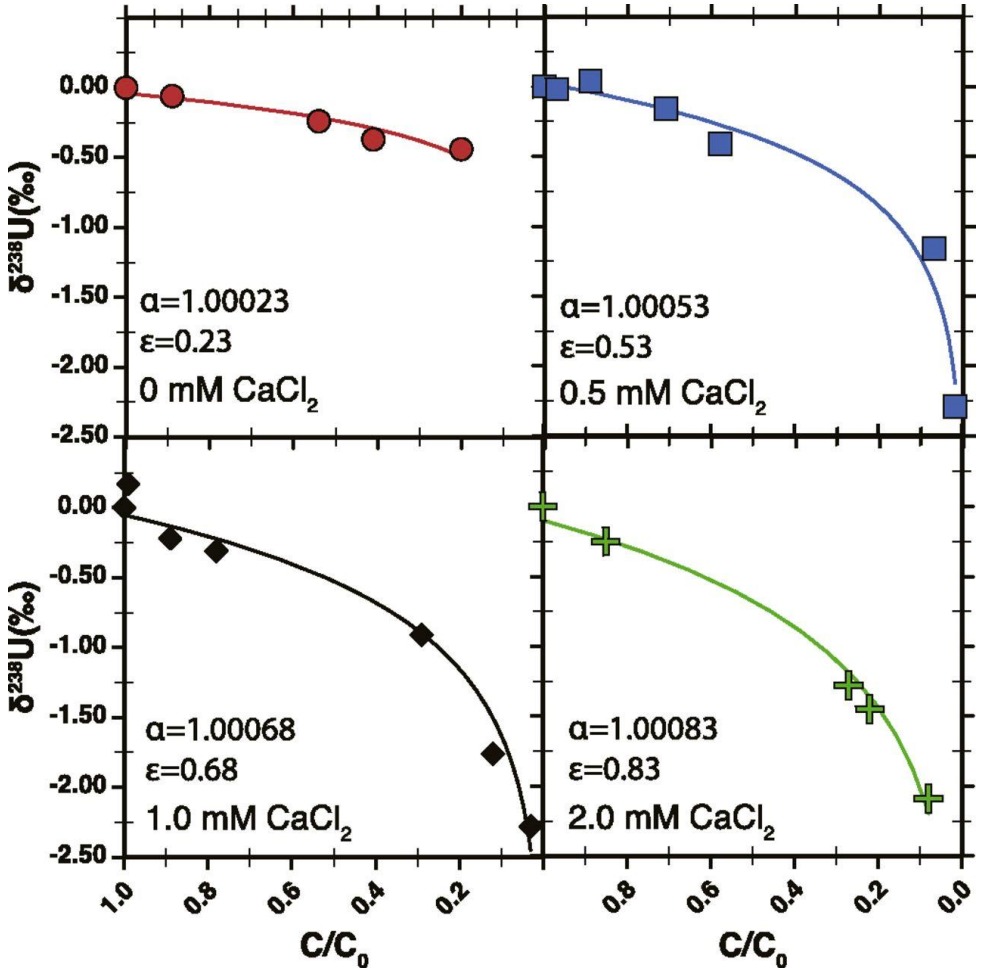
非生物还原铀同位素分馏



部分非生物还原反应导致U(IV)富集^{235}U, 其它无分馏

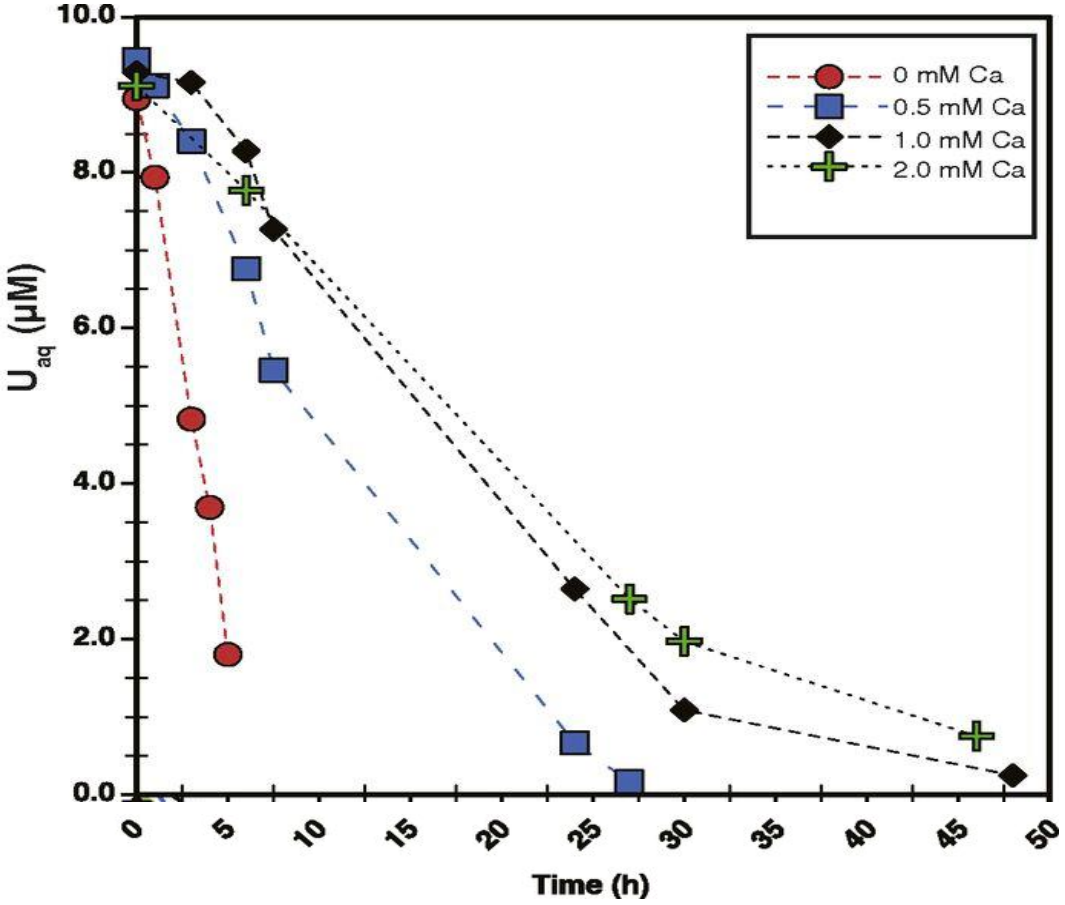
Stirling et al., 2007; Stylo et al., 2015; Rademacher et al., 2006

FeS还原铀同位素分馏



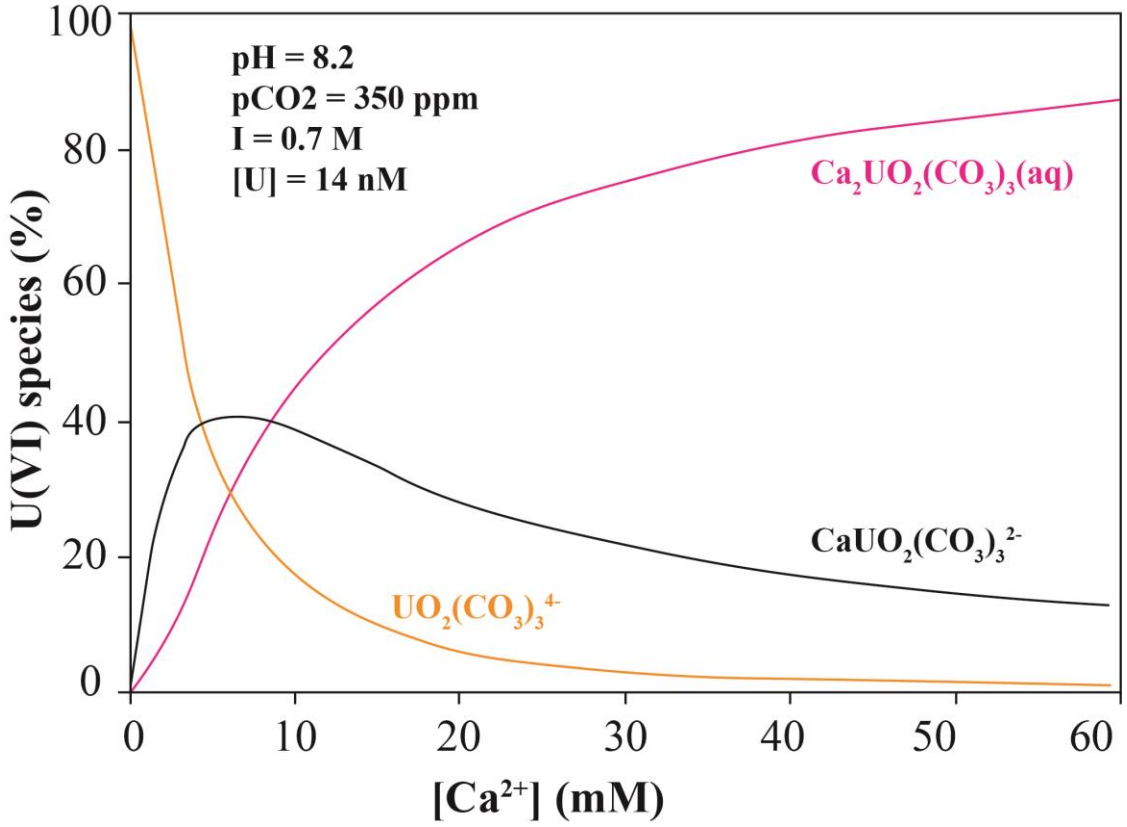
FeS还原导致U(IV)富集

^{238}U

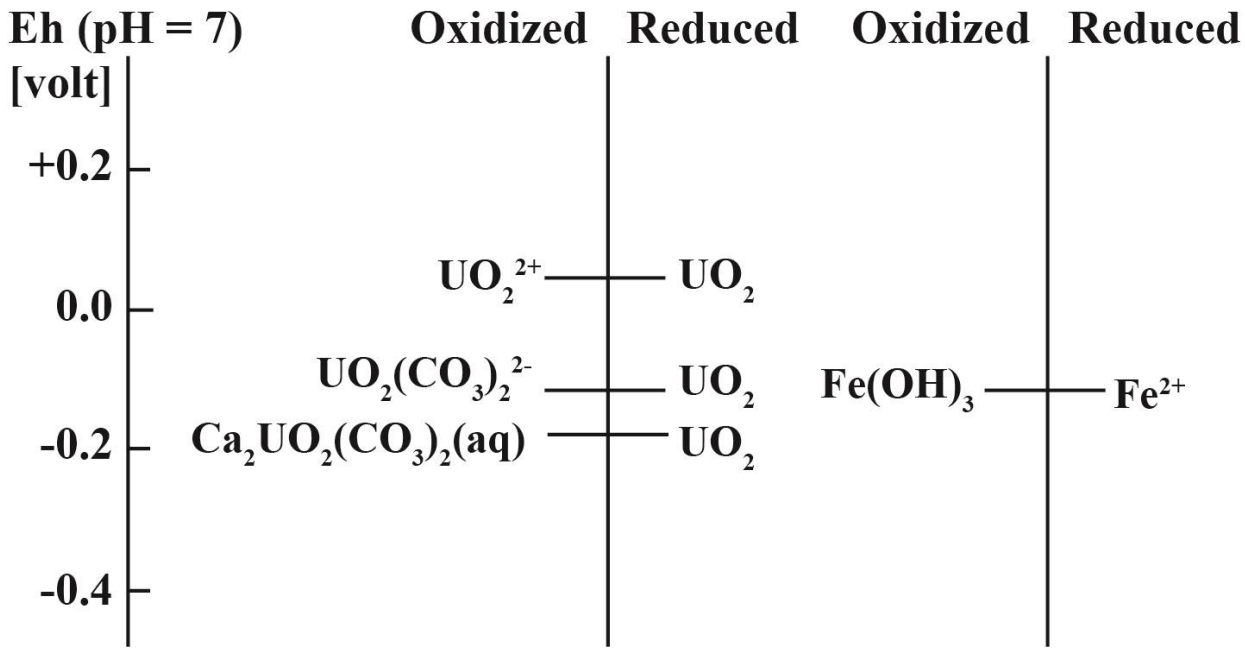


钙离子含量越高，铀还原速率越慢

Brown et al., 2018



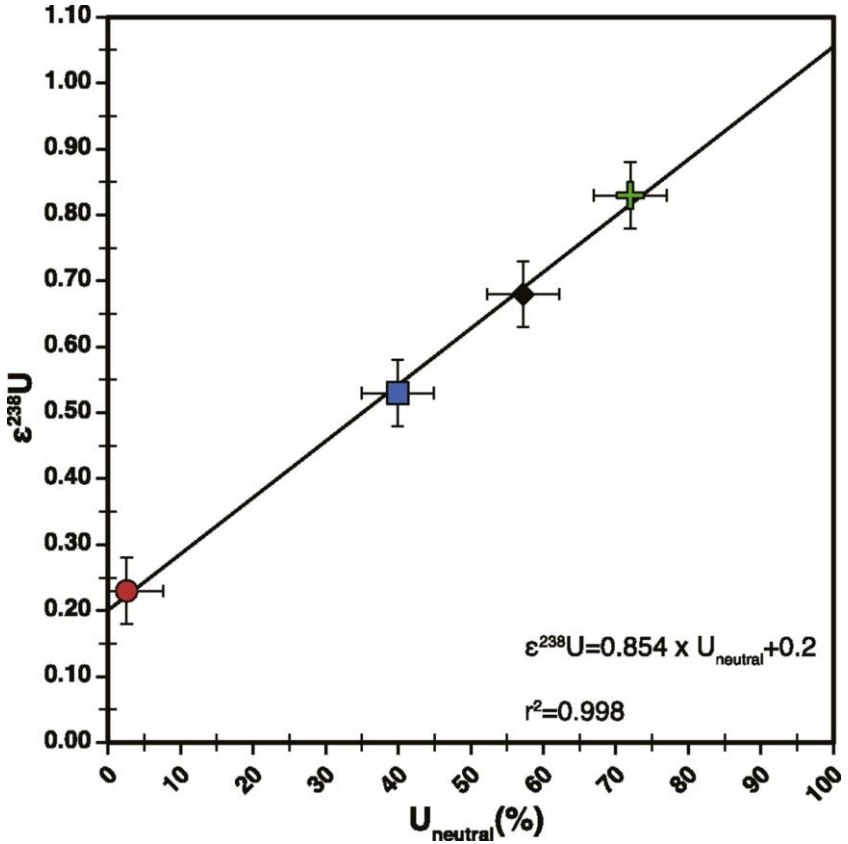
$[Ca_2UO_2(CO_3)_3(aq)$ 随$[Ca^{2+}]$增加而增加

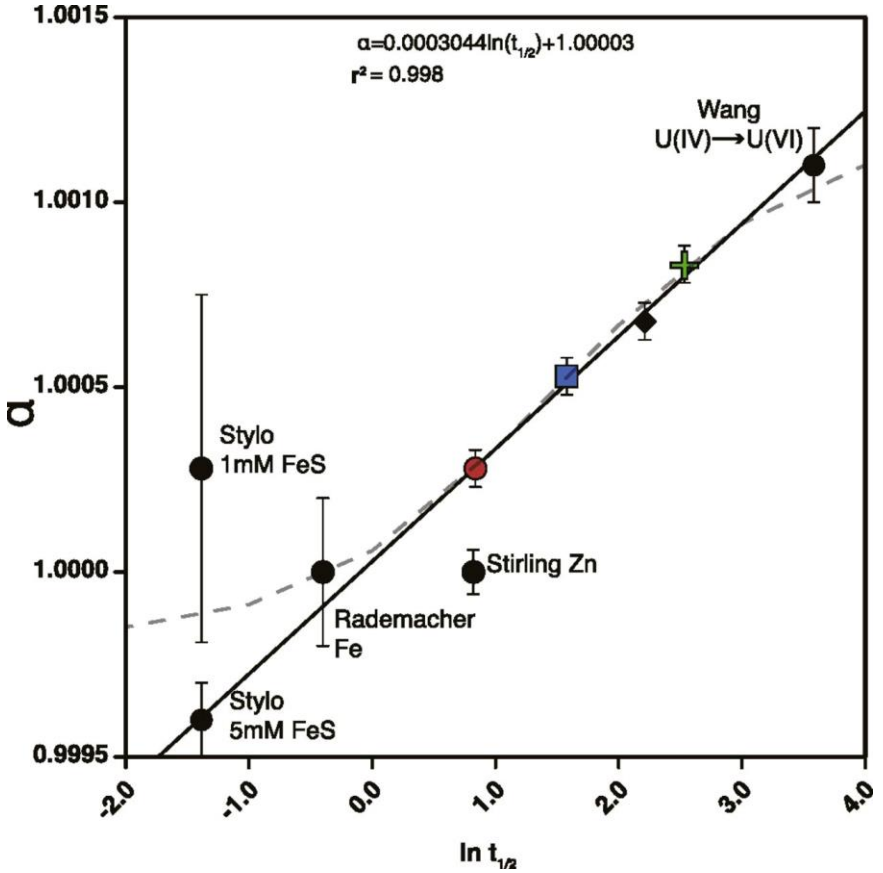


不同铀的组分氧化还原电势不一样

Chen et al., 2017; Vogel and Fendorf, 2008

FeS还原铀同位素分馏—动力学





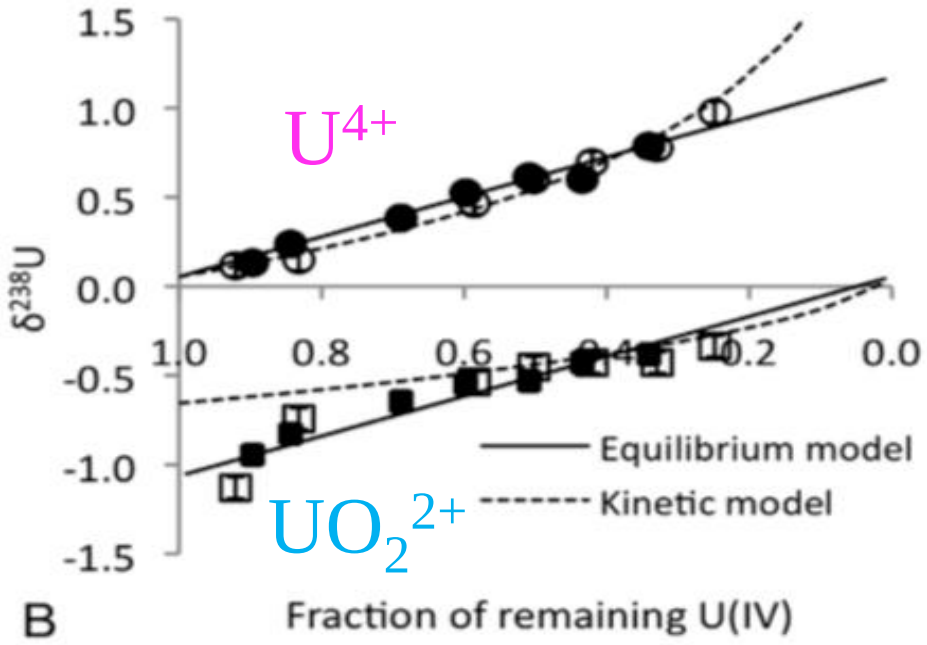
铀还原速率慢：核体积效应 U(IV)富集^{238}U

铀还原速率快：质量相关分馏U(IV)富集^{235}U

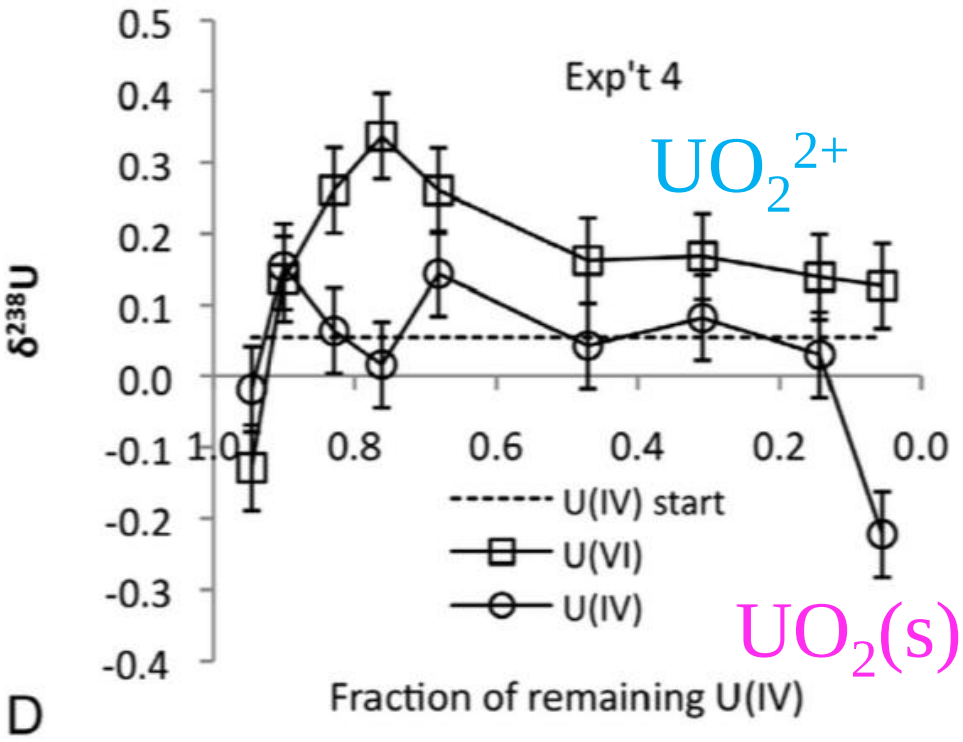
Brown et al., 2018

U(IV)氧化为U(VI)同位素分馏

$$U^{4+} + H_2O + \frac{1}{2}O_2 = UO_2^{2+} + 2H^+$$



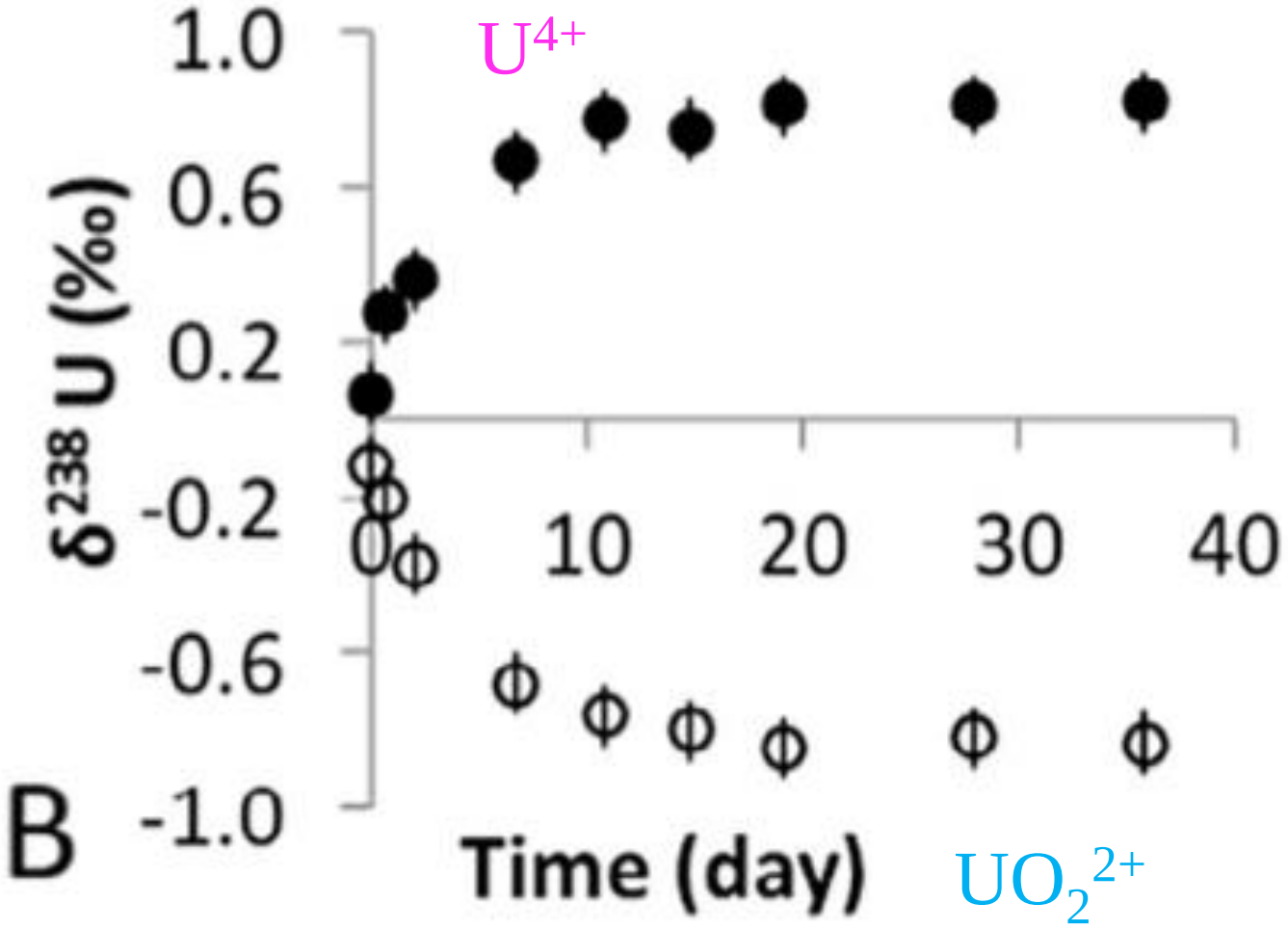
$\Delta^{238}U_{VI-IV}$ = 1.1 ± 0.2 ‰



$\Delta^{238}U$ = -0.1 to -0.3‰

Wang et al., 2015a, 2015b

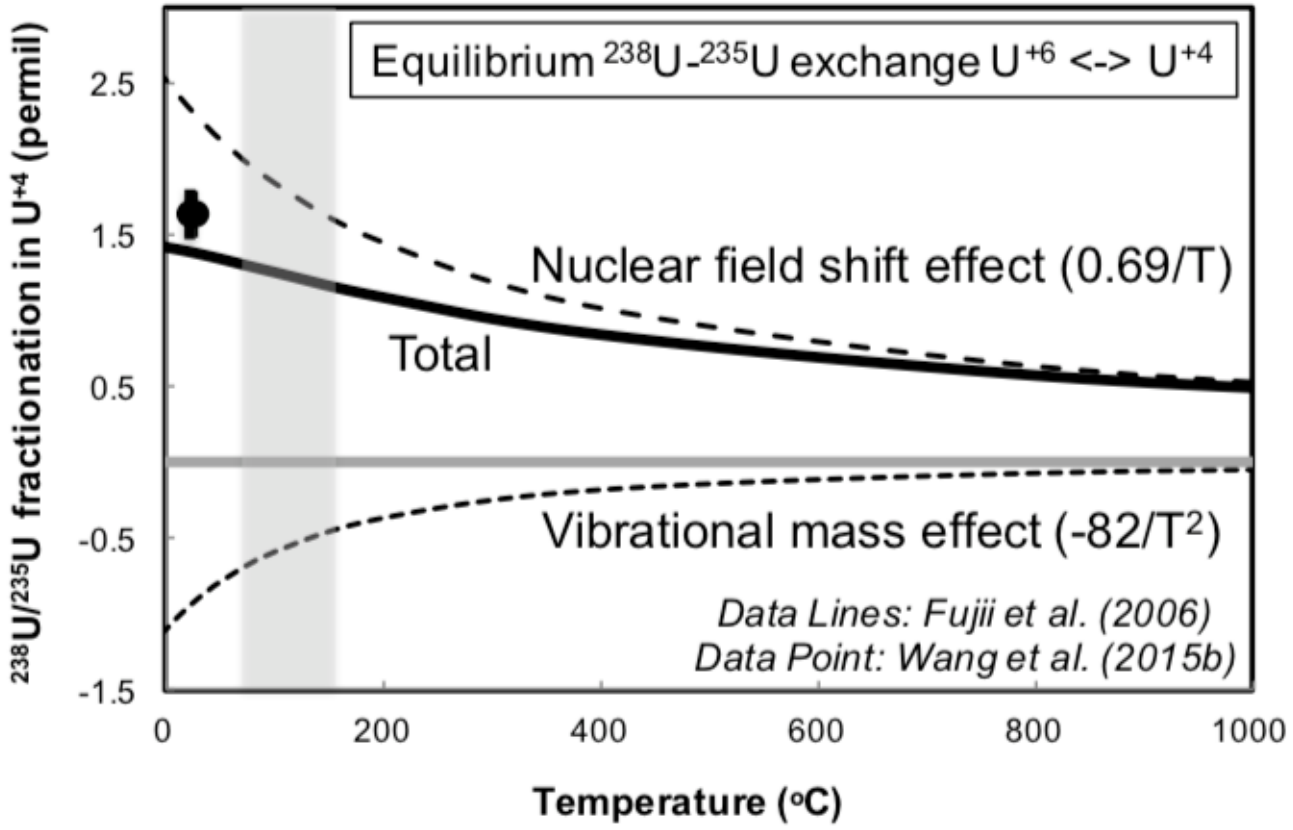
U(IV) ⇌ U(VI)平衡分馏实验



$\Delta^{238}U = 1.64 \pm 0.16$ ‰

Wang et al., 2015b

U(IV) ⇌ U(VI)平衡分馏理论计算



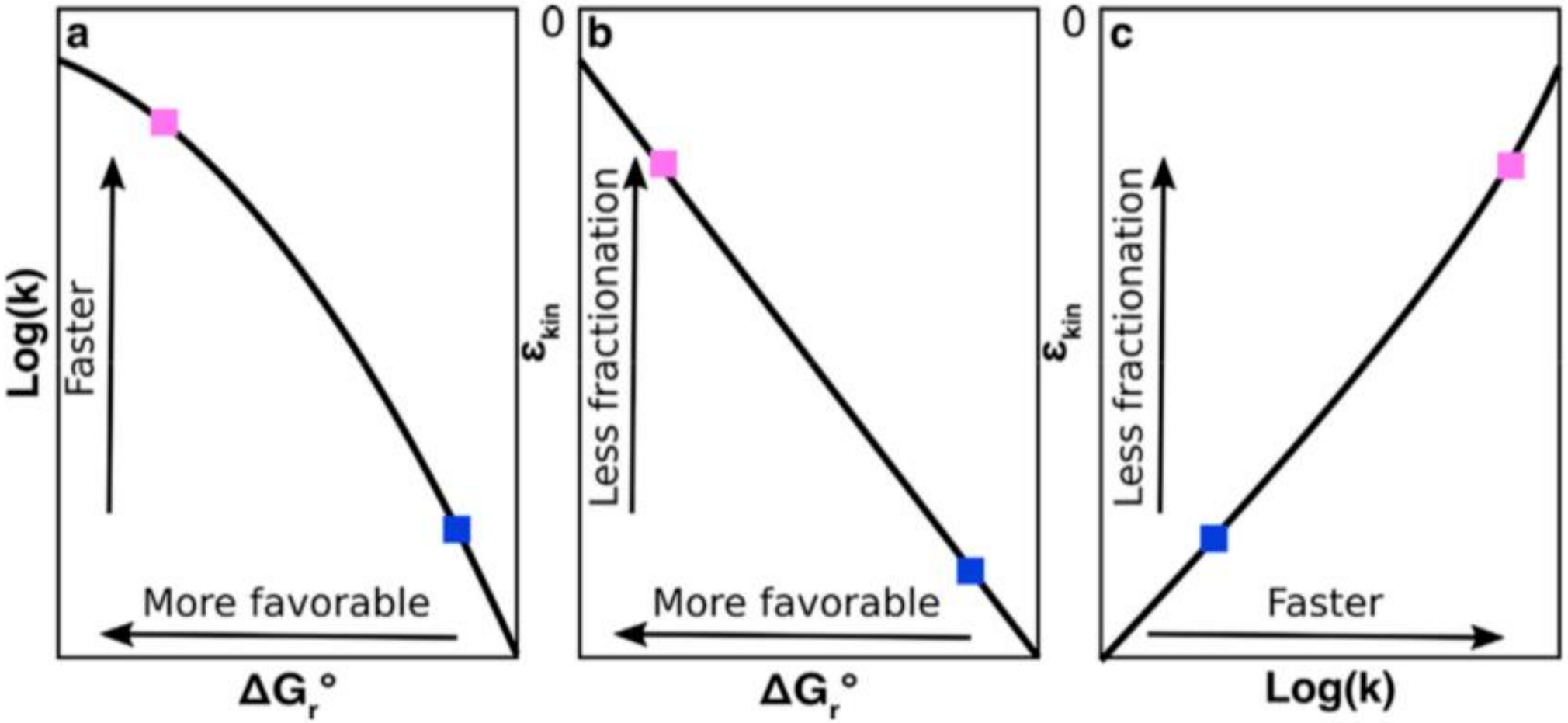
核体积效应：富集^{238}U

质量相关分馏：富集^{235}U

核体积 > 质量相关分馏

Andersen et al., 2017; Wang et et al., 2015a, Fujii et al., 2006; Abe et al., 2008; Bigelesien, 1996

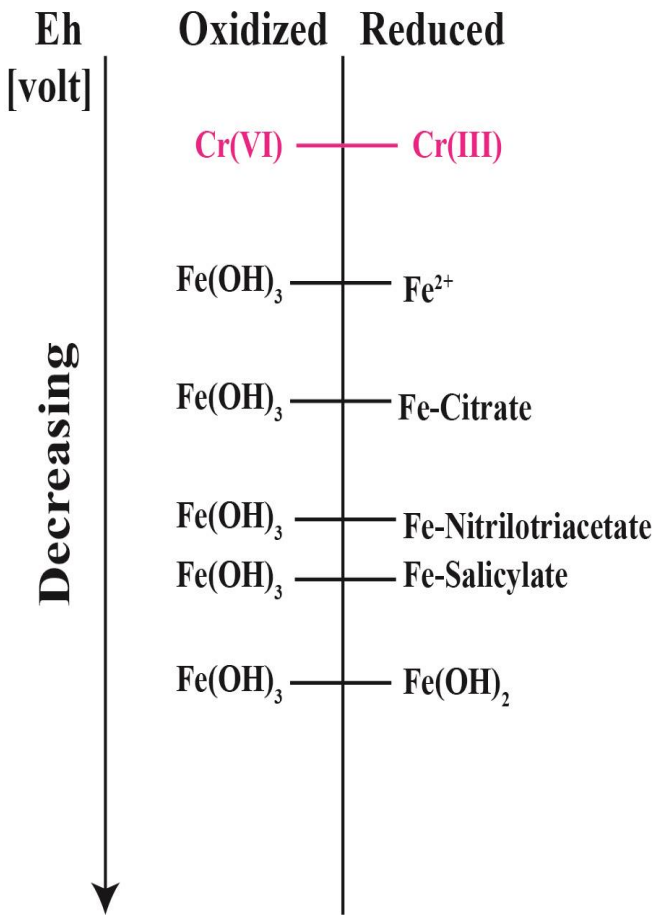
氧化还原反应动力学分馏模型

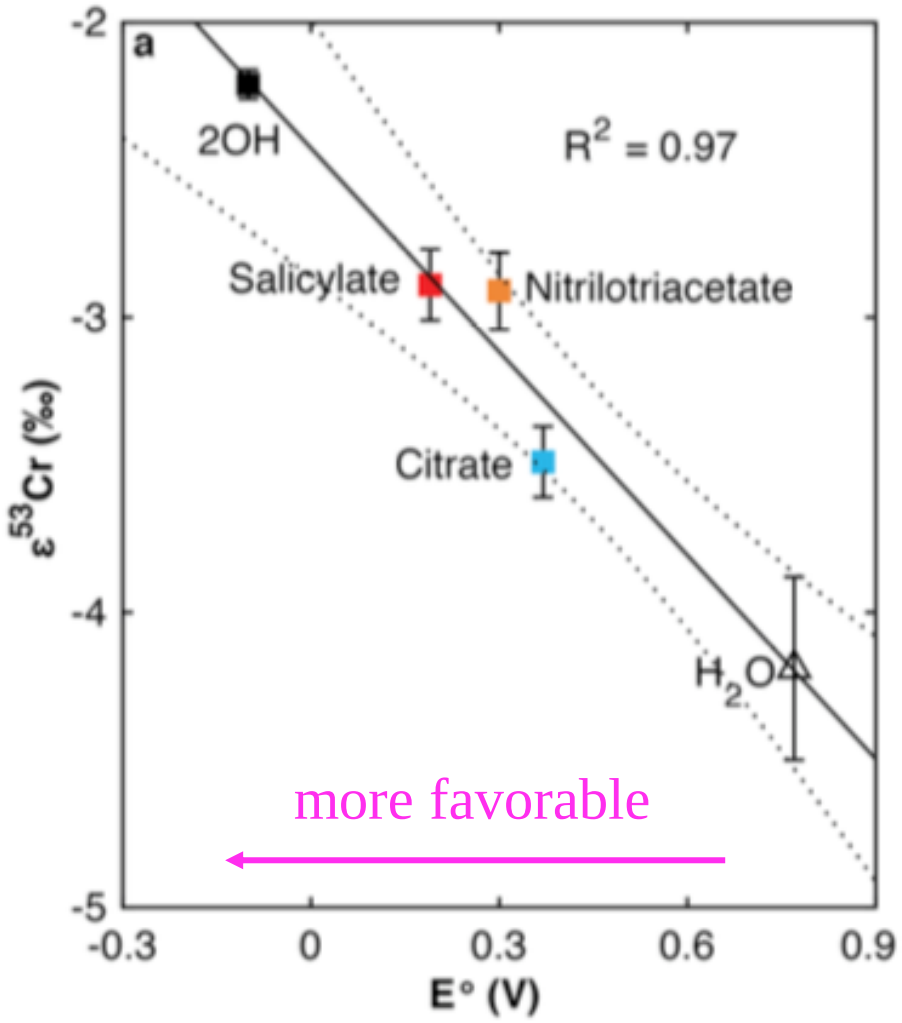


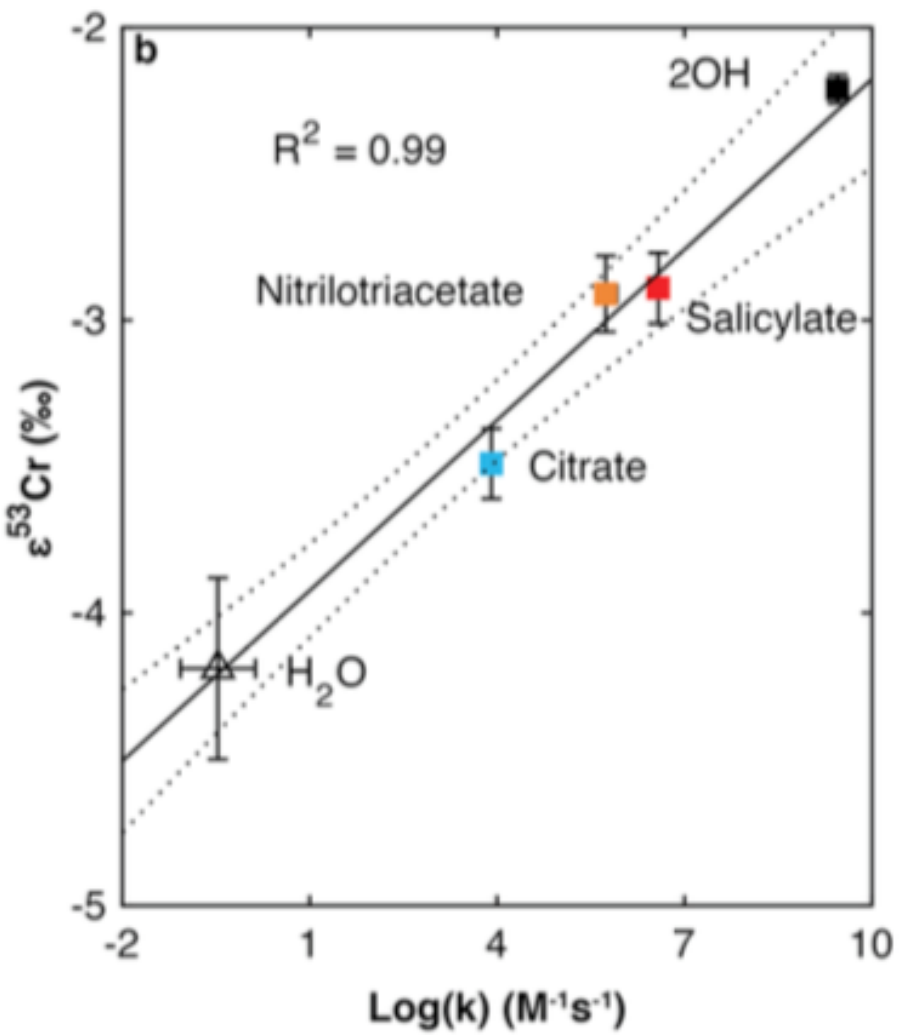
Wong et al., 2020

Marcus theory

Fe(II)还原铬动力学同位素分馏



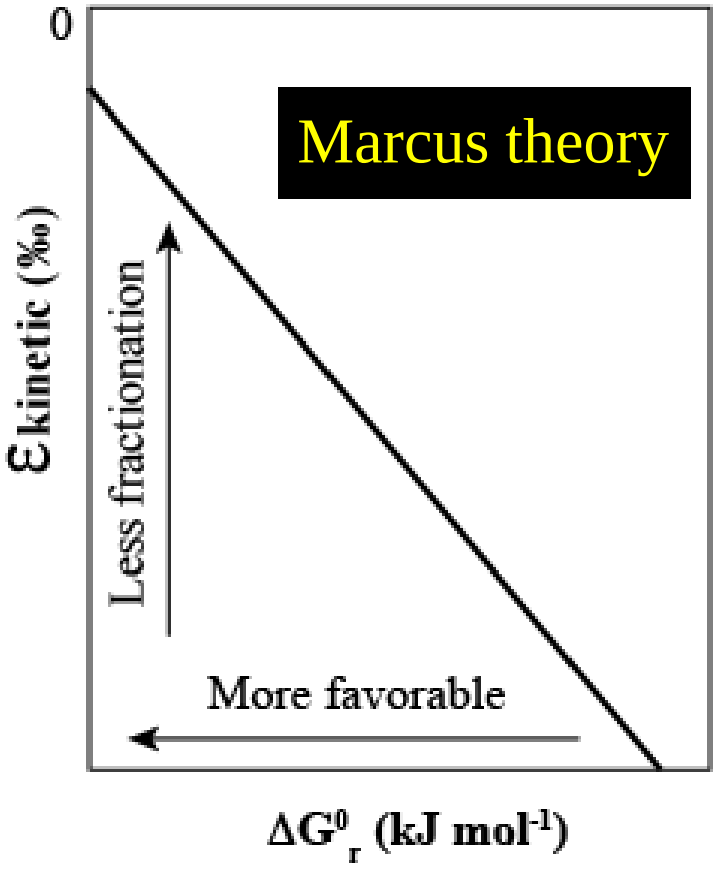


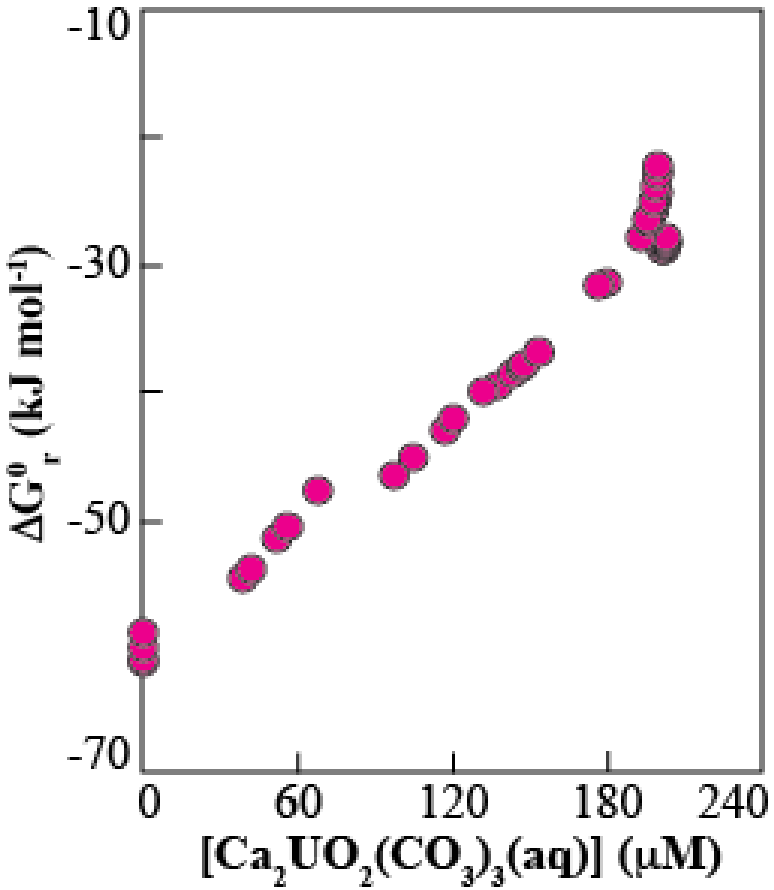


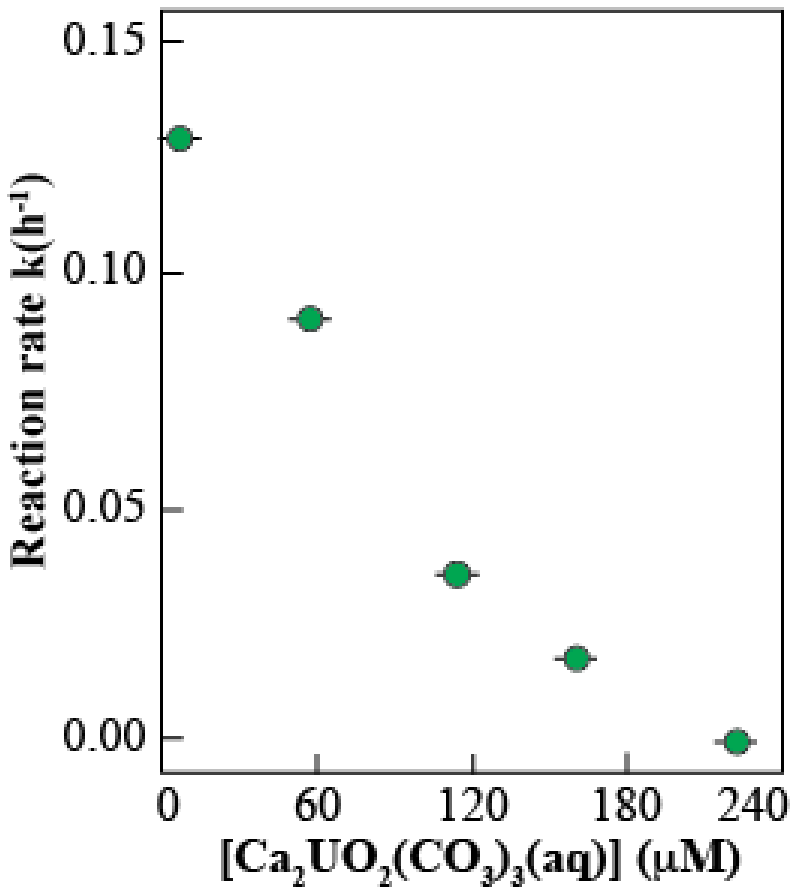
Fe(III) – Fe(II)

Wong et al., 2019, 2020

铀同位素分馏与铀反应动力学相关



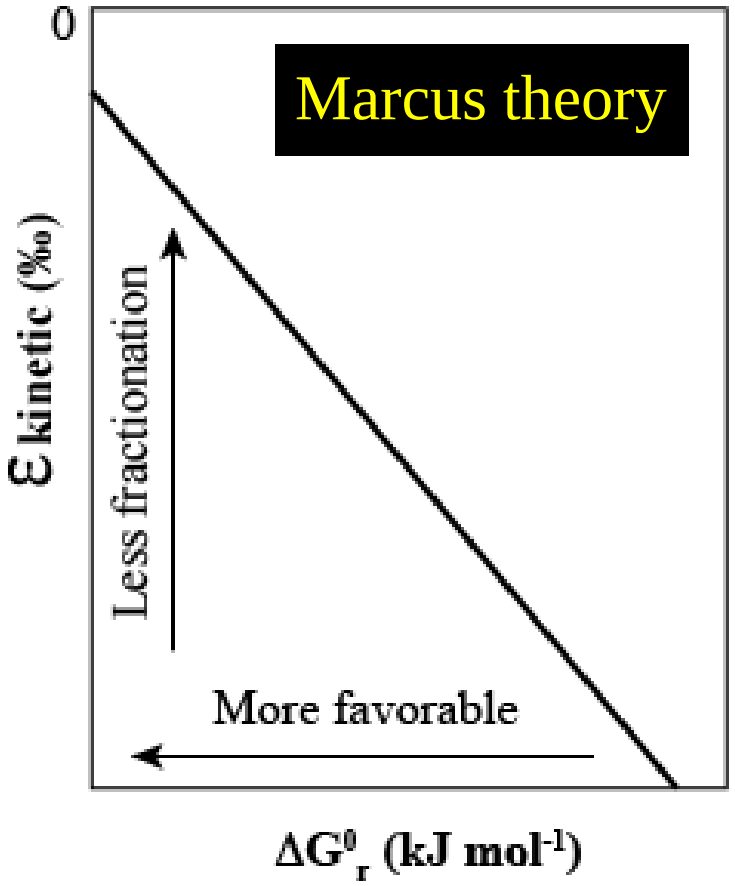


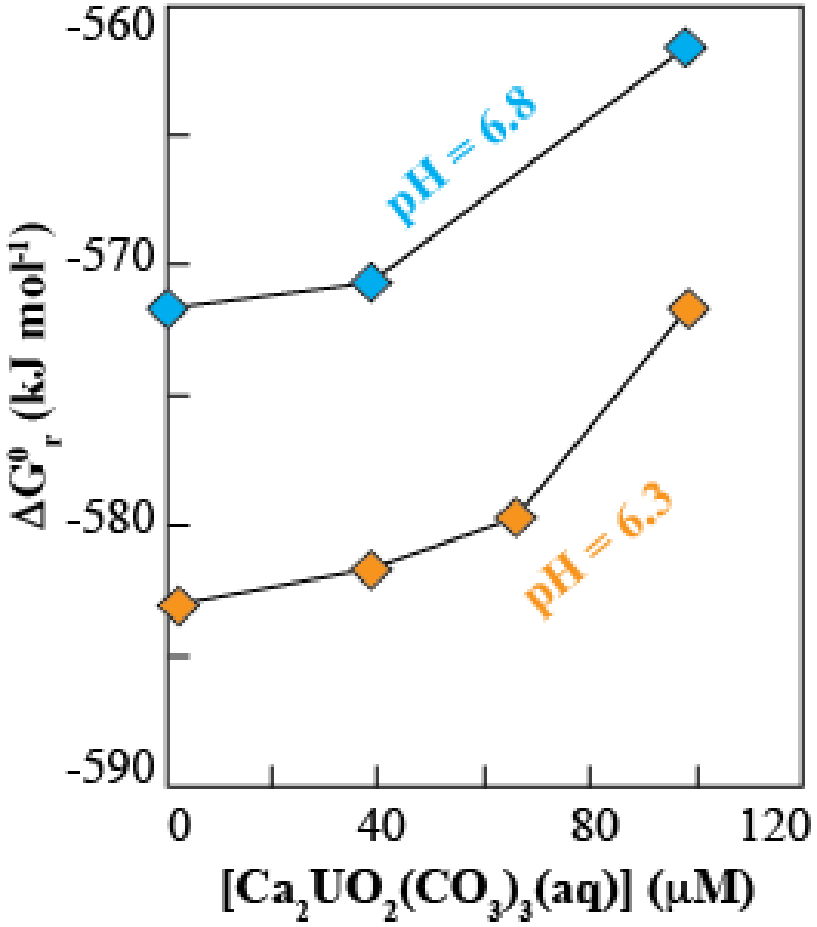


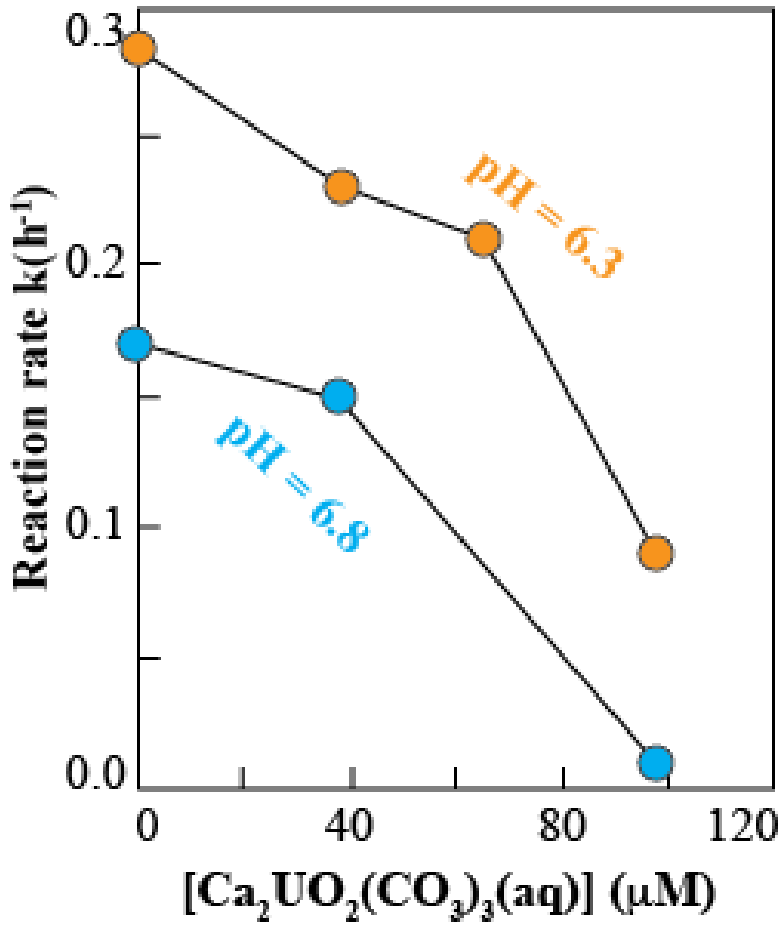
Fe(II)还原U(VI)

Wong et al., 2020; Dewey et al., 2020

铀同位素分馏与反应动力学相关



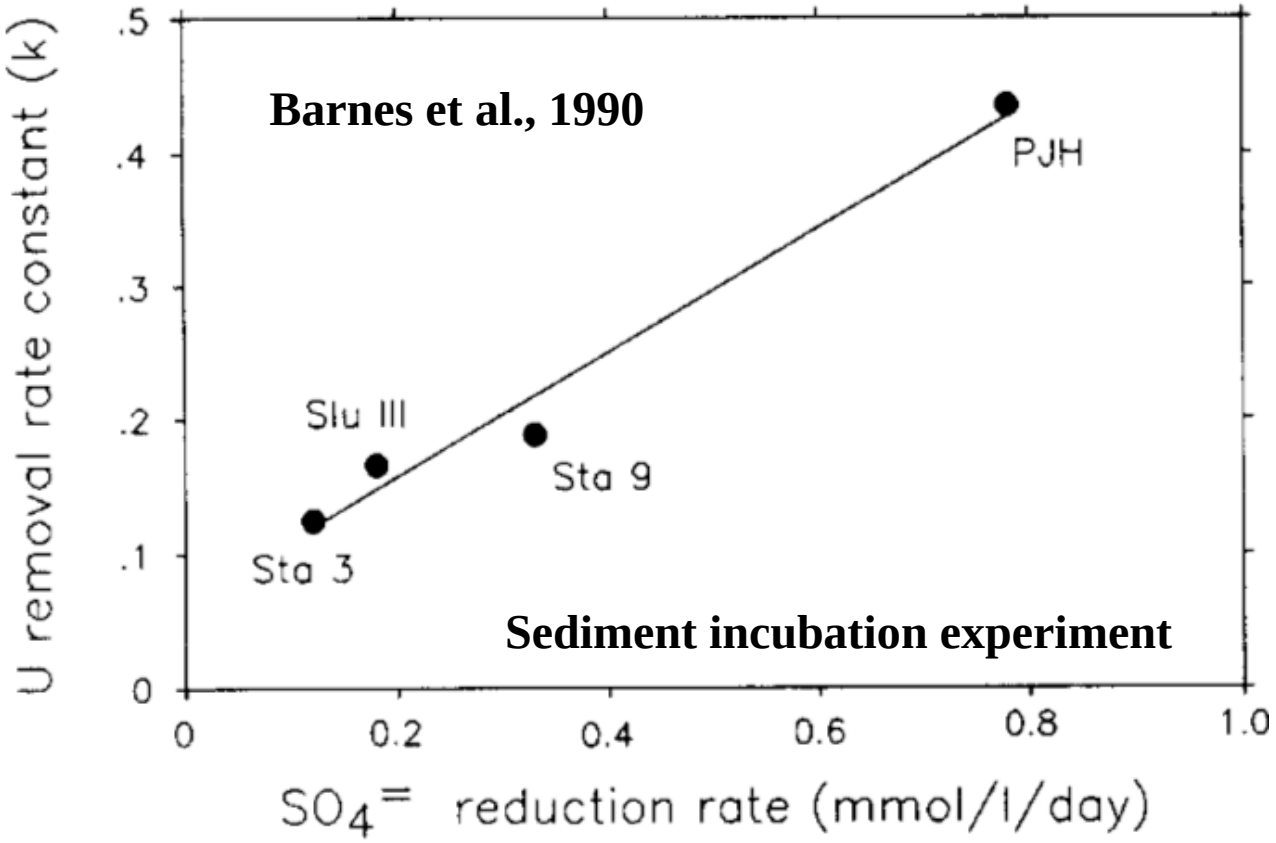


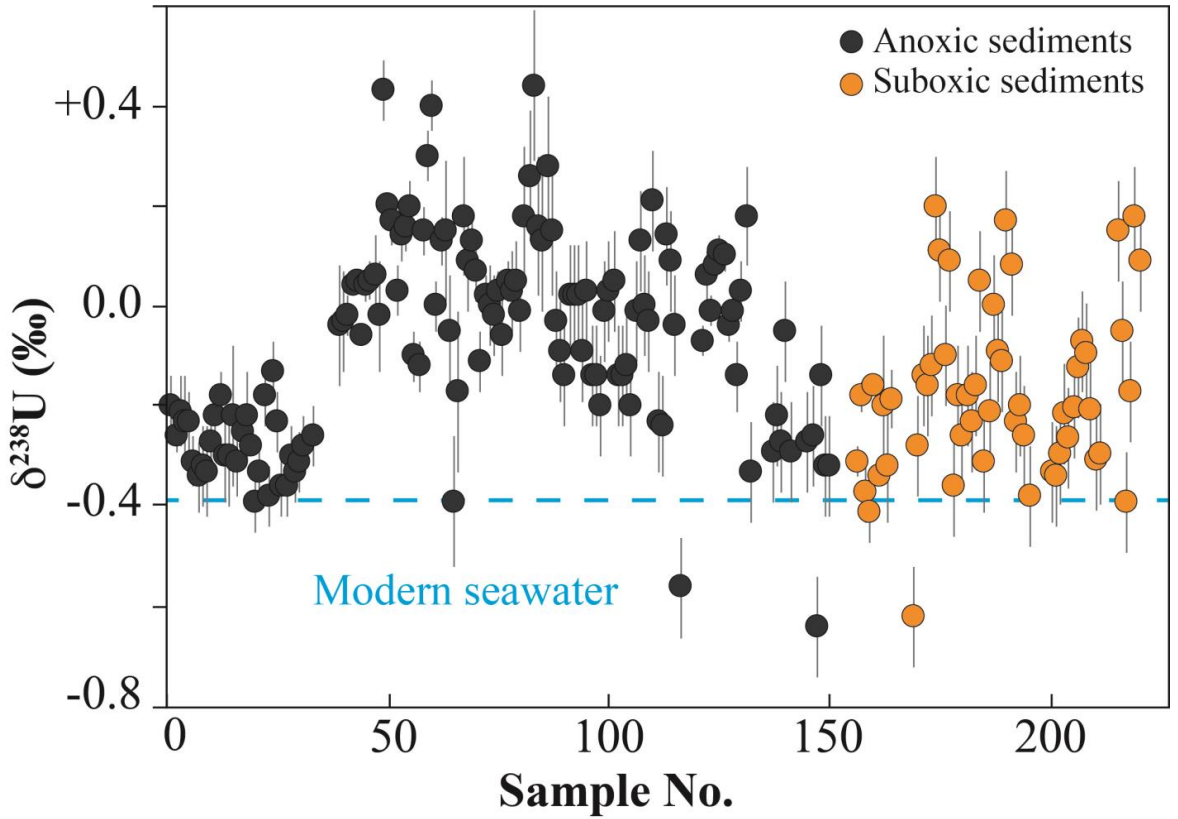


Shewanella oneidensis MR-1 还原U(VI)

Wong et al., 2020; Ulrich et al., 2011

海洋还原沉积物$\delta^{238}U$





铀还原速率是导致还原沉积物$\delta^{238}U$变化的原因之一

氧化还原小结

1. 生物还原过程富集重同位素^{238}U
2. 非生物还原过程可富集^{238}U也可富集^{235}U
3. 生物与非生物还原过程铀同位素分馏主要是铀的反应动力学控制

吸附过程铀同位素分馏

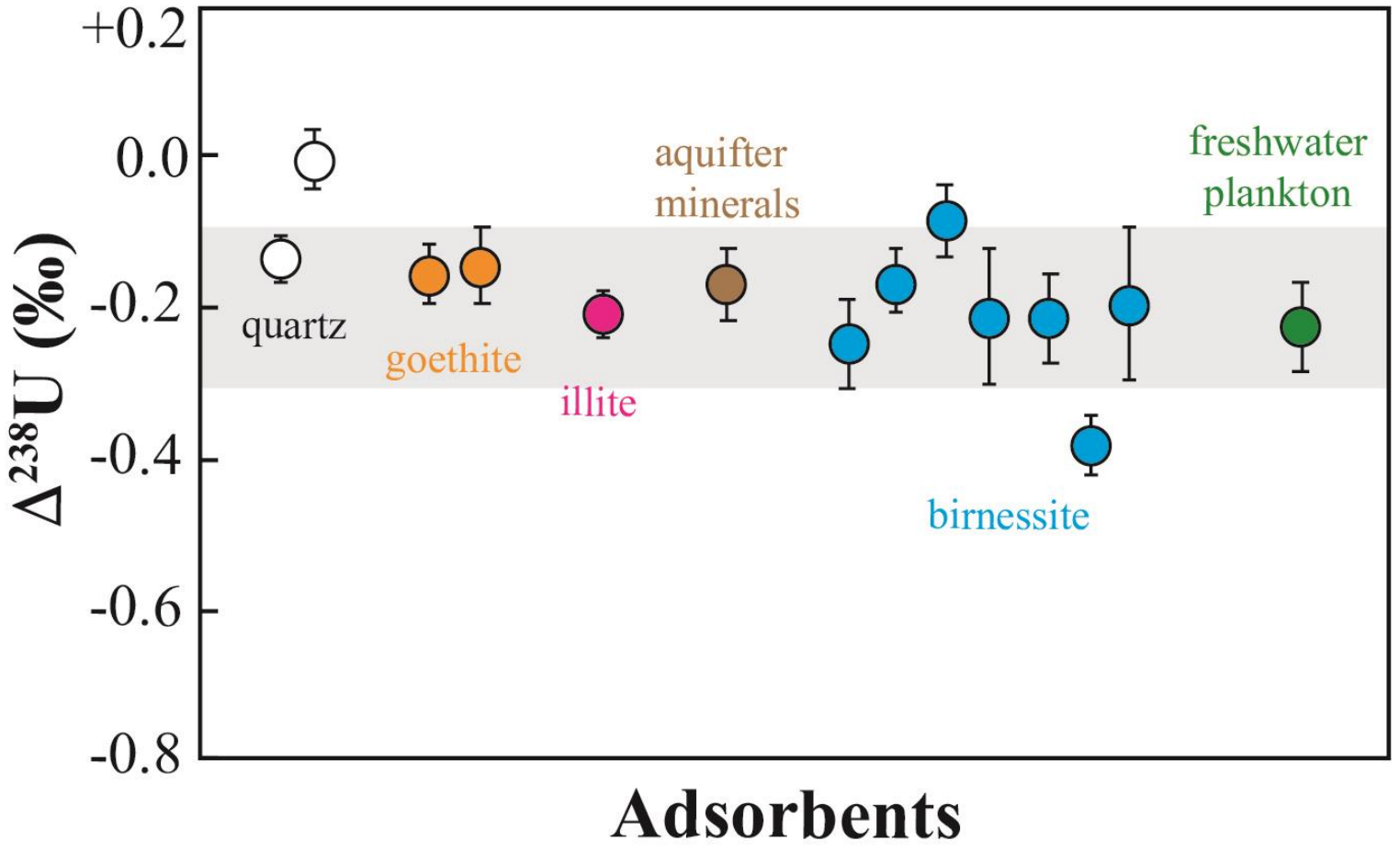
实验研究

- 铁和锰的氧化物
- 含水层介质
- 淡水浮游生物

平衡同位素分馏

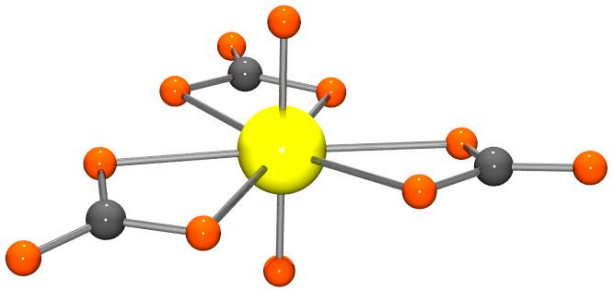
$\Delta^{238}U$ = ~ -0.20 ‰

吸附剂富集^{235}U

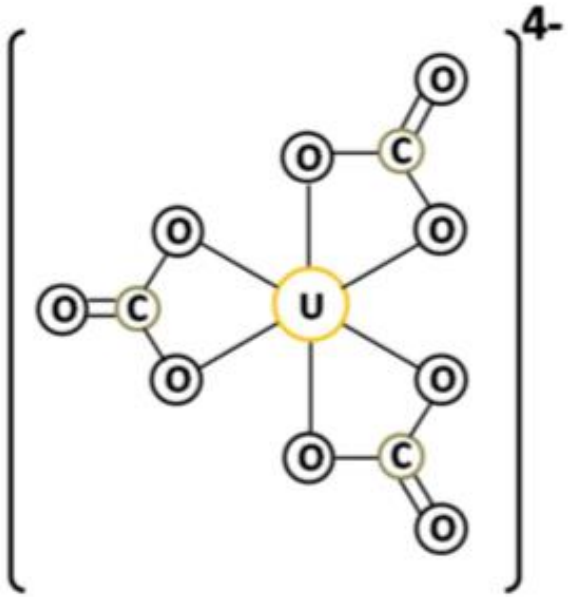


Brennecka et al., 2011; Jemison et al., 2016; Dang et al., 2016; Chen et al., 2020

吸附过程铀同位素分馏

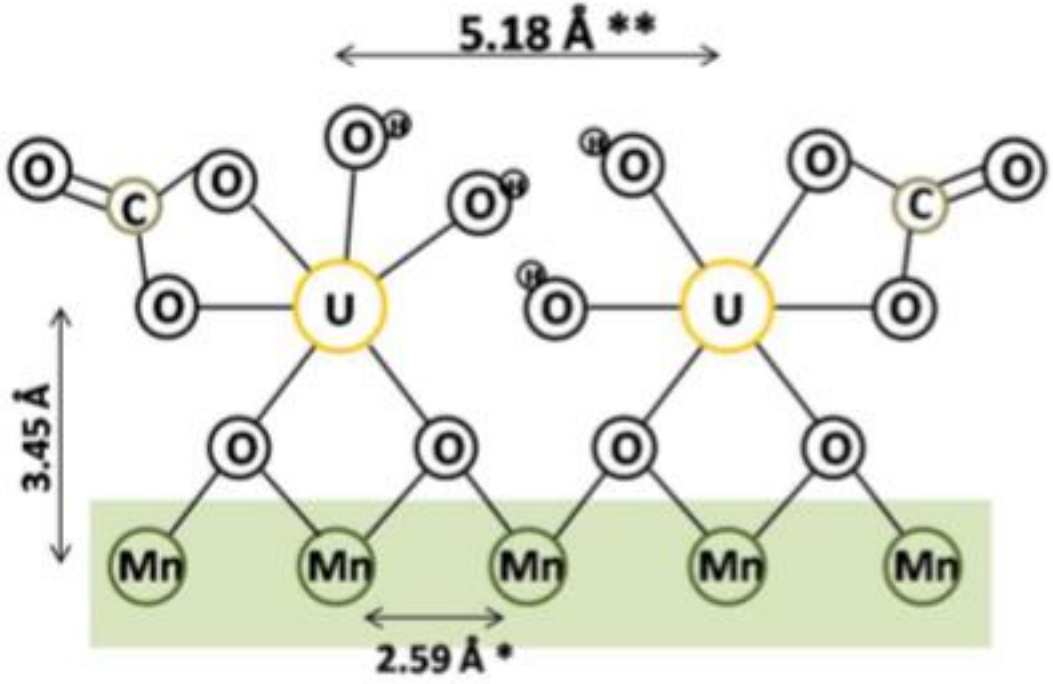


分馏机理：铀的配位数与配位键强度变化



$UO_2(CO_3)_3^{4-}$

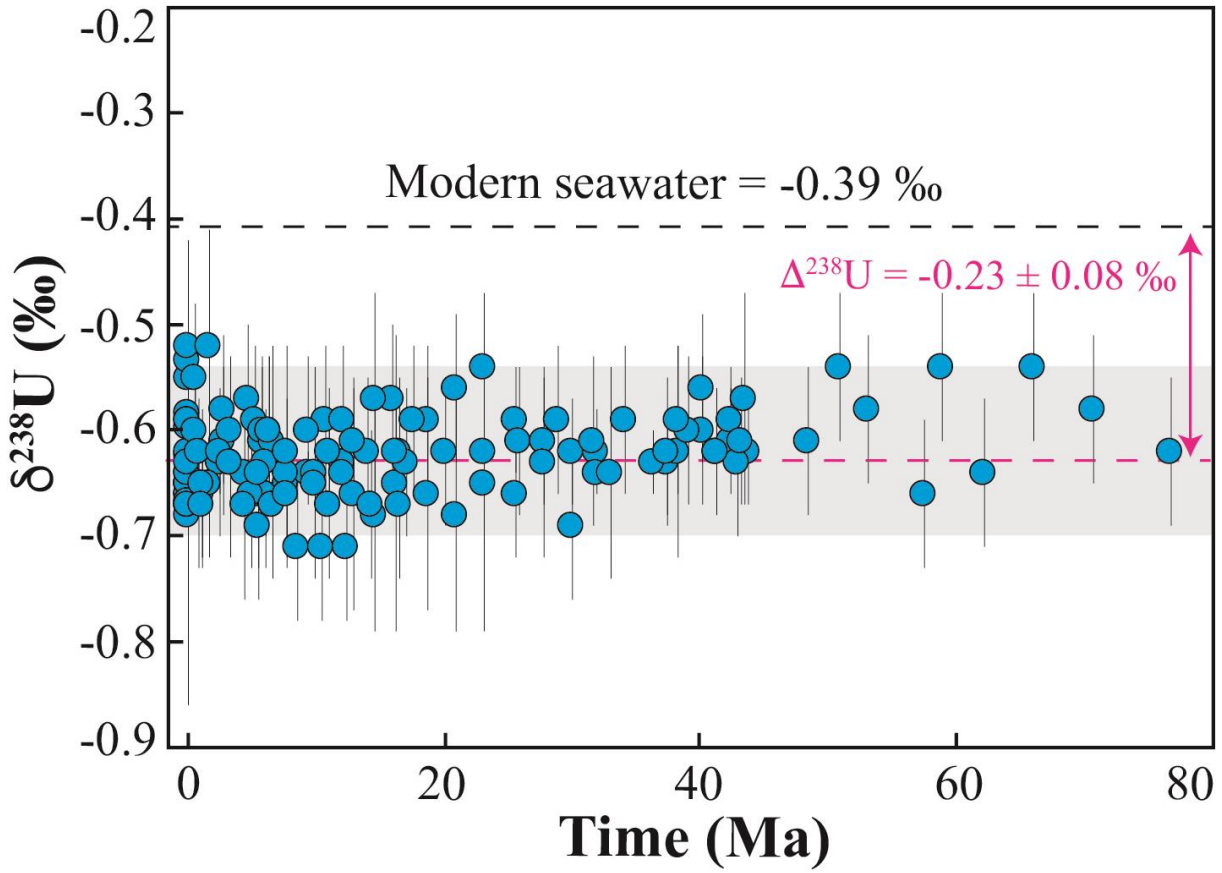
吸附



锰的氧化物表面

Brennecka et al., 2011; Dang et al., 2016

海洋**铁锰**氧化物$\delta^{238}U$



吸附实验

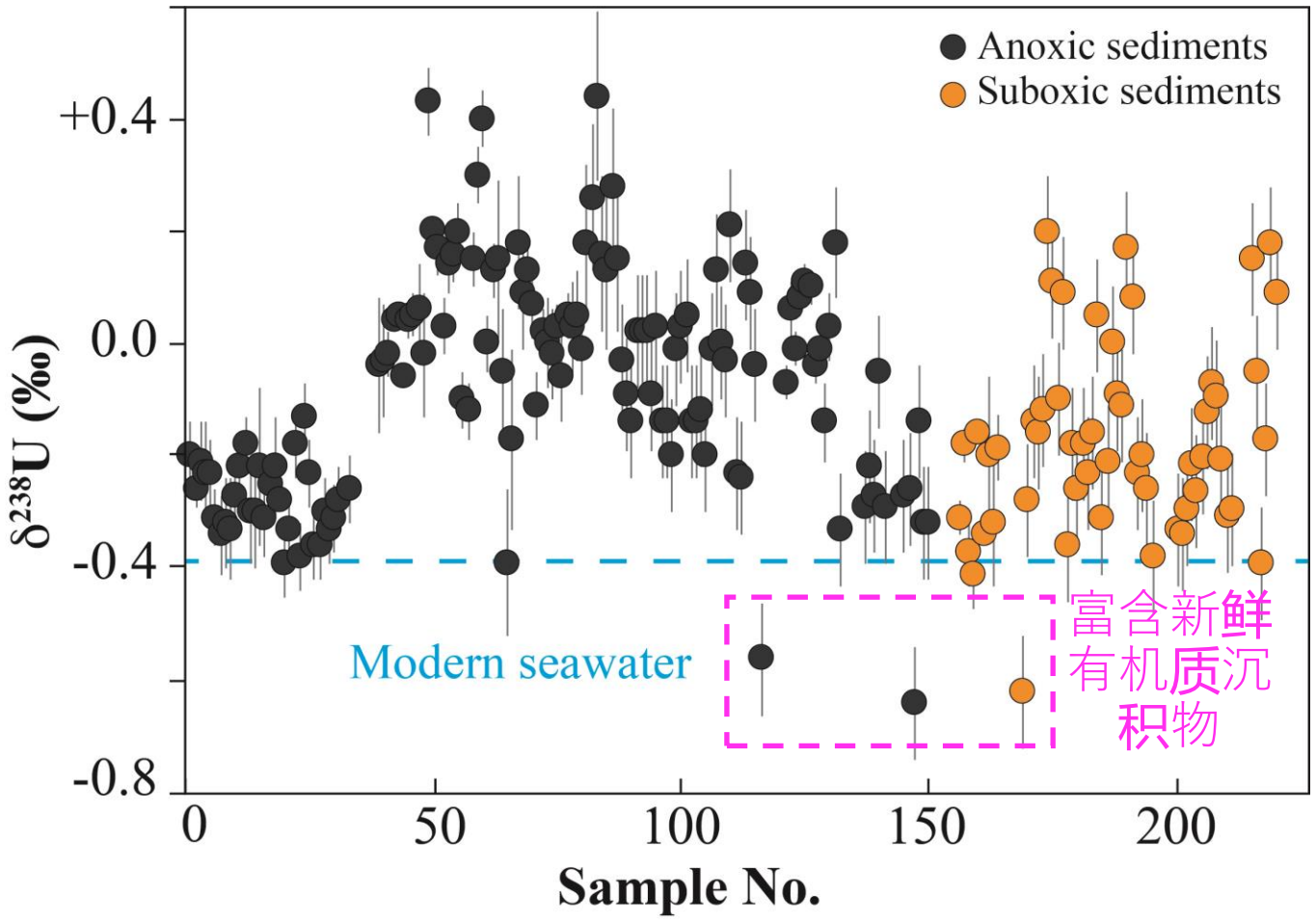
$\Delta^{238}U$ = -0.22 ± 0.10 ‰

海洋Fe-Mn氧化物

$\Delta^{238}U$ = -0.23 ± 0.08 ‰

Goto et al., 2014; Weyer et al., 2008; Stirling et al., 2007; Wang et al., 2016

富有机质海洋沉积物$\delta^{238}U$



浮游生物吸附

$\Delta^{238}U = -0.23 \pm 0.08$ ‰

富含新鲜机质沉积物

$\Delta^{238}U = \sim -0.20$ ‰

Chen et al., 2020; Holmden et al., 2015; Hinojosa et al., 2016; Abshire et al., 2020

吸附小结

1. 吸附过程导致吸附剂富集轻同位素^{235}U
2. 吸附过程导致平衡同位素分馏 ~ -0.20 ‰
3. 实验测定的同位素分馏与自然样品一致

碳酸岩沉淀及成岩过程铀同位素分馏

碳酸岩形成过程

成岩作用

假设：$(^{238}U/^{235}U)_{碳酸钙} = (^{238}U/^{235}U)_{海水}$

原生碳酸钙

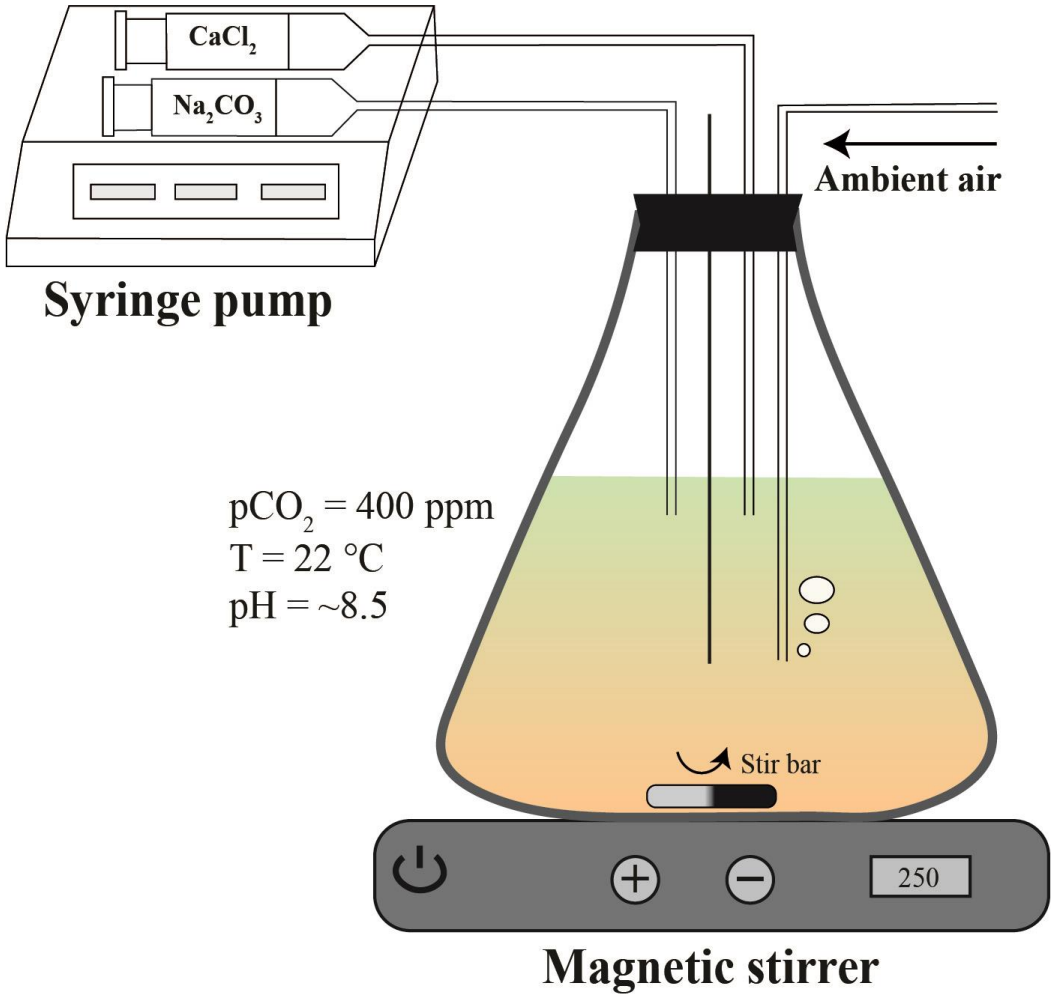
- 无机碳酸钙
- 生物成因碳酸钙

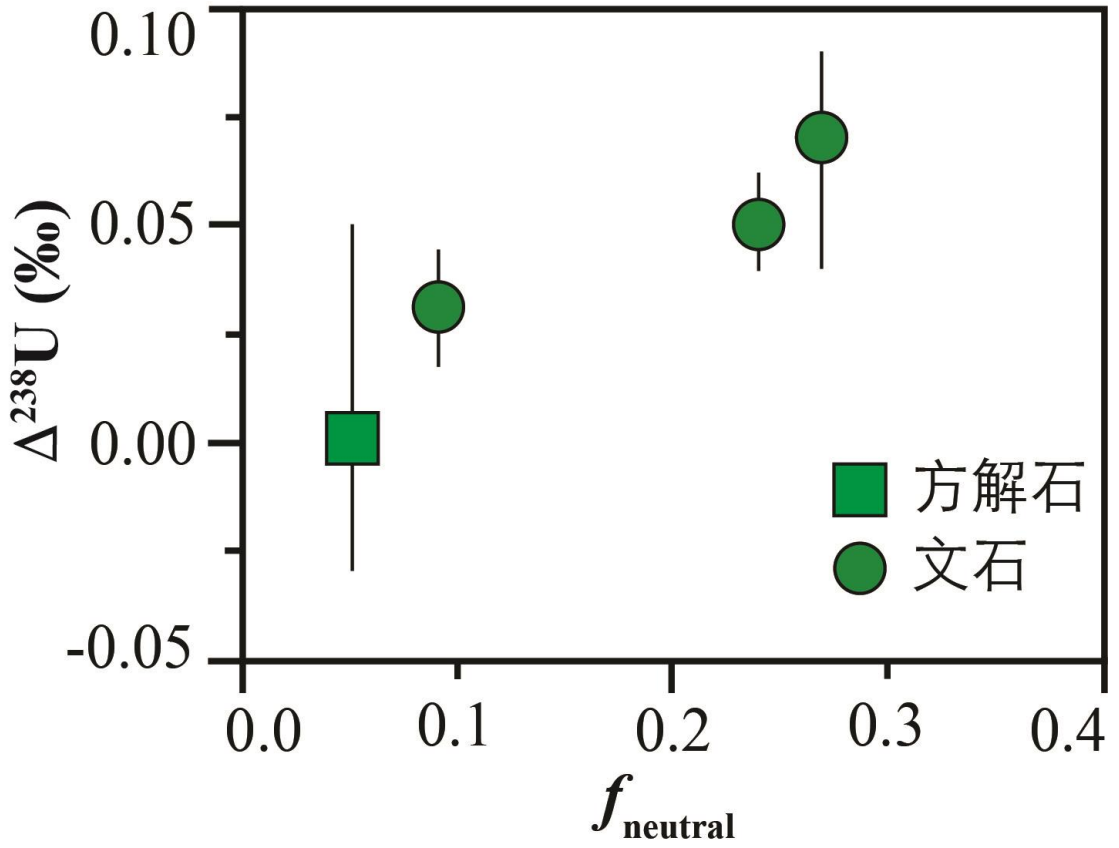
成岩作用

（溶解再沉淀，白云岩化等）

碳酸岩

无机碳酸钙共沉淀过程中铀同位素分馏

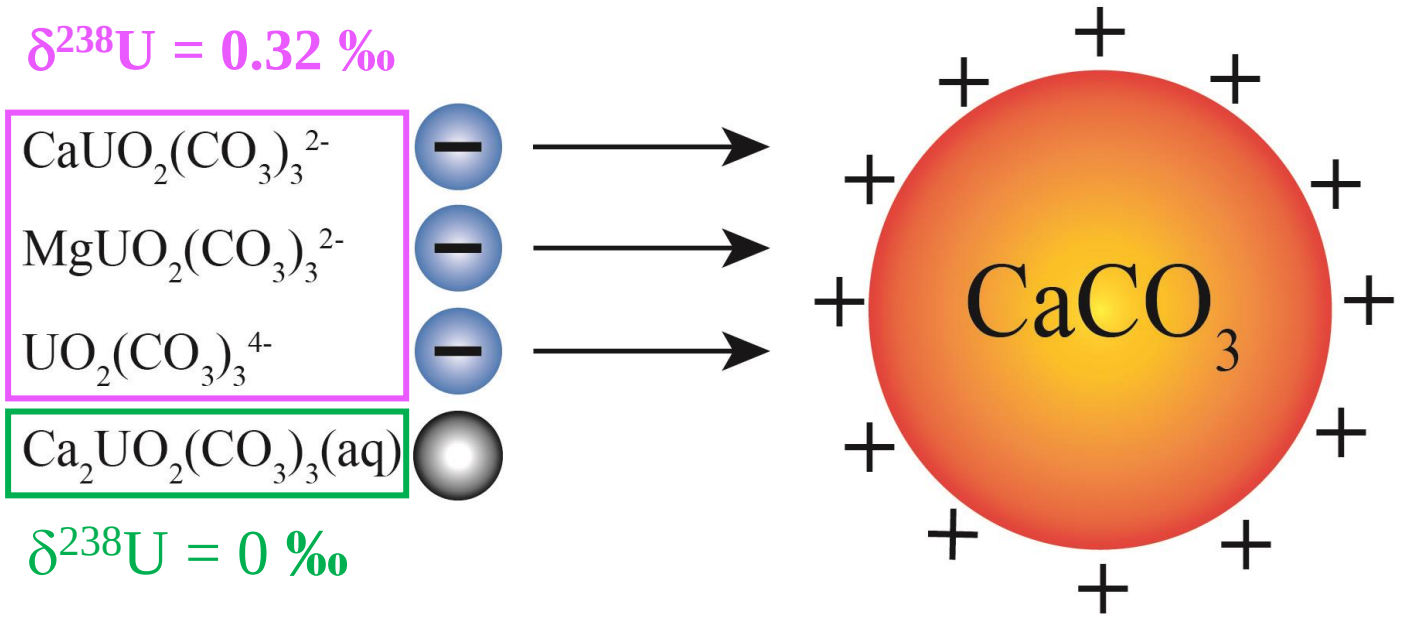


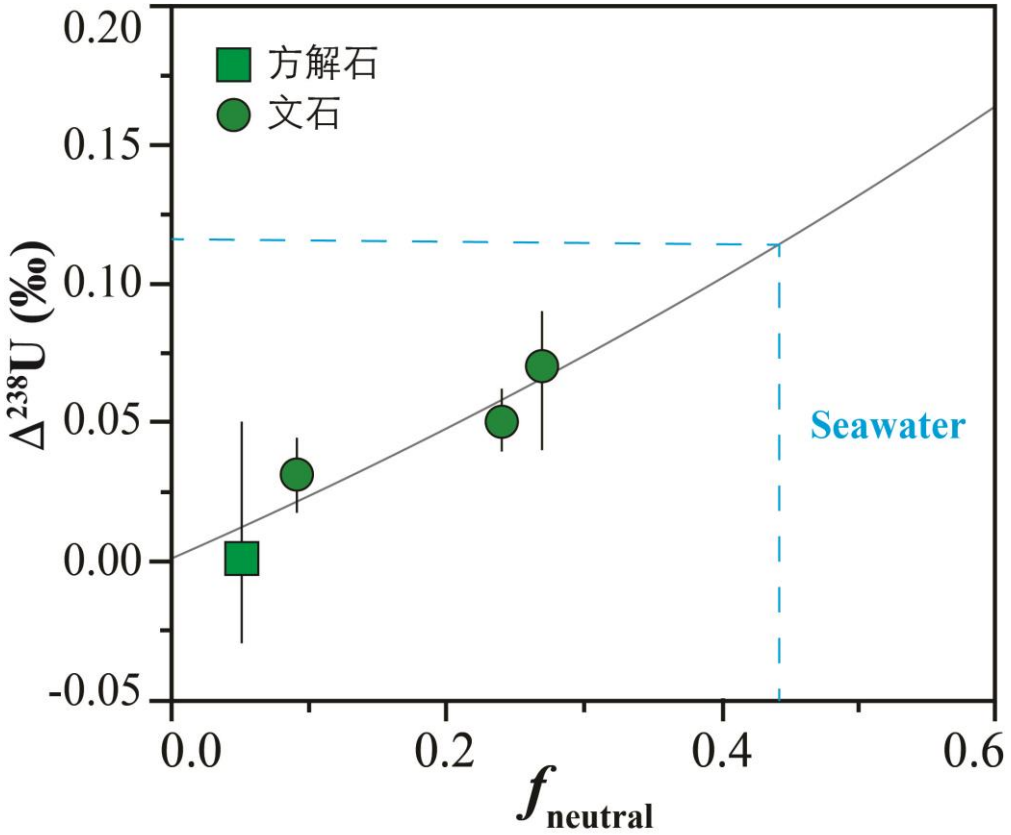


$f_{neutral}$: $Ca_2UO_2(CO_3)_3(aq)$ 的含量

Chen et al., 2016

无机碳酸钙共沉淀过程中铀同位素分馏



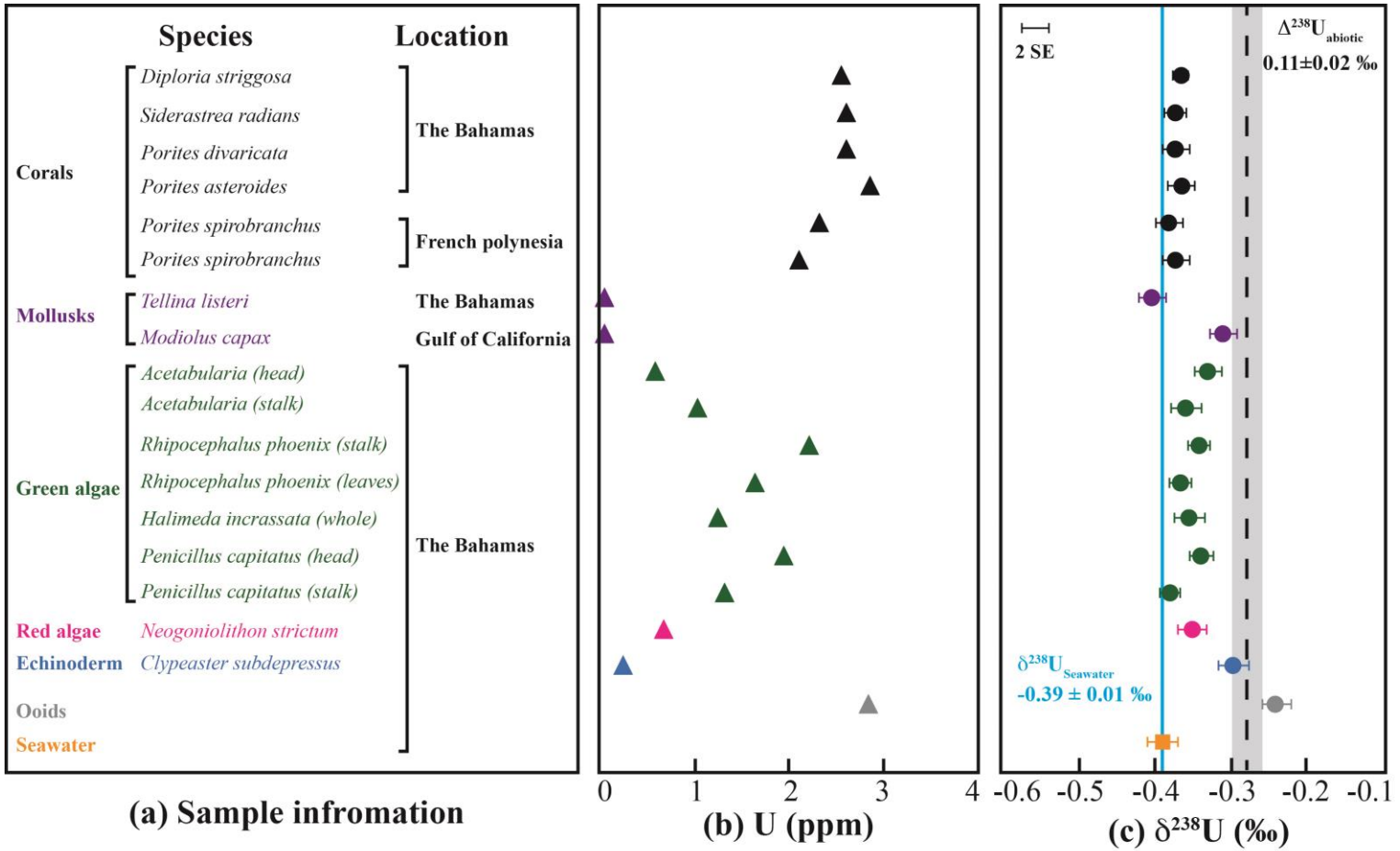


- 碳酸钙共沉淀过程中存在铀同位素分馏
- $\Delta^{238}U$取决于溶解态铀的中性组分含量

Chen et al., 2016

生物成因碳酸钙铀同位素分馏

海洋碳酸钙90%属于生物成因



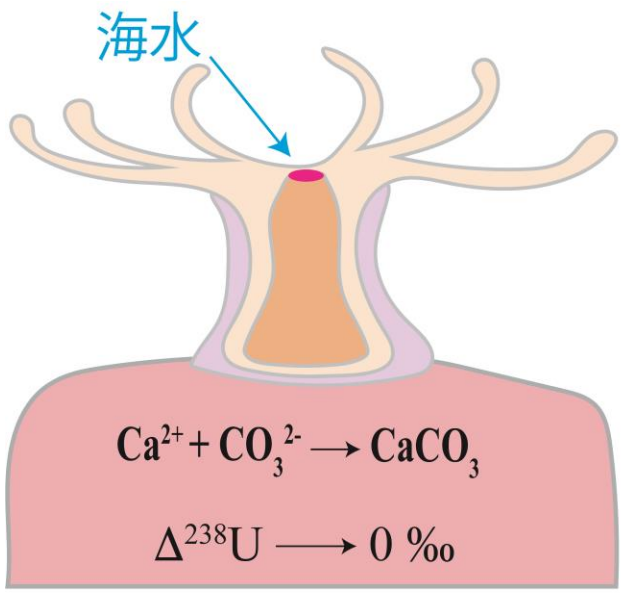
生物效应影响碳酸钙中铀同位素分馏

Chen et al., 2018

生物成因碳酸钙铀同位素分馏

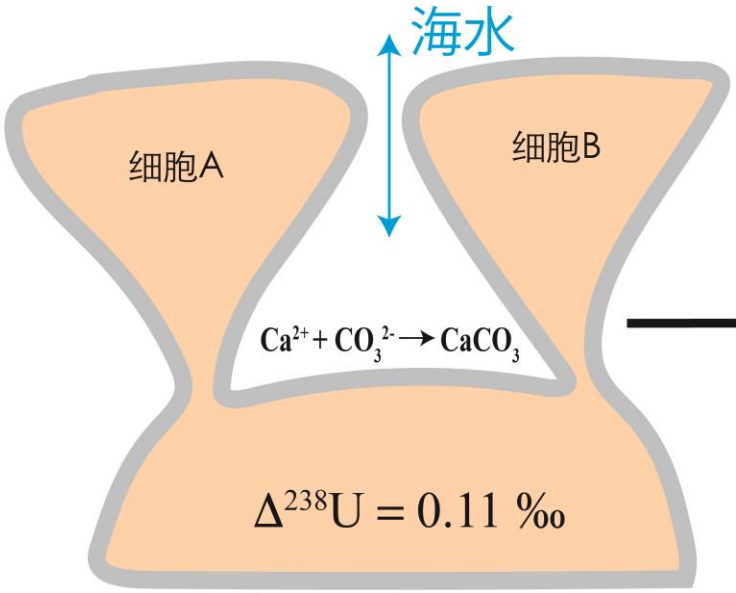
铀同位素分馏大小取决于钙化区的开放程度

封闭系统



珊瑚

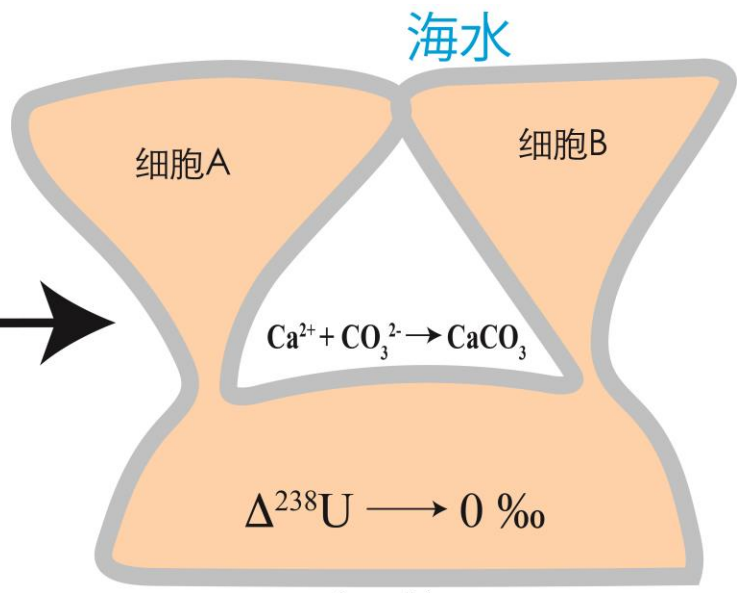
开放



绿藻

未成熟

封闭



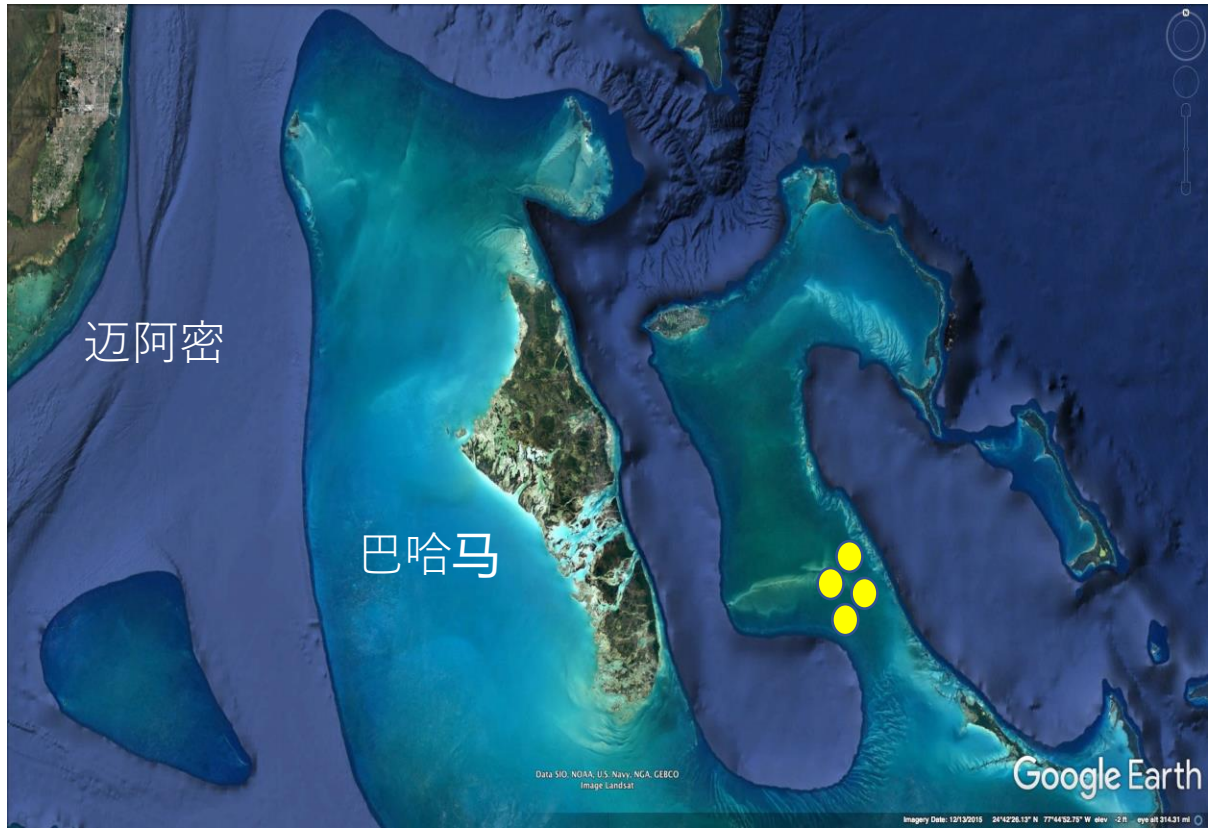
绿藻

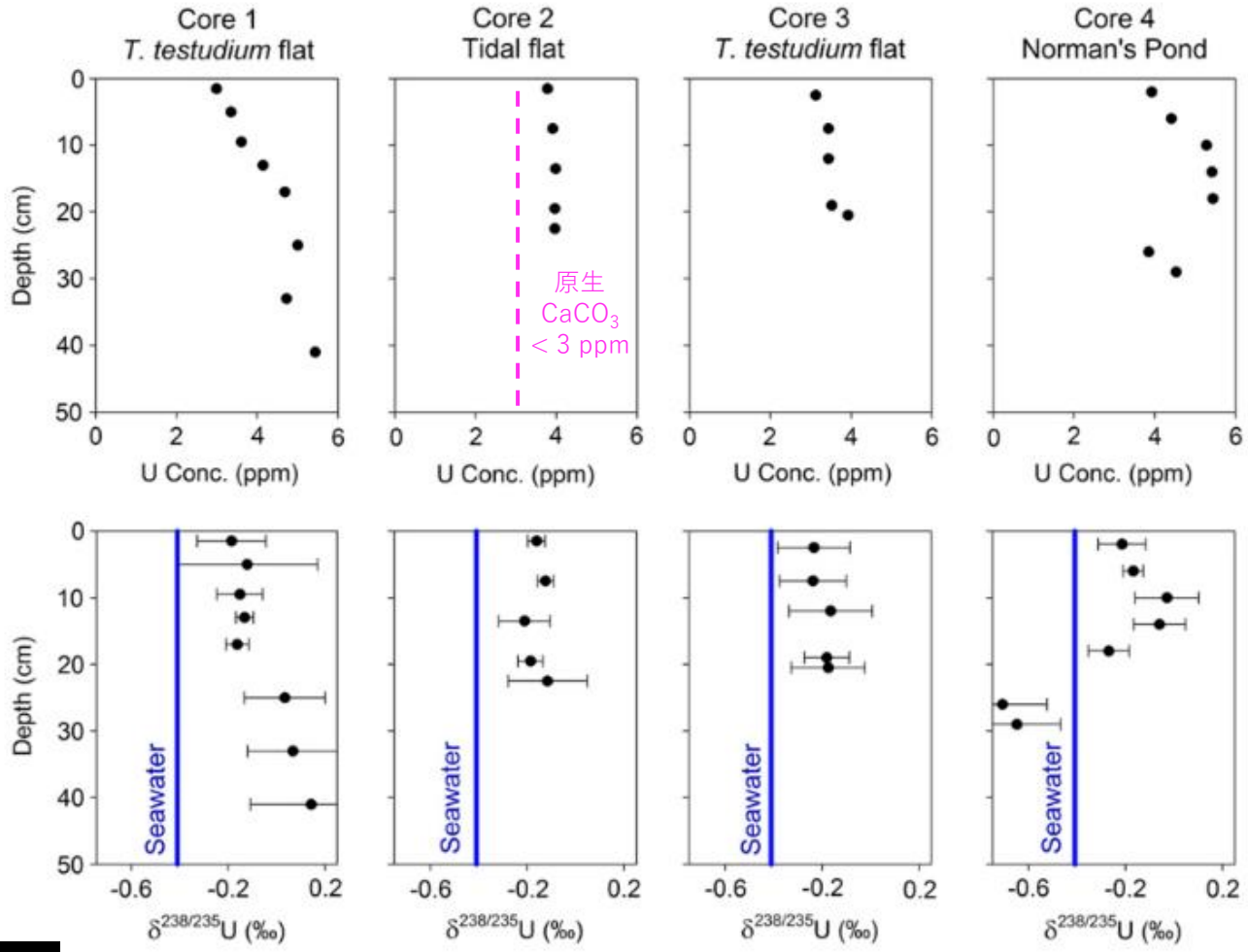
成熟

Chen et al., 2018a

现代碳酸岩沉积物铀同位素分馏

表层碳酸岩沉积物(0 – 5000 year)



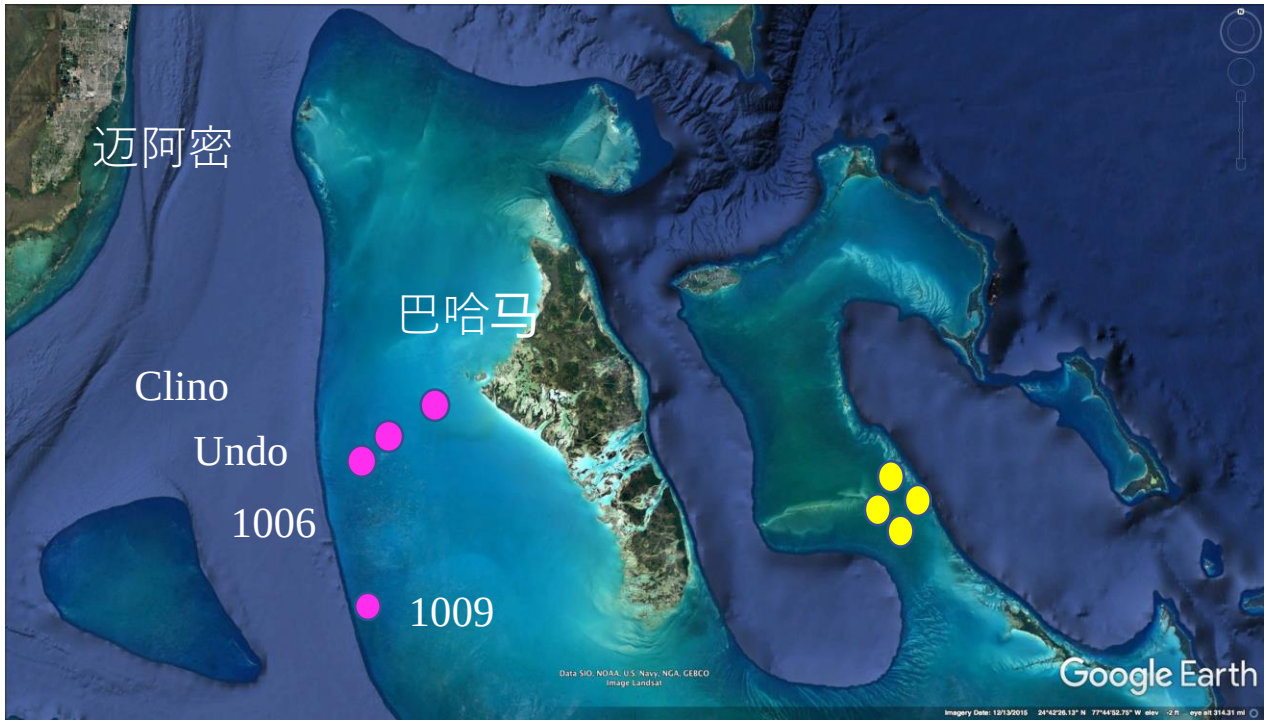


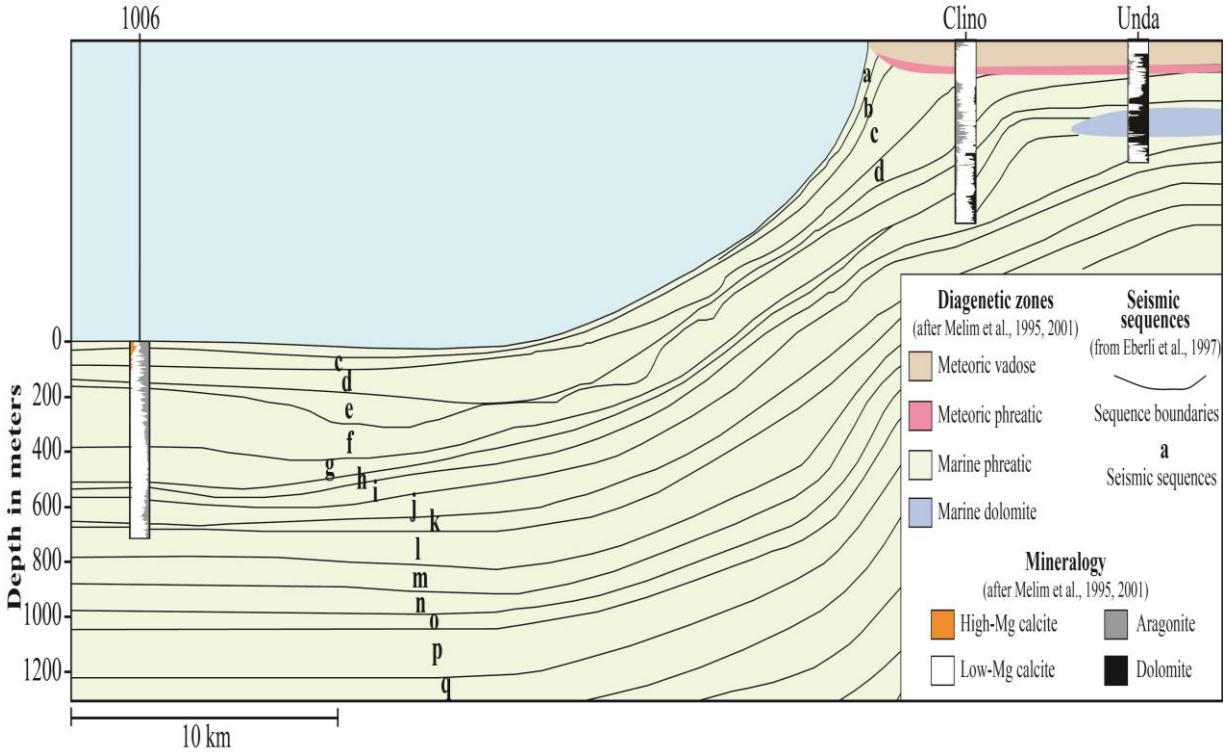
碳酸岩沉积物富集铀及其重同位素(^{238}U)

Romaniello et al., 2013

现代碳酸岩沉积物铀同位素分馏

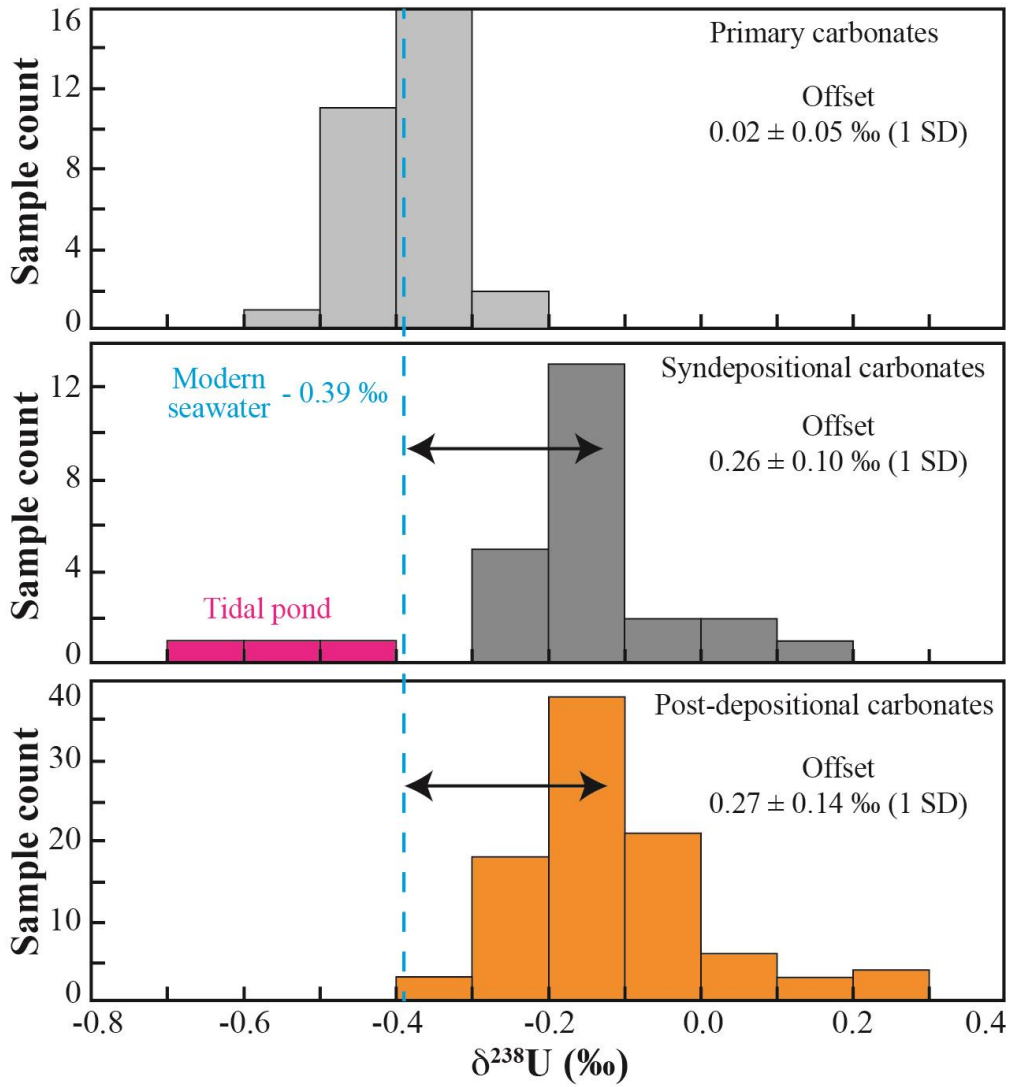
现代碳酸岩沉积物 (0 – 400 万年)





Chen et al., 2018b; Tissot et al., 2018

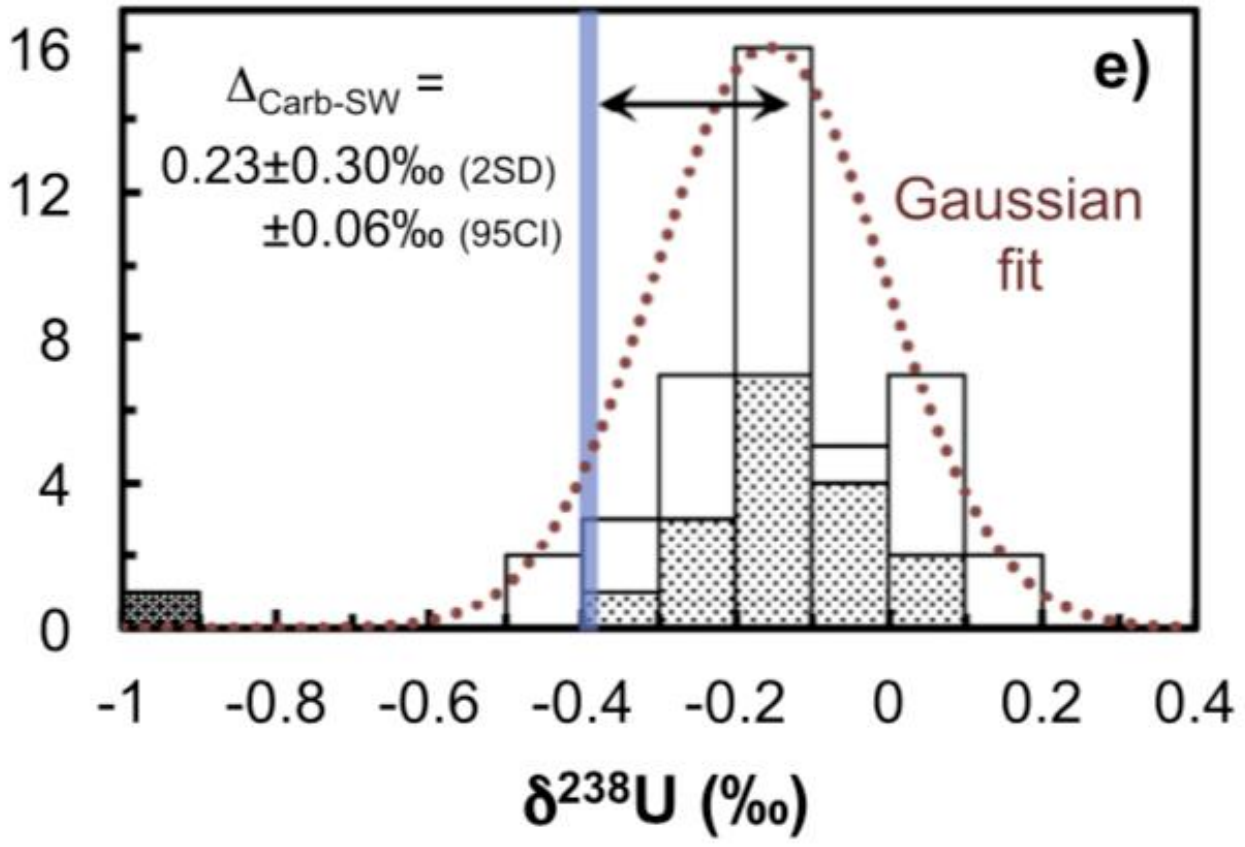
碳酸岩成岩过程中铀同位素分馏



- 成岩作用导致的分馏：0.27 ± 0.14 ‰
- 分馏大小主要有孔隙水铀的还原决定
- 沉积后的成岩作用未导致进一步分馏

Romaniello et al., 2013; Chen et al., 2018a, 2018b

碳酸岩成岩过程中铀同位素分馏



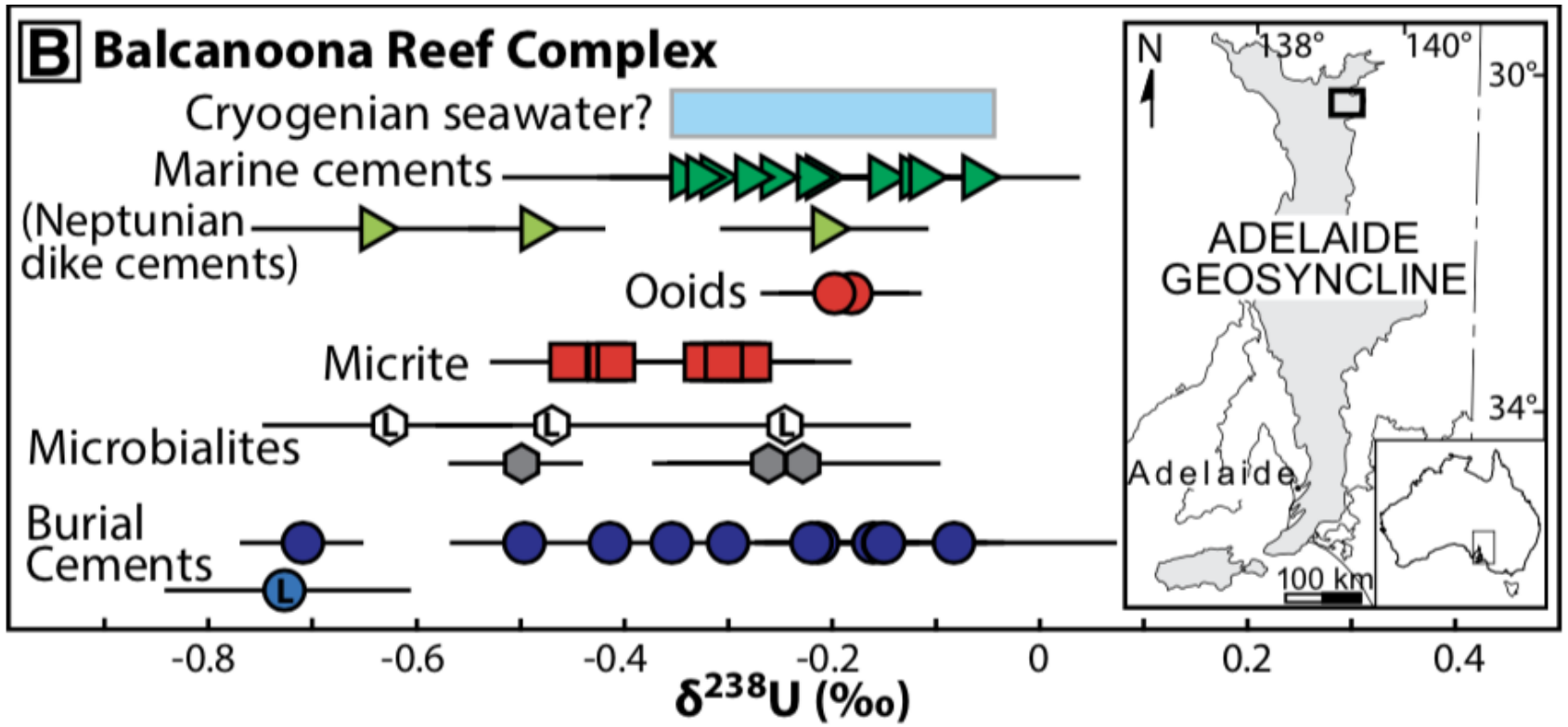
碳酸岩成岩作用导致的分馏

Chen et al. (2018): 0.27 ± 0.14 ‰

Tissot et al. (2018): 0.23 ± 0.10 ‰

Site 1009 from Tissot et al. (2018)

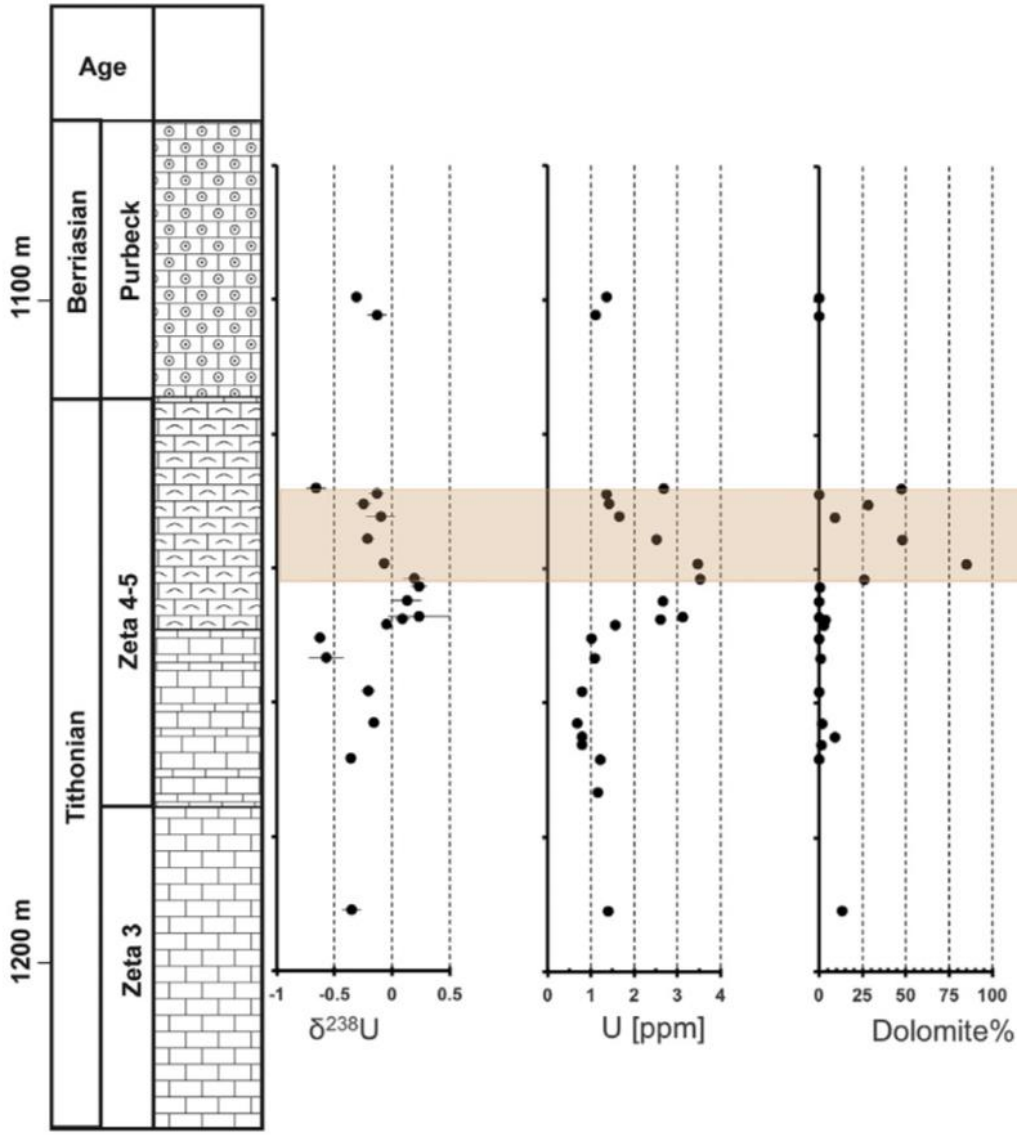
碳酸岩成岩过程中铀同位素分馏

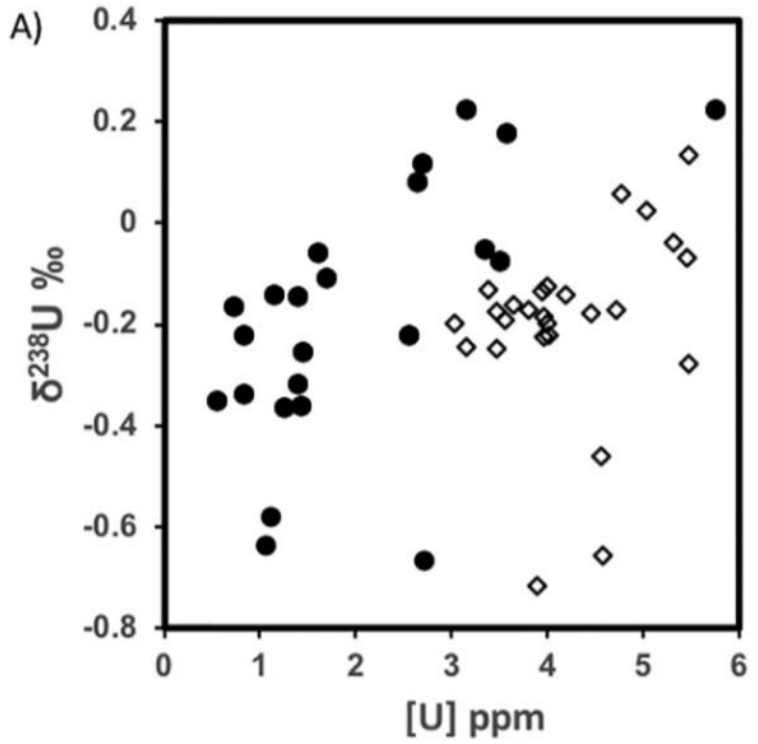


微观尺度$\delta^{238}U$分布不均匀

Hood et al. (2016)

白云岩化过程中铀同位素分馏



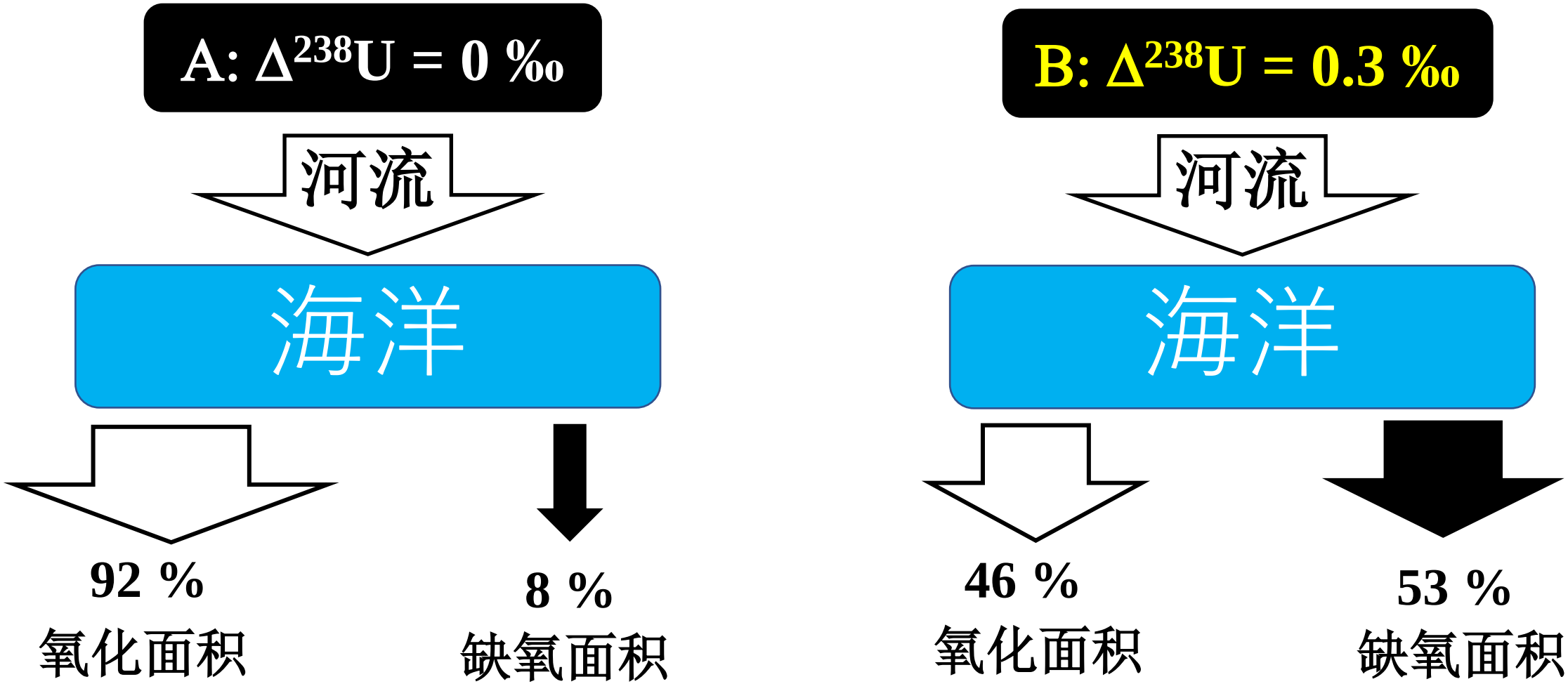


白云岩化不导致进一步铀同位素分馏

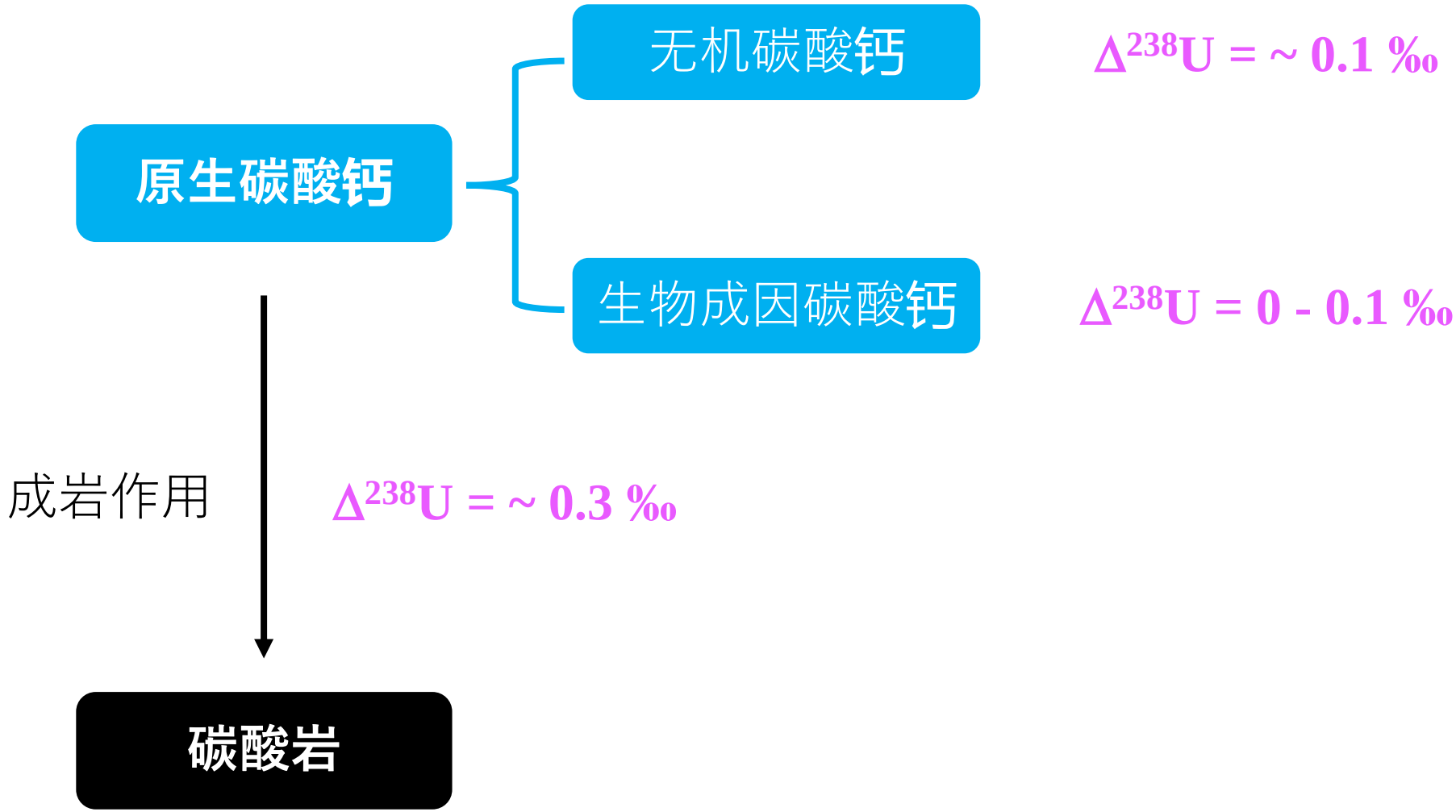
Herrmann et al. (2018)

碳酸岩铀同位素分馏校正

碳酸岩: $\delta^{238}U$ = -0.6 ‰



碳酸岩小结



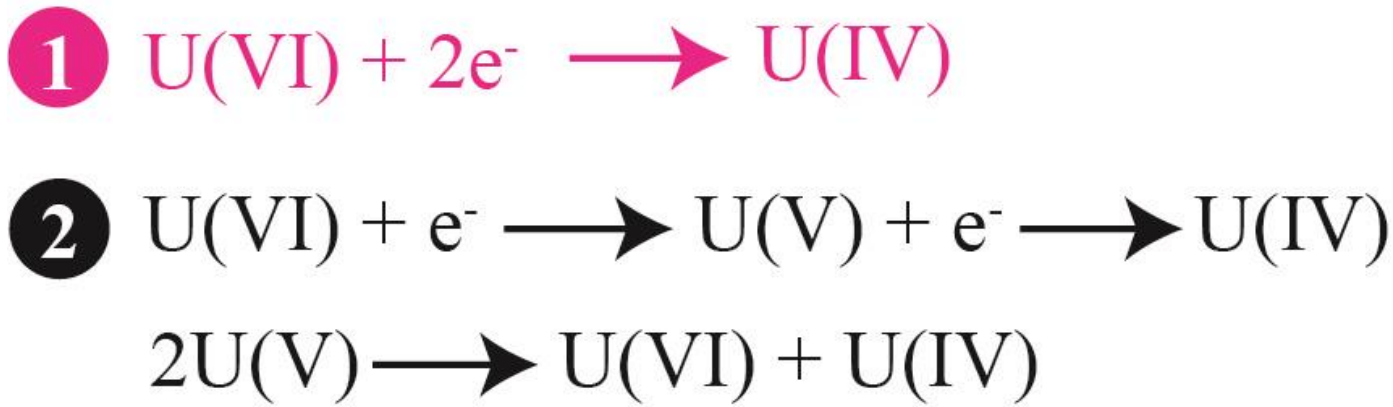
Chen et al., 2016, 2018a, 2018b, Tissot et al., 2018

第四部分: 总结

1. 氧化还原过程铀同位素分馏机理尚不清楚

核体积效应 vs. 质量相关分馏

铀还原反应动力学及其同位素分馏



2. 碳酸钙成岩过程铀同位素分馏机理及如何校正

$$\delta^{238}U = \left[\frac{\left({}^{238}U/_{235}U\right)_{sample}}{\left({}^{238}U/_{235}U\right)_{standard}}\right] \times 1000$$

$$\delta^{238}U = \left[\frac{\left({}^{238}U_0 \times e^{-\lambda_{238}t}/{}^{235}U_0 \times e^{-\lambda_{235}t}\right)_{sample}}{\left({}^{238}U_0 \times e^{-\lambda_{238}t}/{}^{235}U_0 \times e^{-\lambda_{235}t}\right)_{standard}} - 1\right] \times 1000$$

$$\delta^{238}U = \left[\frac{\left({}^{238}U_0/_{235}U_0\right)_{sample}}{\left({}^{238}U_0/_{235}U_0\right)_{standard}} - 1\right] \times 1000$$