重金属稳定同位素与古海洋学：从定性走向定量的进展与思考

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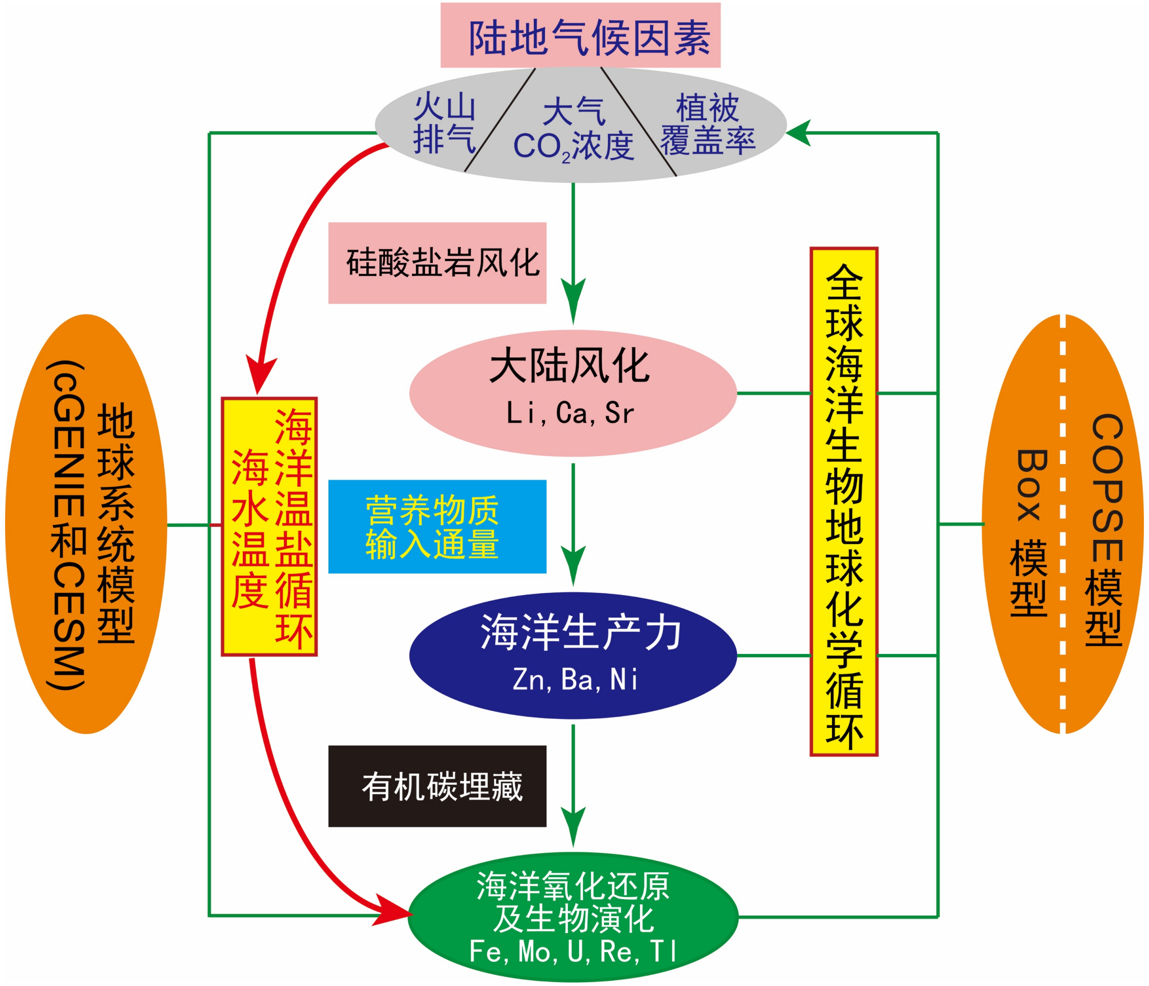
主要研究方向：环境与生命协同演化

- 金属稳定同位素分析测试方法
- 金属稳定同位素低温过程分馏理论与成岩作用改造
- 环境与生命协同演化的过程与机制
- 将实测地球化学数据与不同层次、复杂度模式的定量模型深入融合



古海洋学：我们关心哪些方面？

海洋缺氧导致鱼类大量死亡

海洋酸化导致珊瑚大量死亡

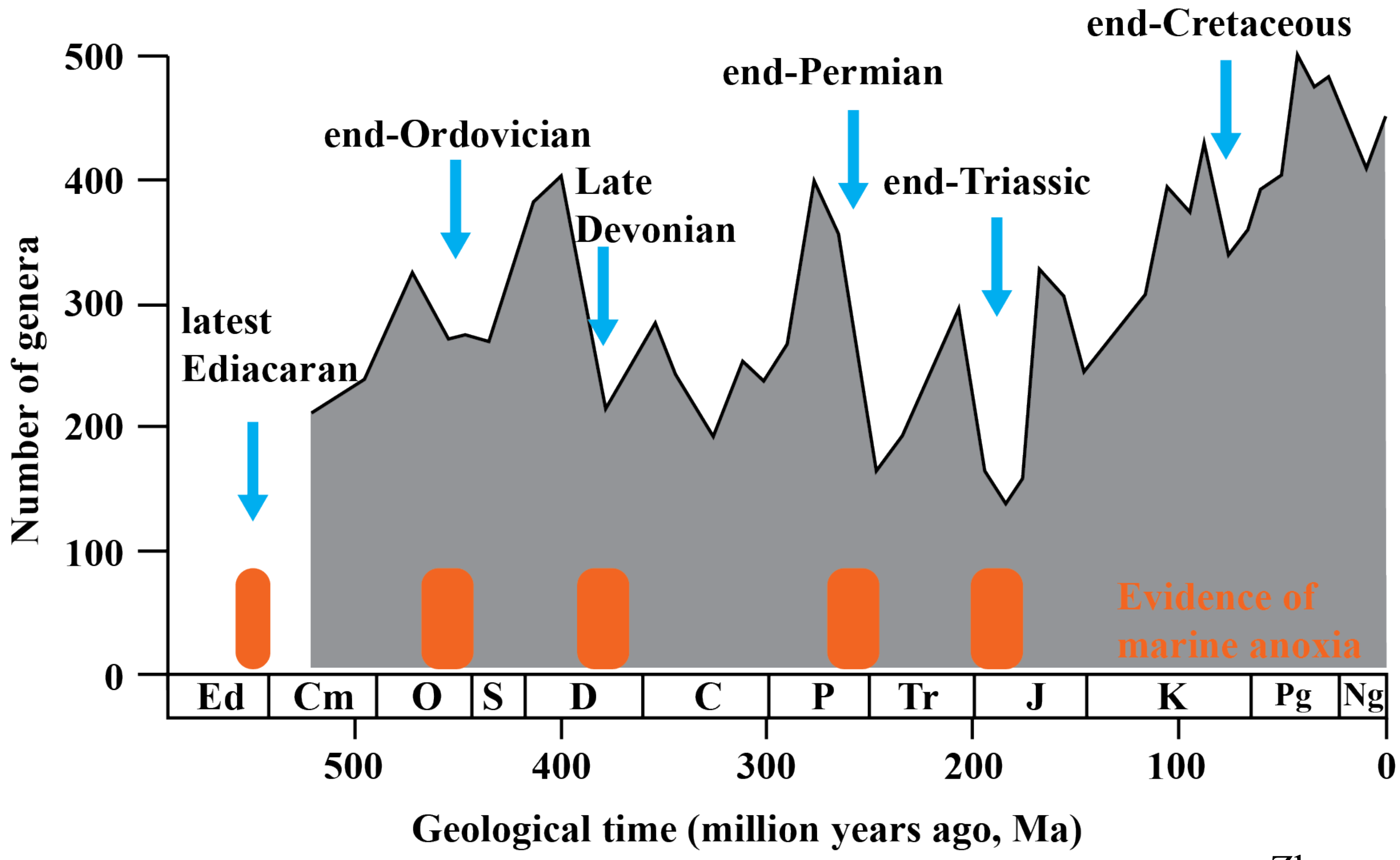
海洋富营养化导致藻类大量繁殖

图片均来自网络

为什么关心海洋氧化还原状态？

海洋与大气中O_2浓度的变化深刻影响/改变了生物的演化历程

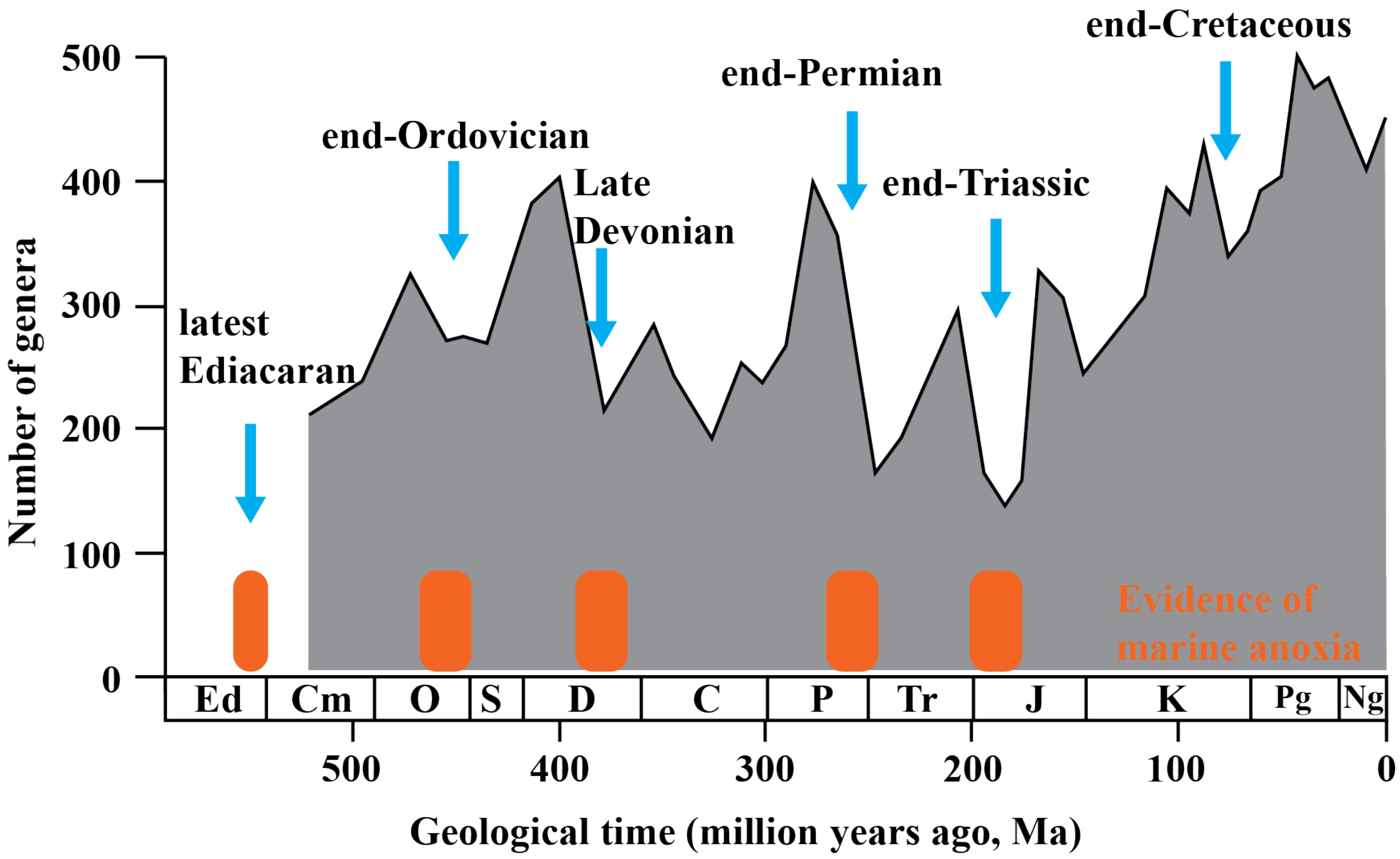
埃迪卡拉纪末期生物灭绝和显生宙五次生物大灭绝中的前4次（奥陶纪末、泥盆纪末、二叠纪末、三叠纪末）都与海洋缺氧相关。



Zhang et al., 2020a, GCA

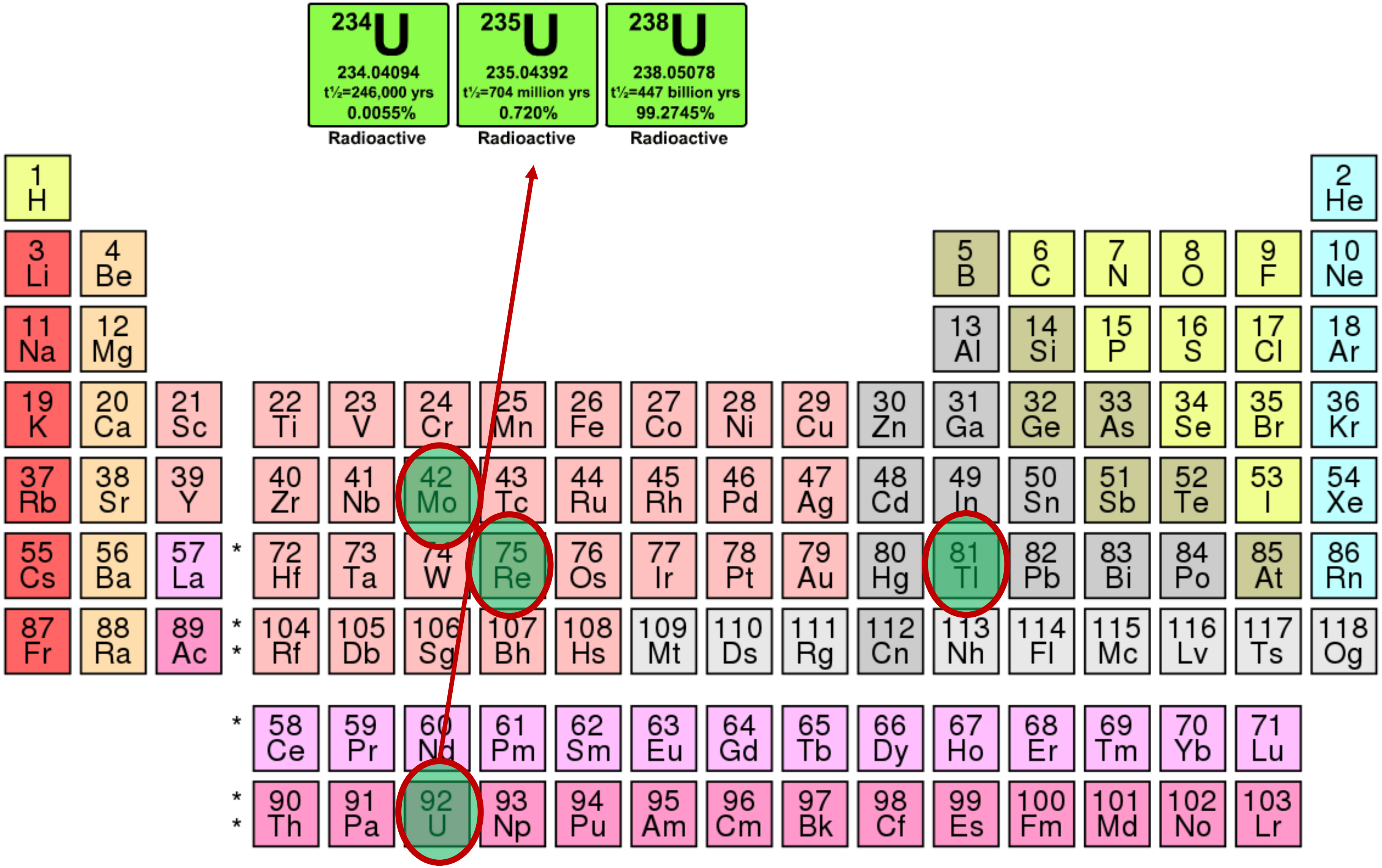
为什么关心海洋氧化还原状态？

精确定量重建地质历史时期海洋和大气的氧化历史，是理解地球生命起源与演化，以及地球是如何逐步演化为一个宜居星球的基础。



Zhang et al., 2020a, GCA

碳酸盐岩U同位素


234U
234.04094
t½=246,000 yrs
0.0055%
Radioactive
235U
235.04392
t½=704 million yrs
0.720%
Radioactive
238U
238.05078
t½=447 billion yrs
99.2745%
Radioactive
1 H
2 He
3 Li
4 Be
5 B
6 C
7 N
8 O
9 F
10 Ne
11 Na
12 Mg
13 Al
14 Si
15 P
16 S
17 Cl
18 Ar
19 K
20 Ca
21 Sc
22 Ti
23 V
24 Cr
25 Mn
26 Fe
27 Co
28 Ni
29 Cu
30 Zn
31 Ga
32 Ge
33 As
34 Se
35 Br
36 Kr
37 Rb
38 Sr
39 Y
40 Zr
41 Nb
42 Mo
43 Tc
44 Ru
45 Rh
46 Pd
47 Ag
48 Cd
49 In
50 Sn
51 Sb
52 Te
53 I
54 Xe
55 Cs
56 Ba
57 La
*
72 Hf
73 Ta
74 W
75 Re
76 Os
77 Ir
78 Pt
79 Au
80 Hg
81 Tl
82 Pb
83 Bi
84 Po
85 At
86 Rn
87 Fr
88 Ra
89 Ac
**
104 Rf
105 Db
106 Sg
107 Bh
108 Hs
109 Mt
110 Ds
111 Rg
112 Cn
113 Nh
114 Fl
115 Mc
116 Lv
117 Ts
118 Og
*
58 Ce
59 Pr
60 Nd
61 Pm
62 Sm
63 Eu
64 Gd
65 Tb
66 Dy
67 Ho
68 Er
69 Tm
70 Yb
71 Lu
**
90 Th
91 Pa
92 U
93 Np
94 Pu
95 Am
96 Cm
97 Bk
98 Cf
99 Es
100 Fm
101 Md
102 No
103 Lr

碳酸盐岩U同位素

$\delta^{238}U = [(^{238}U/^{235}U)_{sample}/(^{238}U/^{235}U)_{CRM\text{-}145a} - 1) \times 10^3$

- U 在表生系统中主要呈现两种化合价态:

  U(VI): 易溶于氧化性海水中

  U(IV): 难溶于氧化性海水中

- U(VI) 还原成U(IV) 过程中，伴随着较大的U同位素分馏

  还原态的U(IV) 富集重铀的同位素^{238}U

  核体积效应主导的同位素分馏效应

Main isotopes of uranium ($_{92}U$)

Isotope			Decay	
	abundance	half-life ($t_{1/2}$)	mode	product
^{232}U	syn	68.9 y	SF	–
			α	^{228}Th
^{233}U	trace	1.592×10^5 y	SF	–
			α	^{229}Th
^{234}U	0.005%	2.455×10^5 y	SF	–
			α	^{230}Th
^{235}U	0.720%	7.04×10^8 y	SF	–
			α	^{231}Th
^{236}U	trace	2.342×10^7 y	SF	–
			α	^{232}Th
^{238}U	99.274%	4.468×10^9 y	α	^{234}Th
			SF	–
			$\beta^-\beta^-$	^{238}Pu

Standard atomic weight $A_{r,\ standard}(U)$ 238.028 91(3)[1]

view · talk · edit

碳酸盐岩U同位素

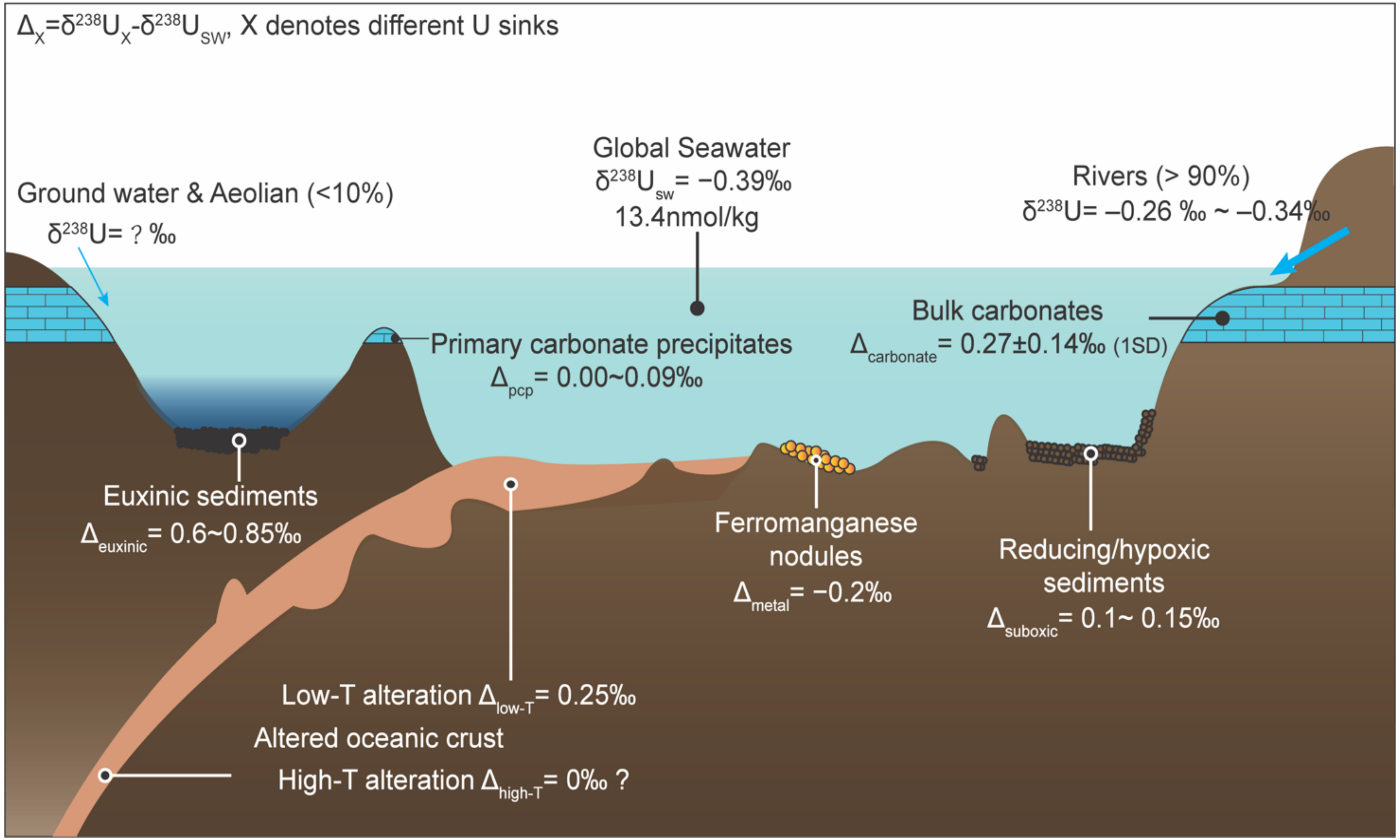
U同位素在海洋中质量平衡示意图

- **Sources:**

  Riverine input
  Ground water
  Aeolian

- **Sinks:**

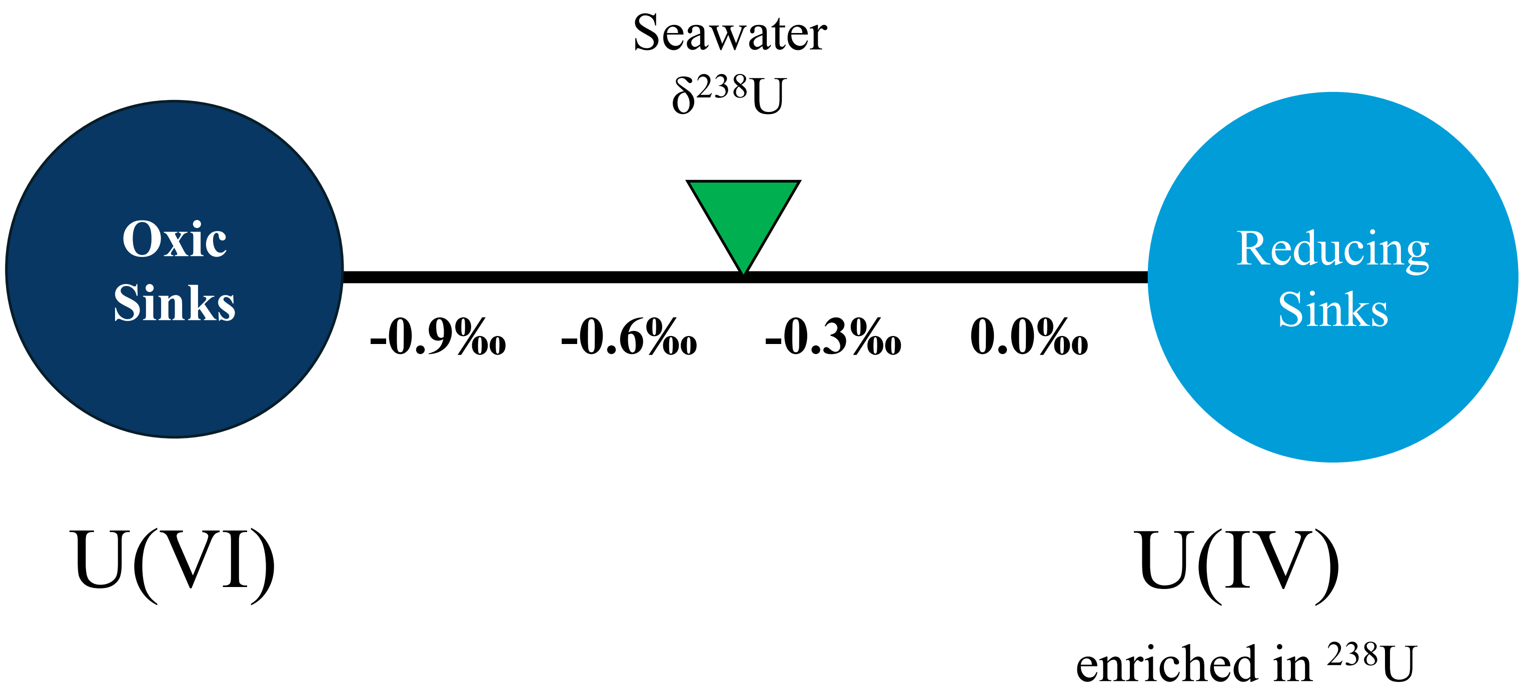
  Euxinic sediments
  Reducing sediments
  Carbonates
  Low-T alteration
  High-T alteration
  Ferromanganese
  Others



Zhang et al., 2020a, GCA

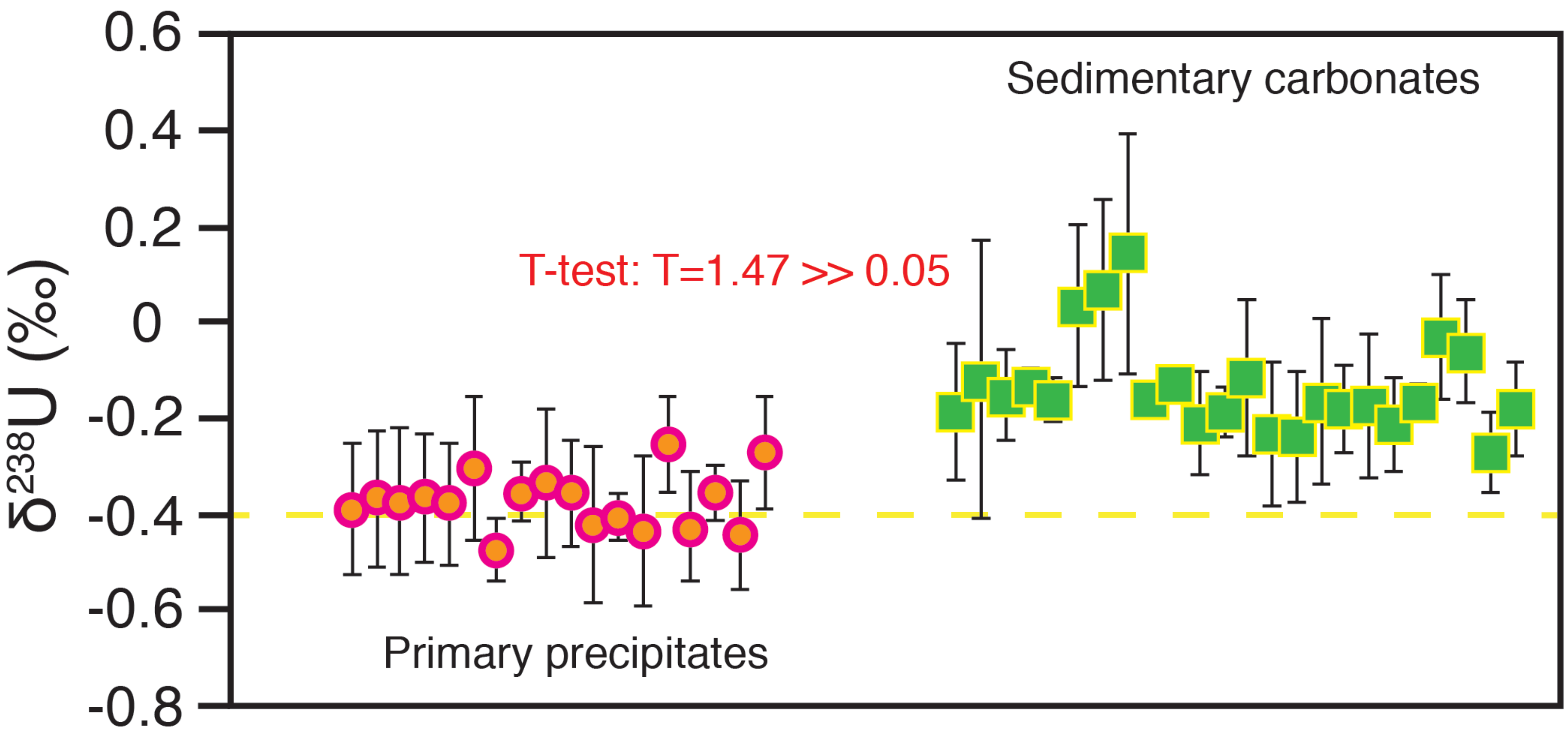
碳酸盐岩U同位素

当海洋出现大面积缺氧时，海水U同位素值逐渐降低



U在海洋中的居留时间为 ~500 kyr，远远长于海水混合时间 (~1 kyr), 因此，$\delta^{238}U$ 在海水中混合十分均一；换而言之，一个剖面的U同位素即可代表全球海水的U同位素变化趋势。

碳酸盐岩U同位素

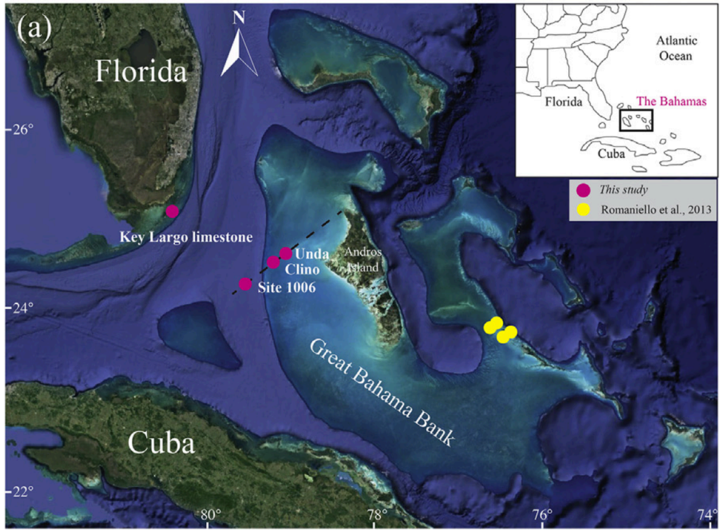


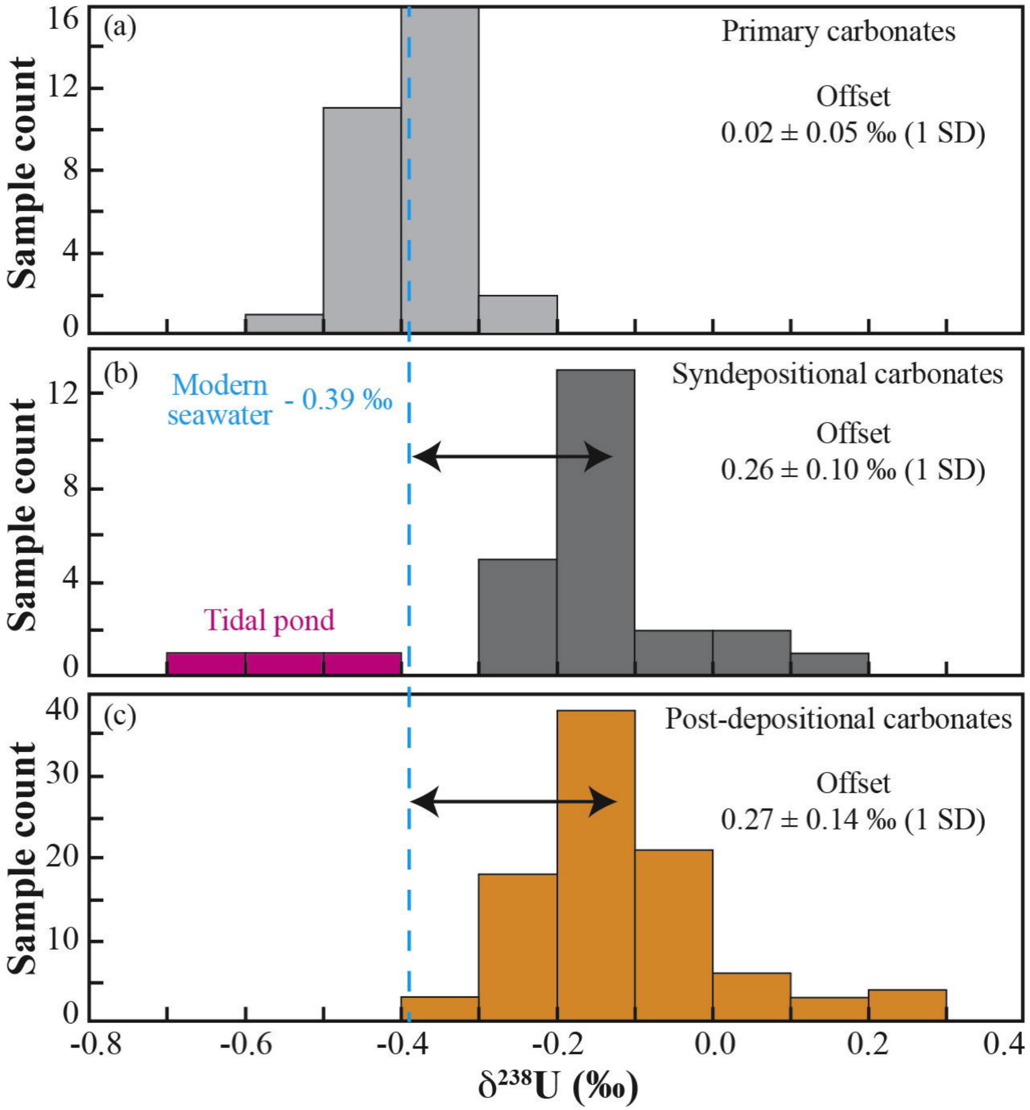
原生生物成因碳酸盐岩可以记录海水的$\delta^{238}U$ 值；沉积碳酸盐岩与上覆海水之间存在一个系统偏差，平均偏差为+0.26‰。

Romaniello et al., 2013, Chem. Geol.

碳酸盐岩U同位素

在早期成岩过程（碳酸盐泥晶被压实变成岩石过程）中，受孔隙水化学性质影响，部分富集^{238}U的U(IV)会进入碳酸盐岩中，造成碳酸盐岩相对上覆海水存在一个系统、相对较稳定的偏差。

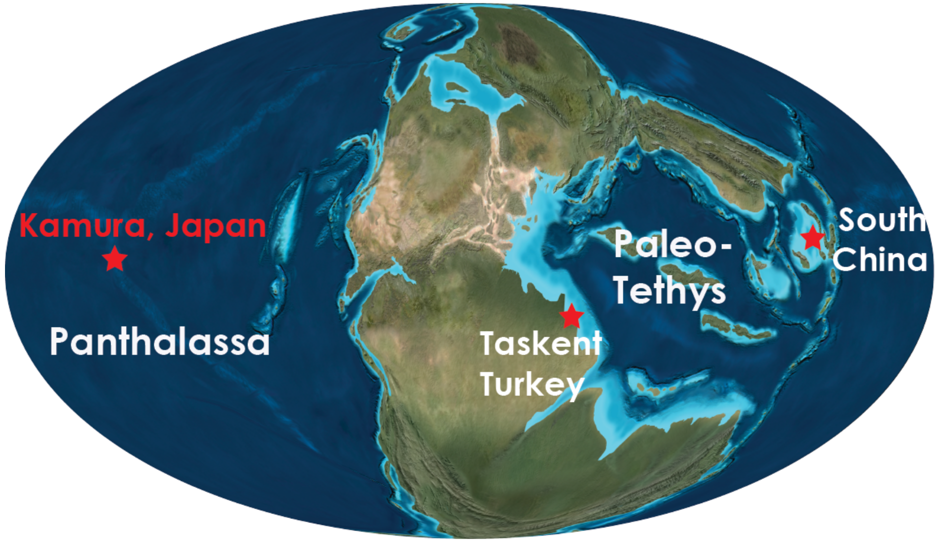


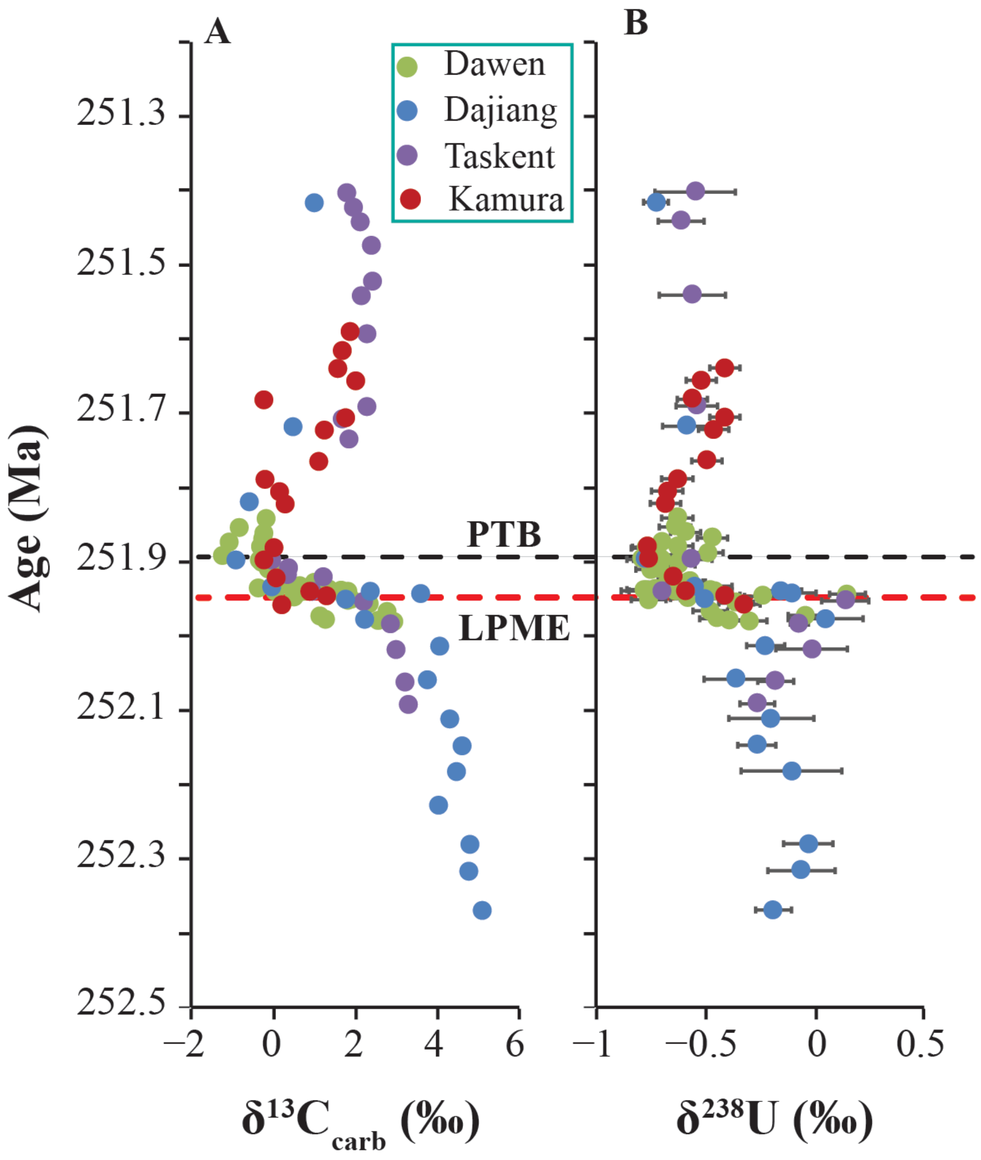


Chen et al., 2018, GCA

碳酸盐岩U同位素

A global compilation of δ238U and δ13C across the end-Permian mass extinction

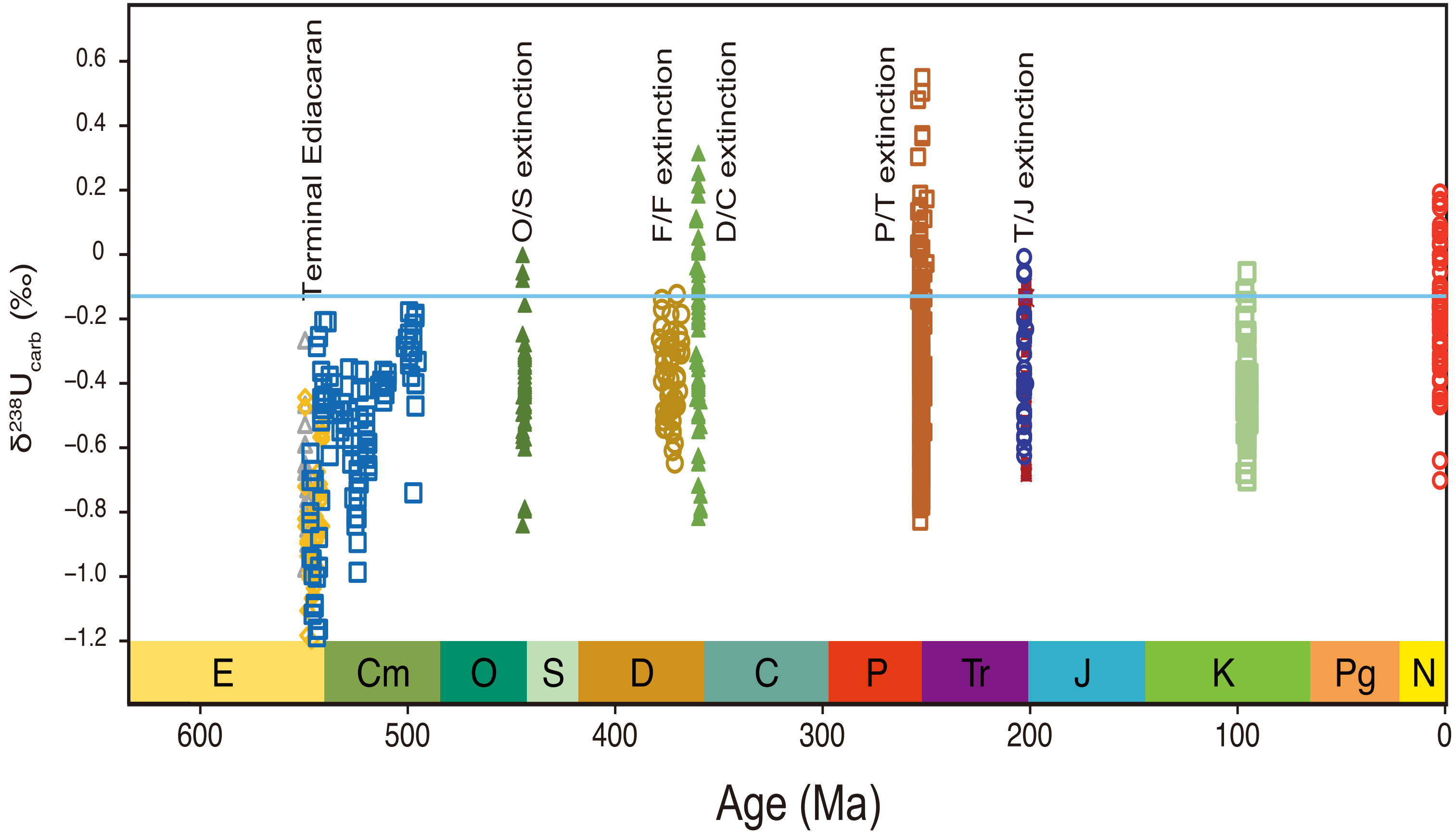




Zhang et al., 2018, Geology

碳酸盐岩U同位素

地质历史时期，重大生物灭绝事件几乎都伴随着显著的海洋缺氧事件



Zhang et al., 2020a, GCA

U同位素的基本质量平衡计算

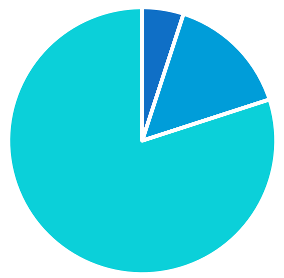
The rate of change of N_{sw} is equal to the source of U (rivers) minus the various sinks for U (e.g. anoxic, suboxic, oxic, etc):

$$\frac{\mathrm{d}N_{sw}}{dt} = F_{input} - F_{anoxic} - F_{suboxic} - F_{oxic}$$

We can write a similar equation for the U isotopic composition of seawater which depends on the mass-weighted isotopic composition of each sink:

$$\frac{\mathrm{d}(N_{sw} \cdot \delta^{238}U_{sw})}{dt} = F_{input} \cdot \delta^{238}U_{input} - F_{anoxic} \cdot \delta^{238}U_{anoxic} - F_{suboxic} \cdot \delta^{238}U_{suboxic} - F_{oxic} \cdot \delta^{238}U_{oxic}$$

distribution of seafloor areas



Zhang et al., 2020a, GCA

U同位素的基本质量平衡计算

Steady State Solutions: at steady state, the sum of all inputs and outputs of U to seawater are equal, and thus the concentration and U isotopic composition of seawater through time is constant.

$$\frac{\mathrm{d}N_{sw}}{dt} = F_{input} - F_{anoxic} - F_{suboxic} - F_{oxic} = 0$$

$$\frac{\mathrm{d}(N_{sw} \cdot \delta^{238}U_{sw})}{dt} = F_{input} \cdot \delta^{238}U_{input} - F_{anoxic} \cdot \delta^{238}U_{anoxic} - F_{suboxic} \cdot \delta^{238}U_{suboxic} - F_{oxic} \cdot \delta^{238}U_{oxic} = 0$$

The source and sink terms are equal

$$F_{input} = F_{anoxic} + F_{suboxic} + F_{oxic}$$

$$F_{input} \cdot \delta^{238}U_{input} = F_{anoxic} \cdot \delta^{238}U_{anoxic} + F_{suboxic} \cdot \delta^{238}U_{suboxic} + F_{oxic} \cdot \delta^{238}U_{oxic}$$

Zhang et al., 2020a, GCA

U同位素的基本质量平衡计算

Defining Metal Burial Rates:

$$F_{anoxic} = k_{anoxic} \cdot A_{anoxic} \cdot [U]$$

$$F_{suboxic} = k_{suboxic} \cdot A_{suboxic} \cdot [U]$$

$$F_{oxic} = k_{oxic} \cdot A_{oxic} \cdot [U]$$

Defining the δ values of each sink:

$$\delta^{238}U_{anoxic} = \delta^{238}U_{sw} + \Delta_{anoxic}$$

$$\delta^{238}U_{suboxic} = \delta^{238}U_{sw} + \Delta_{suboxic}$$

$$\delta^{238}U_{oxic} = \delta^{238}U_{sw} + \Delta_{oxic}$$

Defining fraction of each seafloor areas:

$$f_{anoxic} = \frac{A_{anoxic}}{A_{ocean}}$$

$$f_{suboxic} = \frac{A_{suboxic}}{A_{ocean}}$$

$$f_{oxic} = \frac{A_{oxic}}{A_{ocean}}$$

$$\delta^{238}U_{sw} = \delta^{238}U_{input} - \frac{f_{anoxic} \cdot k_{anoxic} \cdot \Delta_{anoxic} + f_{suboxic} \cdot k_{suboxic} \cdot \Delta_{suboxic} + f_{oxic} \cdot k_{oxic} \cdot \Delta_{oxic}}{f_{anoxic} \cdot k_{anoxic} + f_{suboxic} \cdot k_{suboxic} + f_{oxic} \cdot k_{oxic}}$$

Zhang et al., 2020a, GCA

U同位素的基本质量平衡计算

$$\frac{\mathrm{d}N_{sw}}{dt} = F_{input} - F_{anoxic} - F_{suboxic} - F_{oxic}$$

$$\frac{\mathrm{d}(N_{sw} \cdot \delta^{238}U_{sw})}{dt} = F_{input} \cdot \delta^{238}U_{input} - F_{anoxic} \cdot \delta^{238}U_{anoxic} - F_{suboxic} \cdot \delta^{238}U_{suboxic} - F_{oxic} \cdot \delta^{238}U_{oxic}$$

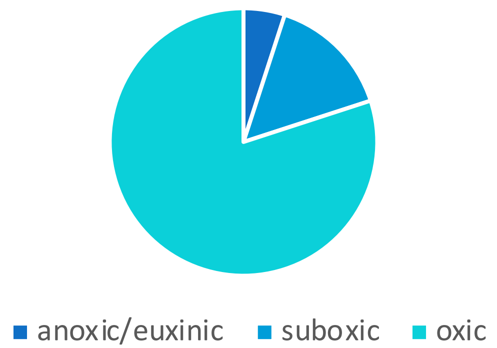
$$F_{anoxic} = k_{anoxic} \cdot A_{anoxic} \cdot [U] \qquad F_{suboxic} = k_{suboxic} \cdot A_{suboxic} \cdot [U] \qquad F_{oxic} = k_{oxic} \cdot A_{oxic} \cdot [U]$$

$$\delta^{238}U_{anoxic} = \delta^{238}U_{sw} + \Delta_{anoxic} \qquad \delta^{238}U_{suboxic} = \delta^{238}U_{sw} + \Delta_{suboxic} \qquad \delta^{238}U_{oxic} = \delta^{238}U_{sw} + \Delta_{oxic}$$

$$f_{anoxic} = \frac{A_{anoxic}}{A_{ocean}} \qquad f_{suboxic} = \frac{A_{suboxic}}{A_{ocean}} \qquad f_{oxic} = \frac{A_{oxic}}{A_{ocean}}$$

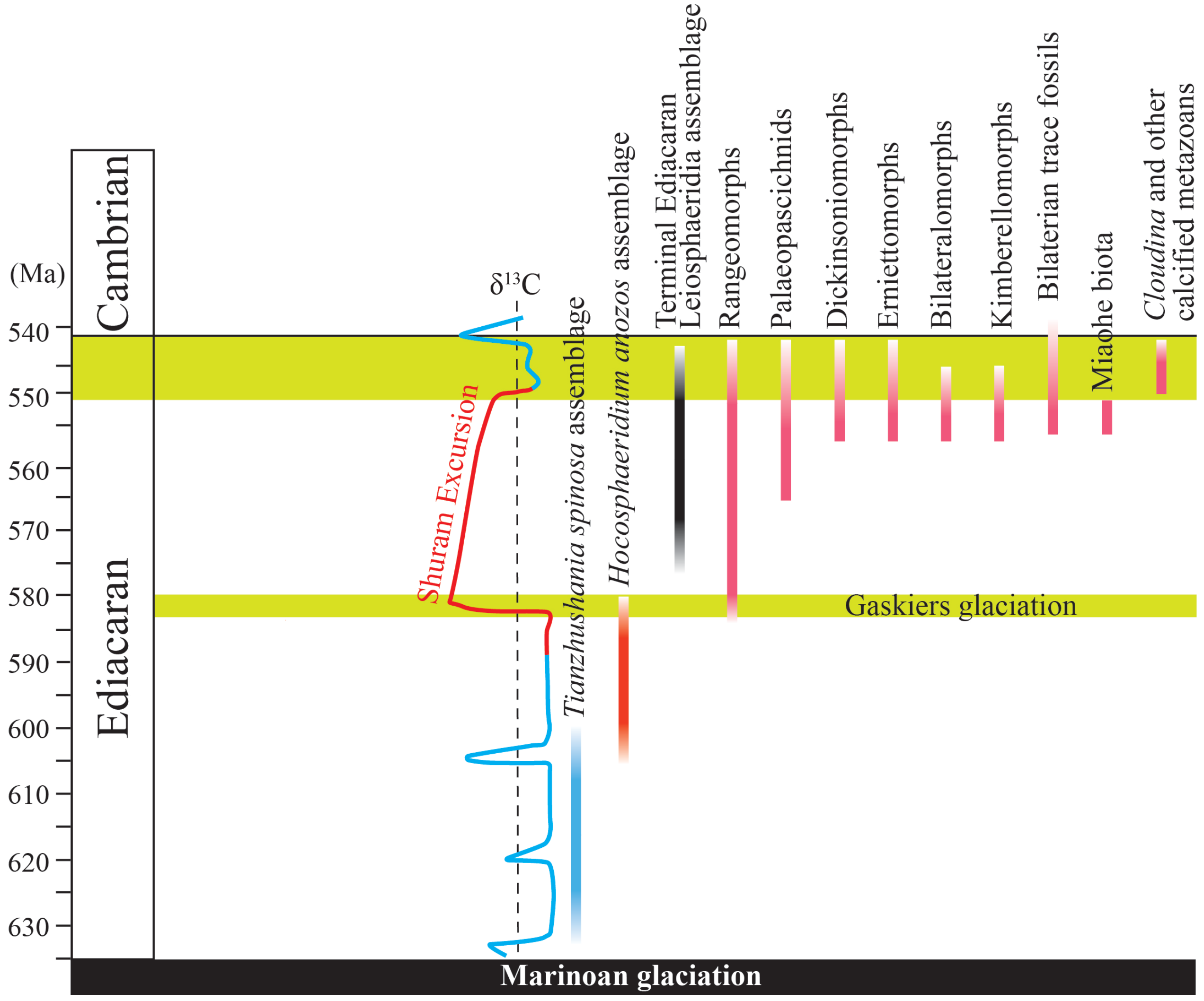
$$\delta^{238}U_{sw} = \delta^{238}U_{input} - \frac{f_{anoxic} \cdot k_{anoxic} \cdot \Delta_{anoxic} + f_{suboxic} \cdot k_{suboxic} \cdot \Delta_{suboxic} + f_{oxic} \cdot k_{oxic} \cdot \Delta_{oxic}}{f_{anoxic} \cdot k_{anoxic} + f_{suboxic} \cdot k_{suboxic} + f_{oxic} \cdot k_{oxic}}$$

distribution of seafloor areas



Zhang et al., 2020a, GCA

伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系



Xiao et al., 2016

- The complex animals (the Ediacara biota) first appeared about 575 Ma, shortly postdate the Shuram Excursion (SE)
- The Ediacara biota begun to decline at ~560 Ma and eventually disappeared at the Ediacaran-Cambrian transition at about 541 Ma

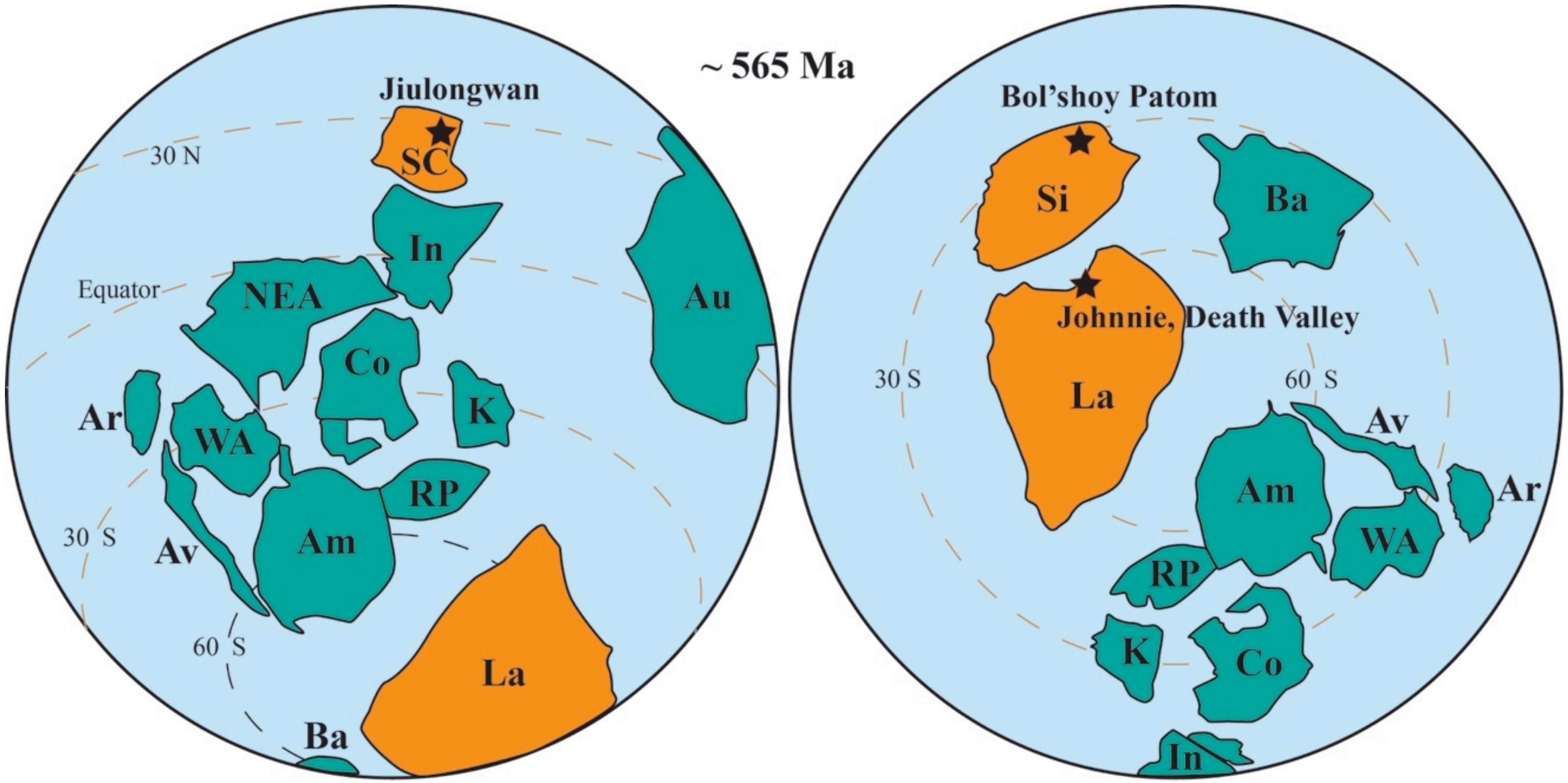
伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系

- What was the global marine redox state across the Ediacaran Shuram Excursion?

- What was the global marine redox state during the last 10 Ma of the Ediacaran Period?

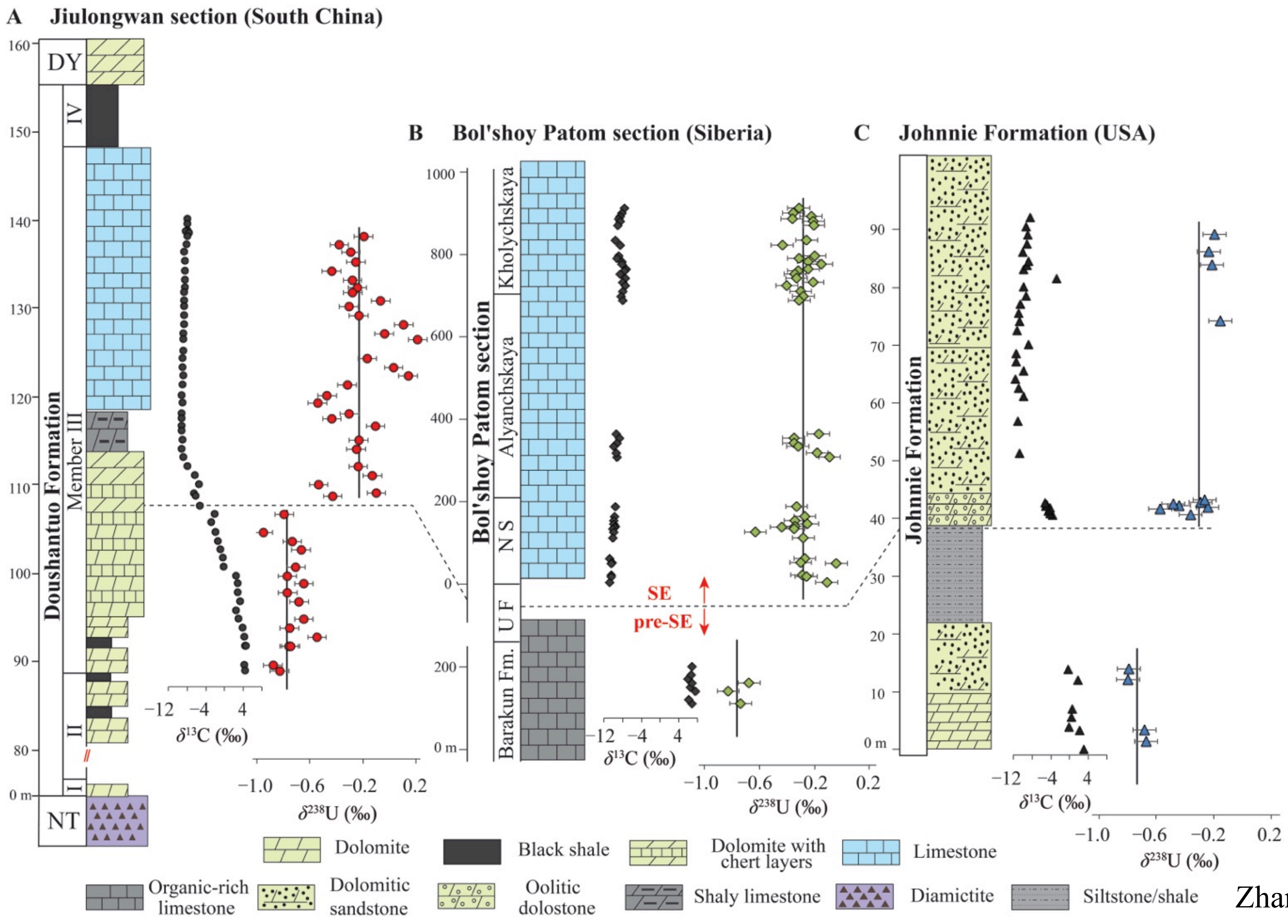
伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系

Three classic Shuram sections



modified after Meert and Lieberman, 2008

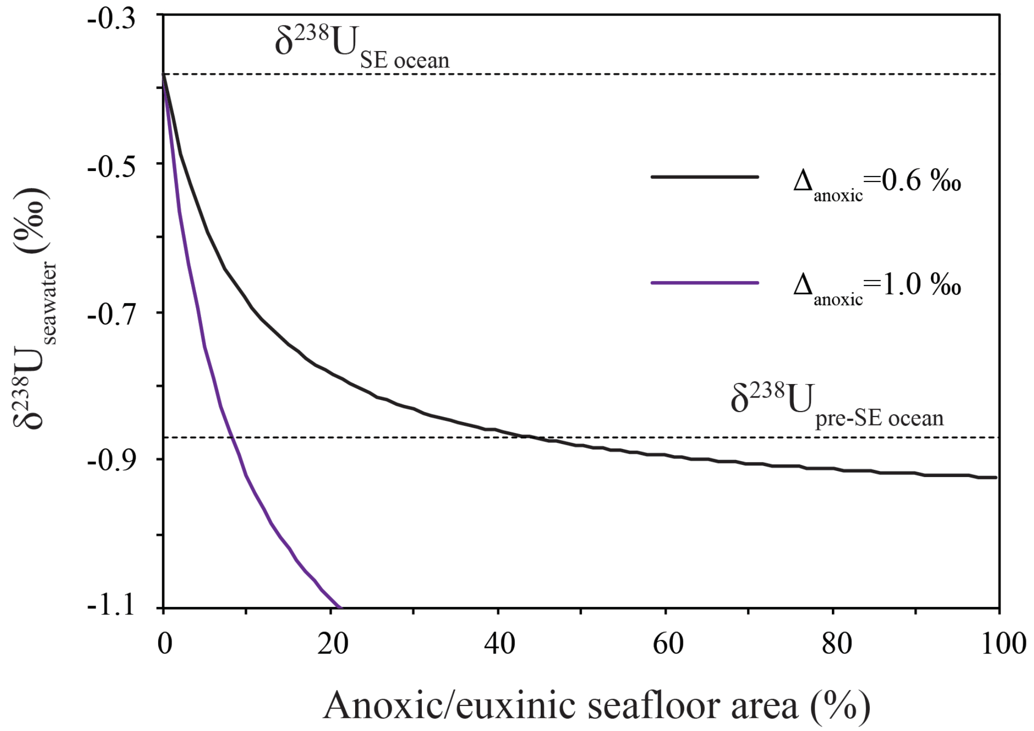
伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系



Zhang et al., 2019, Geobiology

伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系

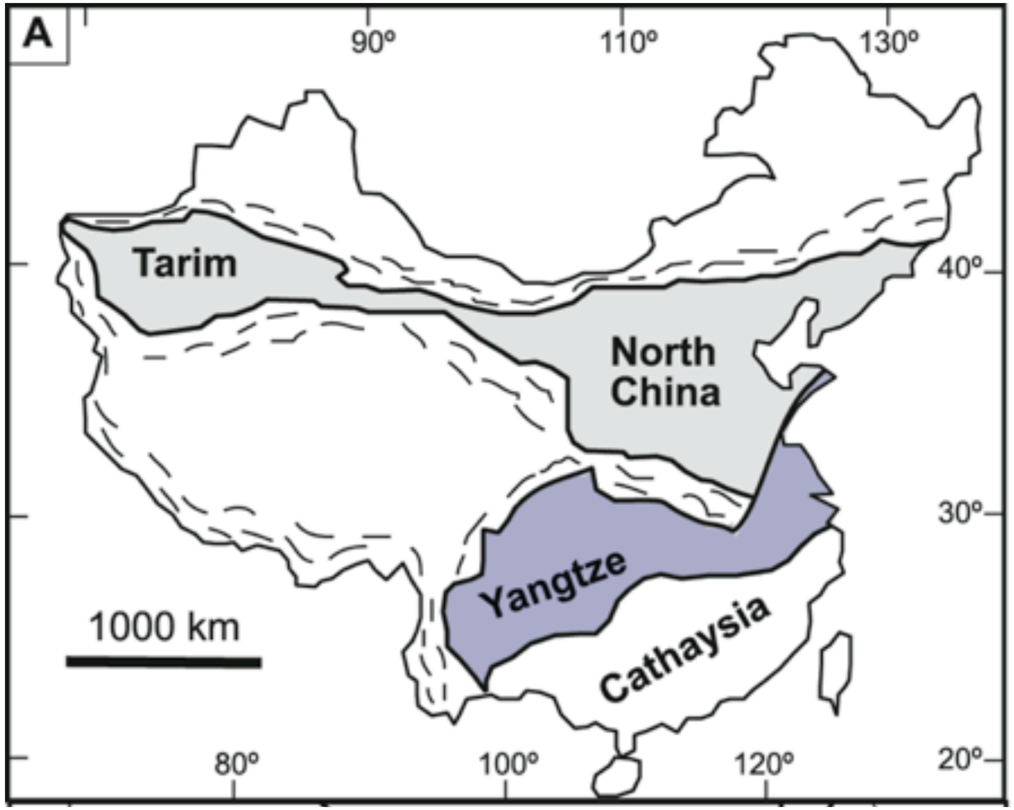
$$\delta^{238}U_{sw} = \delta^{238}U_{input} - \frac{f_{anoxic} \cdot k_{anoxic} \cdot \Delta_{anoxic} + f_{suboxic} \cdot k_{suboxic} \cdot \Delta_{suboxic} + f_{oxic} \cdot k_{oxic} \cdot \Delta_{oxic}}{f_{anoxic} \cdot k_{anoxic} + f_{suboxic} \cdot k_{suboxic} + f_{oxic} \cdot k_{oxic}}$$

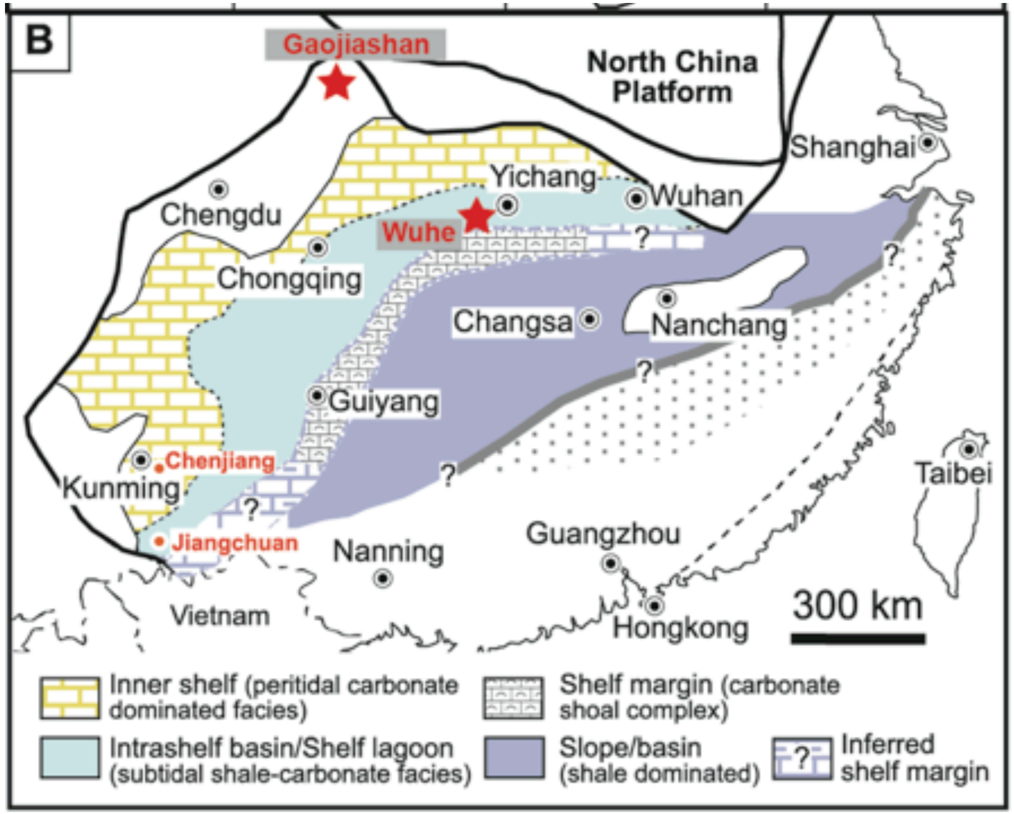


In the pre-SE ocean: >45% of seafloor was overlain by anoxic waters

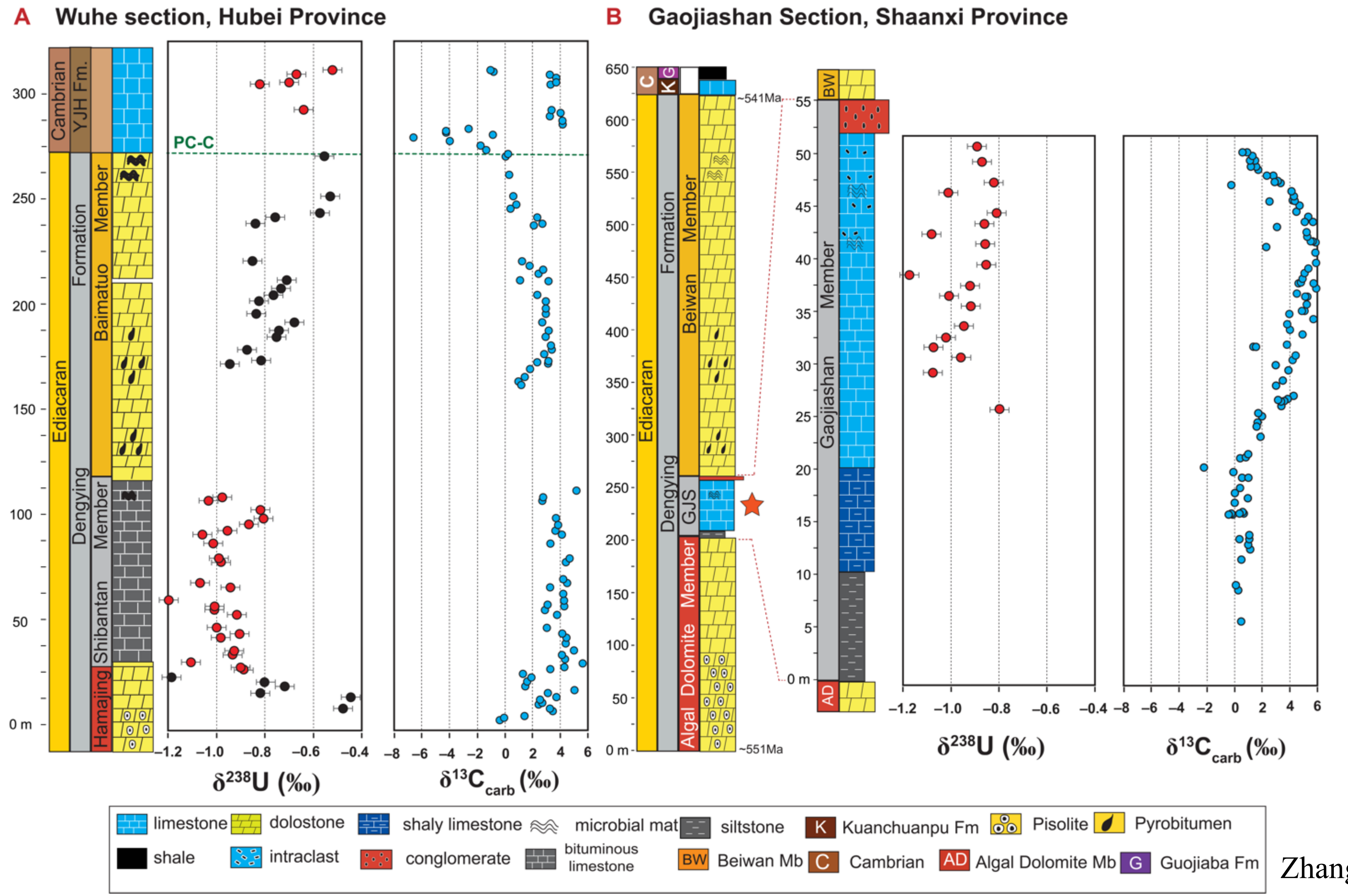
In the SE ocean: ~0.6% of seafloor was overlain by anoxic waters

伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系





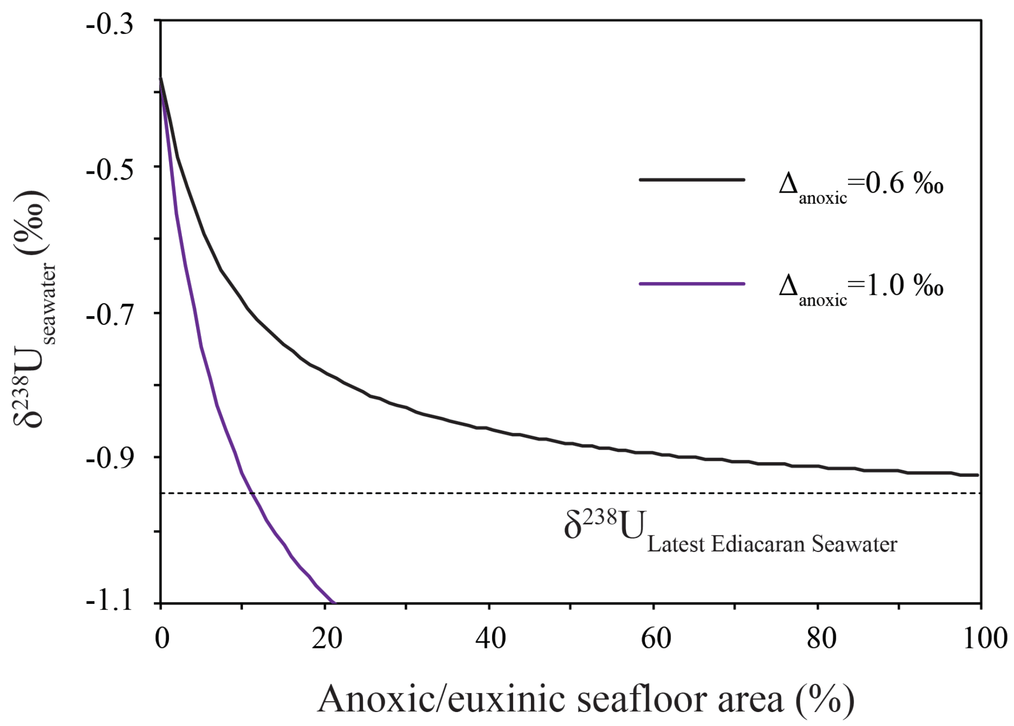
伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系



Zhang et al., 2018, Sci. Adv.

伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系

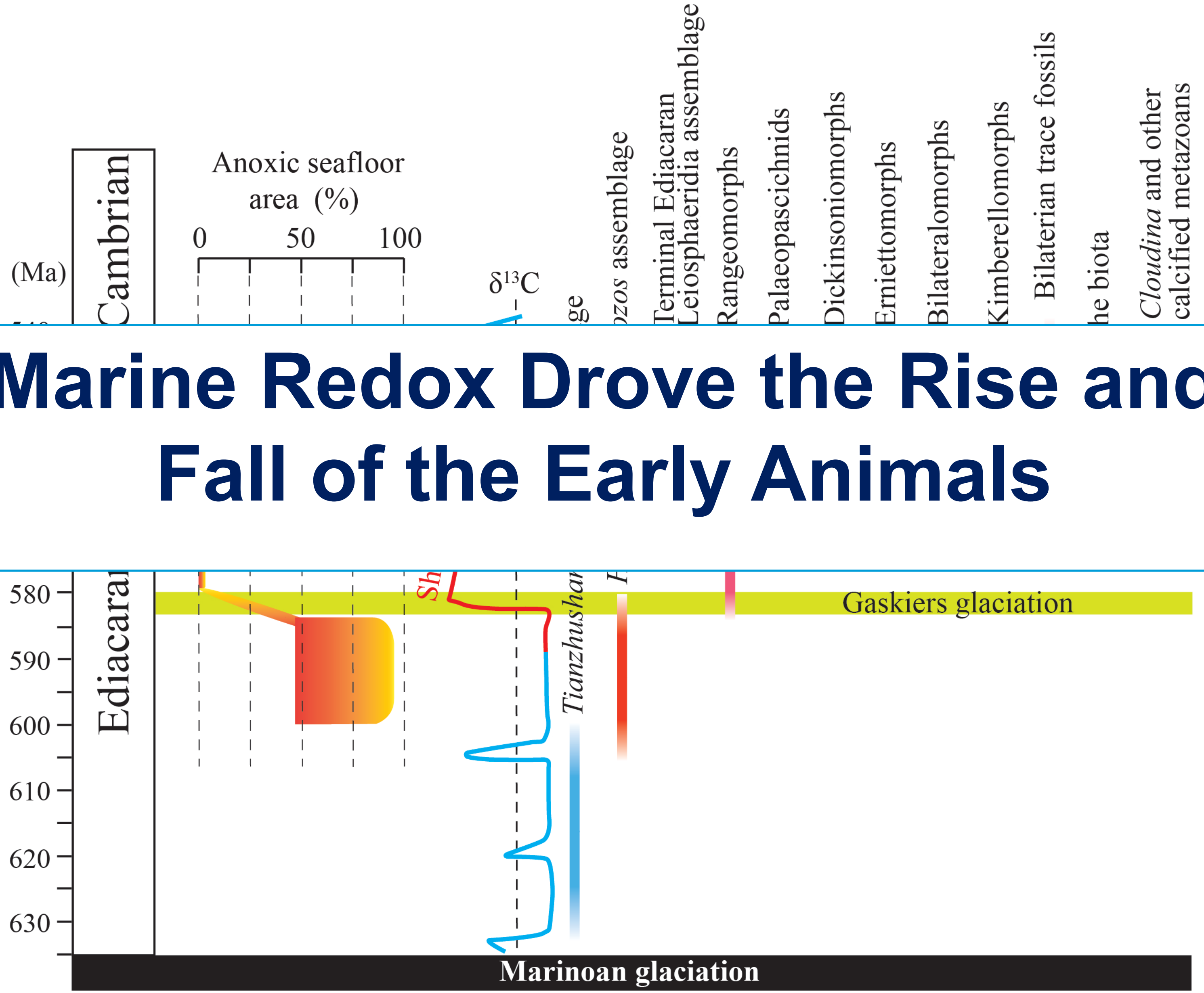
$$\delta^{238}U_{sw} = \delta^{238}U_{input} - \frac{f_{anoxic} \cdot k_{anoxic} \cdot \Delta_{anoxic} + f_{suboxic} \cdot k_{suboxic} \cdot \Delta_{suboxic} + f_{oxic} \cdot k_{oxic} \cdot \Delta_{oxic}}{f_{anoxic} \cdot k_{anoxic} + f_{suboxic} \cdot k_{suboxic} + f_{oxic} \cdot k_{oxic}}$$



In the latest Ediacaran ocean: almost 100% of seafloor was overlain by anoxic waters

Zhang et al., 2018, Sci. Adv.

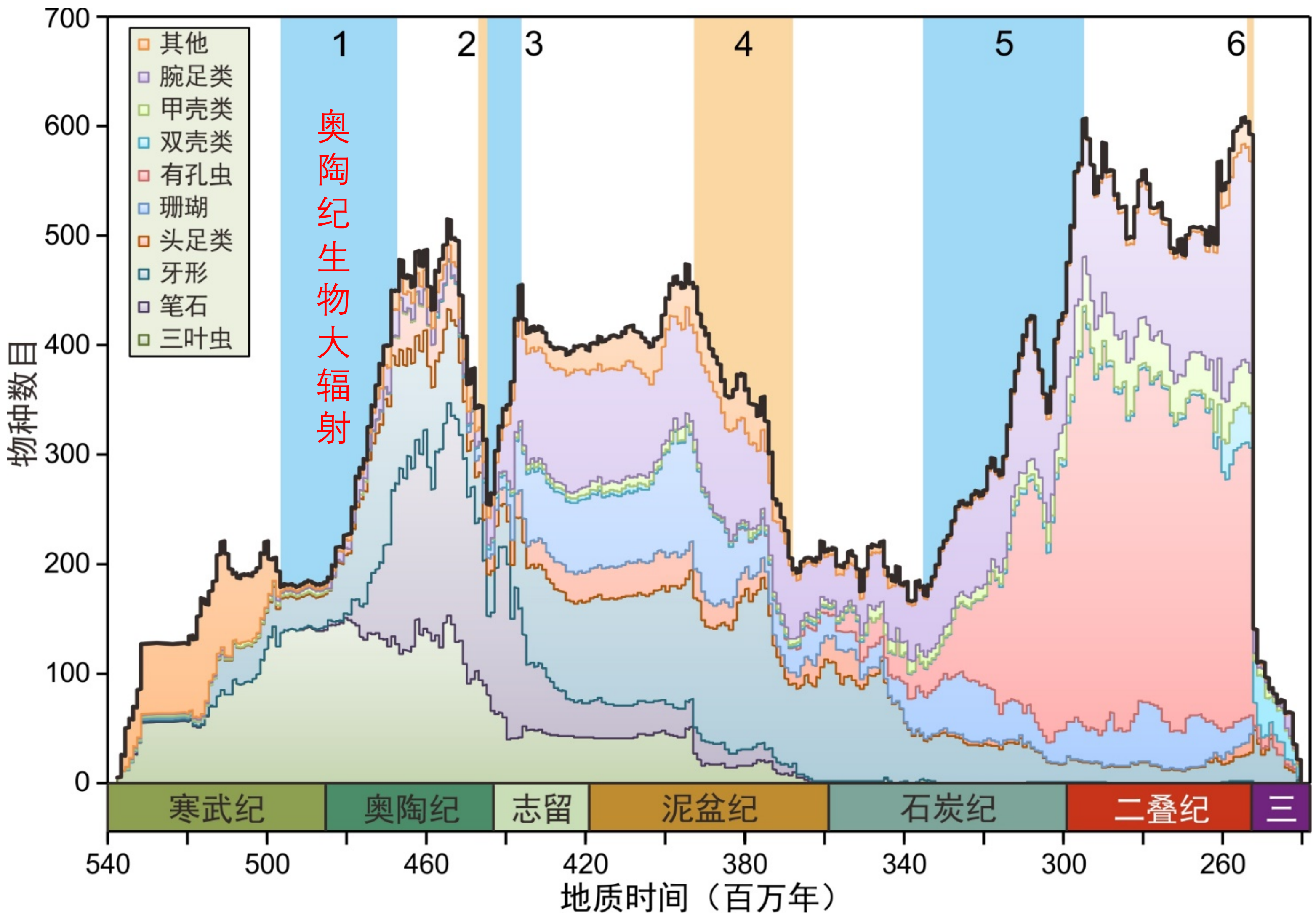
伊迪卡拉纪多细胞动物出现与消亡与海洋环境的关系



Marine Redox Drove the Rise and Fall of the Early Animals

Zhang et al., 2019, Geobiology

奥陶纪生物大辐射与全球海洋氧化还原状态变化



Fan and Shen et al., 2020, Science

奥陶纪生物大辐射与全球海洋氧化还原状态变化

Minimum and maximum values
From modern trace metal oceanography and lab experiments

24 variables
treated as constants in conventional mass balance models

Table 1 Minimum and maximum values included in metal mass balances.

Variable	Minimum value	Maximum value
$\Delta^{238}U_{eux}$ ‰	0.4 [20]	0.8 [20]
$\Delta^{238}U_{eux.loc}$ ‰	0.4 [20]	0.8 [20]
$\Delta^{98}Mo_{eux}$ ‰	−0.8 [47]	0 [31]
$\Delta^{98}Mo$ ‰	−0.8 [47]	0 [31]
F_{riv}		
F_{riv}		
b_U		
b_M		
b_U		
b_M		
b_U		
b_M		
b_U		
b_M		
δ^{23}		
δ^{98}		
Δ^{23}		
Δ^{98}		
Δ^{23}		
Δ^{98}		
$\Delta^{238}U_{carb.loc}$ ‰	0.2 [48]	0.4 [48]
$f_{ox.lim}$ %	83.89 [36]	100 (physical limit)
f_{red} %	0	100-f_{eux}

[a]Calculated by unit conversion.
[b]Calculated as 5th and 95th percentile of ocean-draining rivers.
[c]References indicate that negative fractionations are possible under reducing conditions. As quantitative constraint on the magnitude of these fractionations is poor, the magnitude of the negative fractionation is parameterized to match the positive fractionation. See Supplementary Fig. 6 for alternative parameterizations.

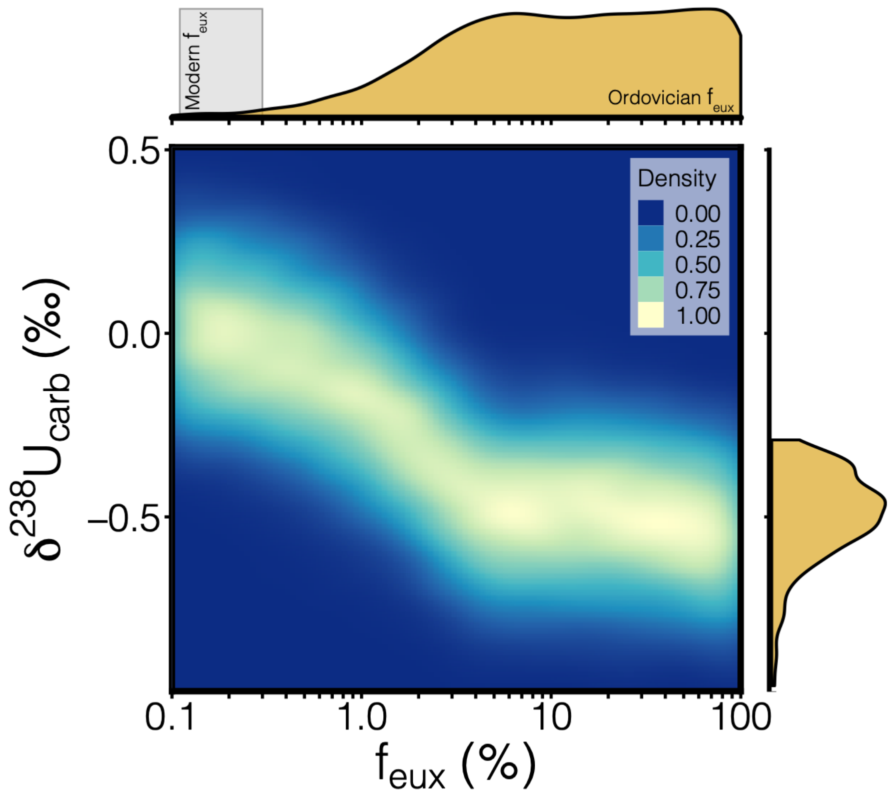
Mass balance models run 1000 times

Each run uses a random subsample between minimum and maximum 'constant' values

Stockey et al. (2020) *Nat. Comm.; Zhang et al., in review*

奥陶纪生物大辐射与全球海洋氧化还原状态变化

- Fully coupled concentration-isotope model: 3 redox sensitive sinks, Monte Carlo mass balance



$$\frac{d[U]_{sw}}{dt} = F_{riv} - F_{oxic} - F_{red} - F_{eux}$$

$$\frac{d[U]_{sw}\delta^{238}U_{sw}}{dt} = F_{riv}\delta^{238}U_{riv} - F_{oxic}(\delta^{238}U_{sw} + \Delta^{238}U_{oxic}) - F_{red}(\delta^{238}U_{sw} + \Delta^{238}U_{red}) - F_{eux}(\delta^{238}U_{sw} + \Delta^{238}U_{eux})$$

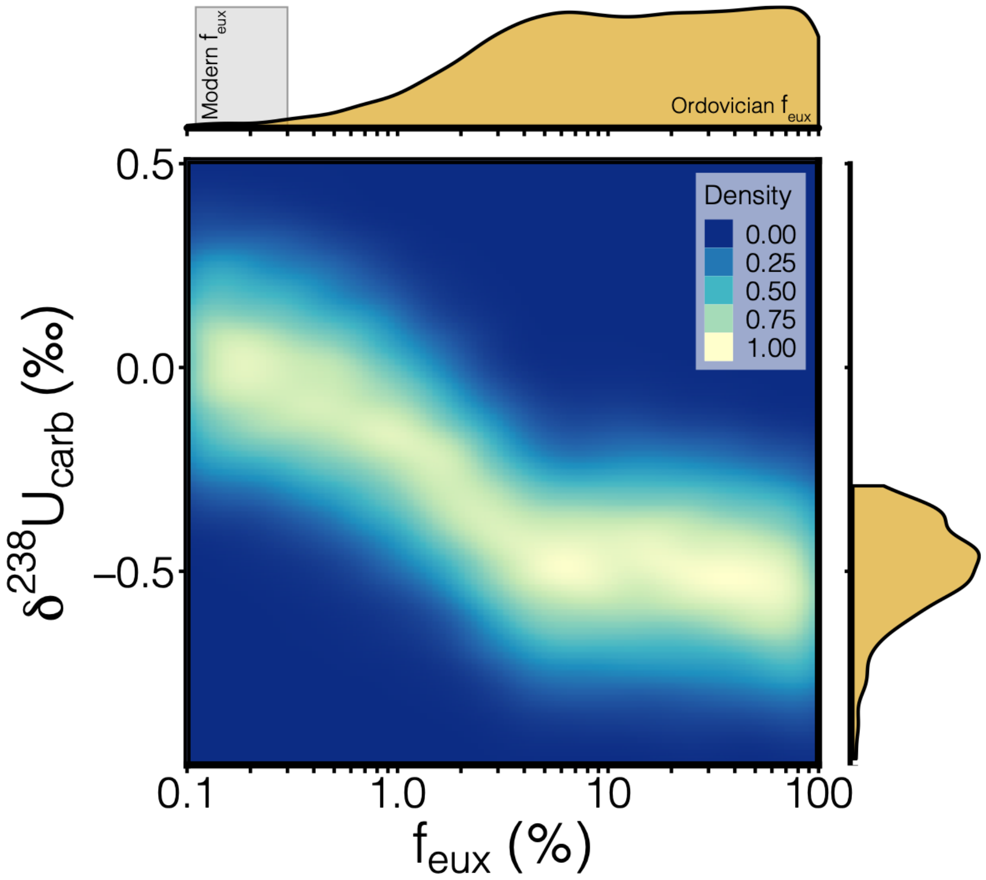
Fluxes for redox-sensitive sinks are defined as

$$F_i = b_i A_i \alpha_i \frac{[Me]_{sw}}{[Me]_{M.sw}}$$

Zhang et al., in review

奥陶纪生物大辐射与全球海洋氧化还原状态变化

- Fully coupled concentration-isotope model: 3 redox sensitive sinks, monte carlo



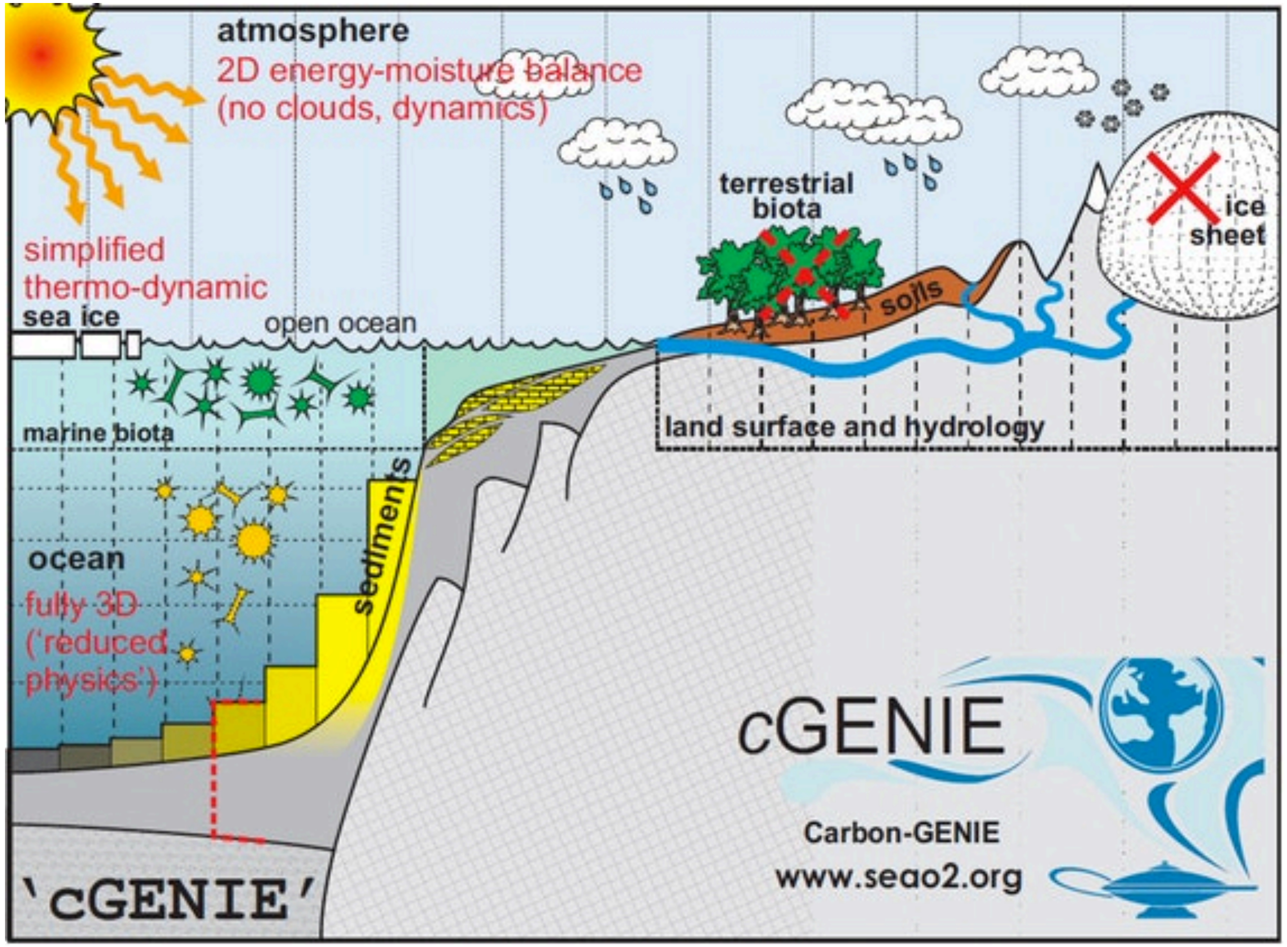
But what about interpretations of global cooling and atmospheric oxygenation through the Ordovician?...

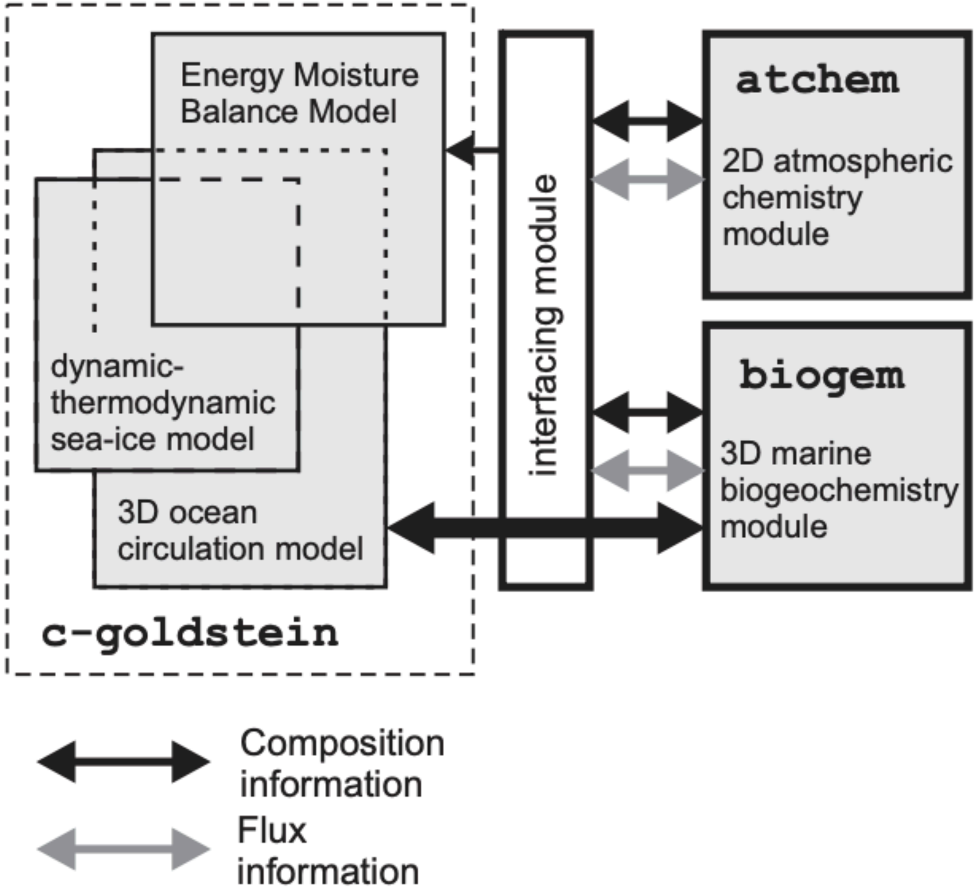
...we use the cGENIE Earth system model to evaluate whether these trends are compatible.

Zhang et al., in review

奥陶纪生物大辐射与全球海洋氧化还原状态变化

- cGENIE Earth System model

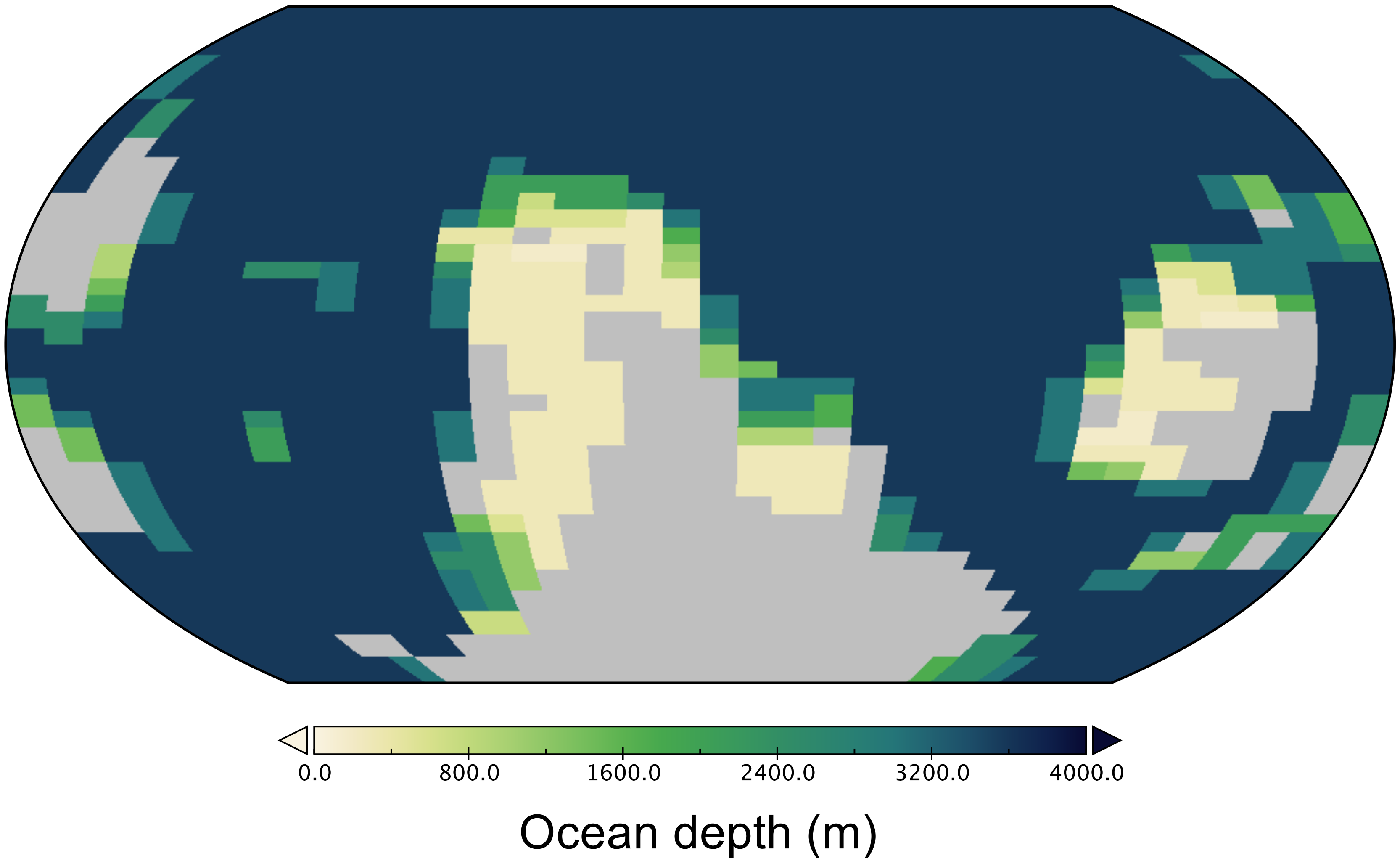




Ridgwell et al. (2007) *Biogeosciences*

奥陶纪生物大辐射与全球海洋氧化还原状态变化

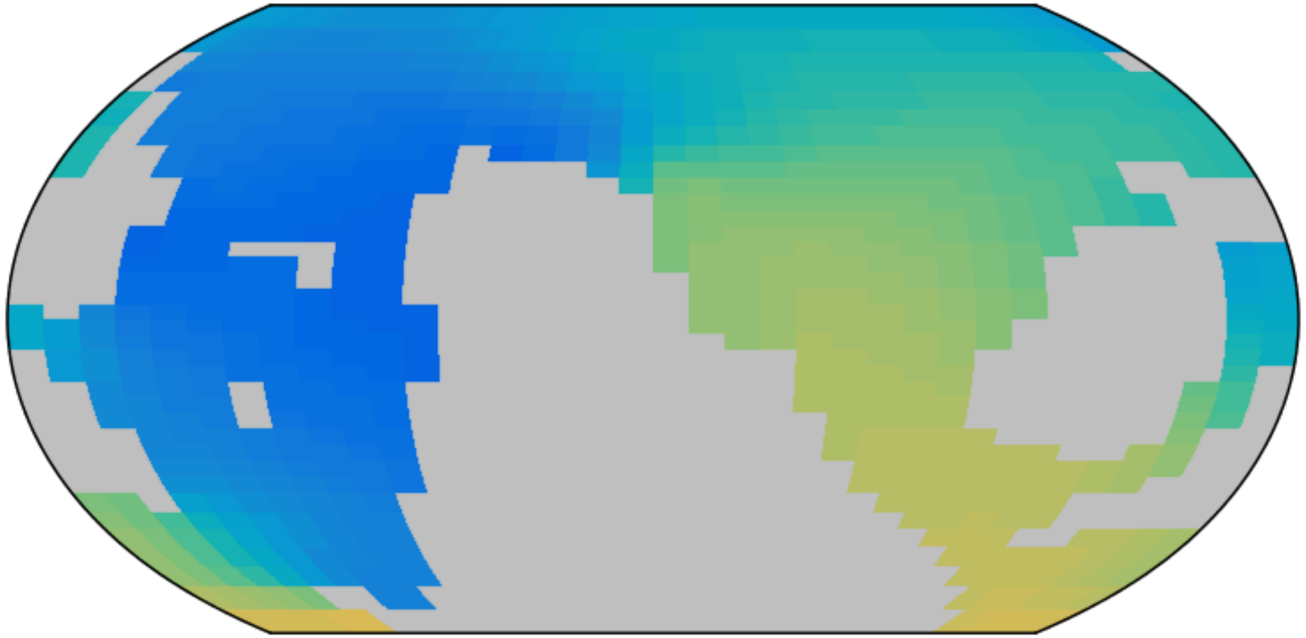
- Ordovician tectonic configuration in cGENIE



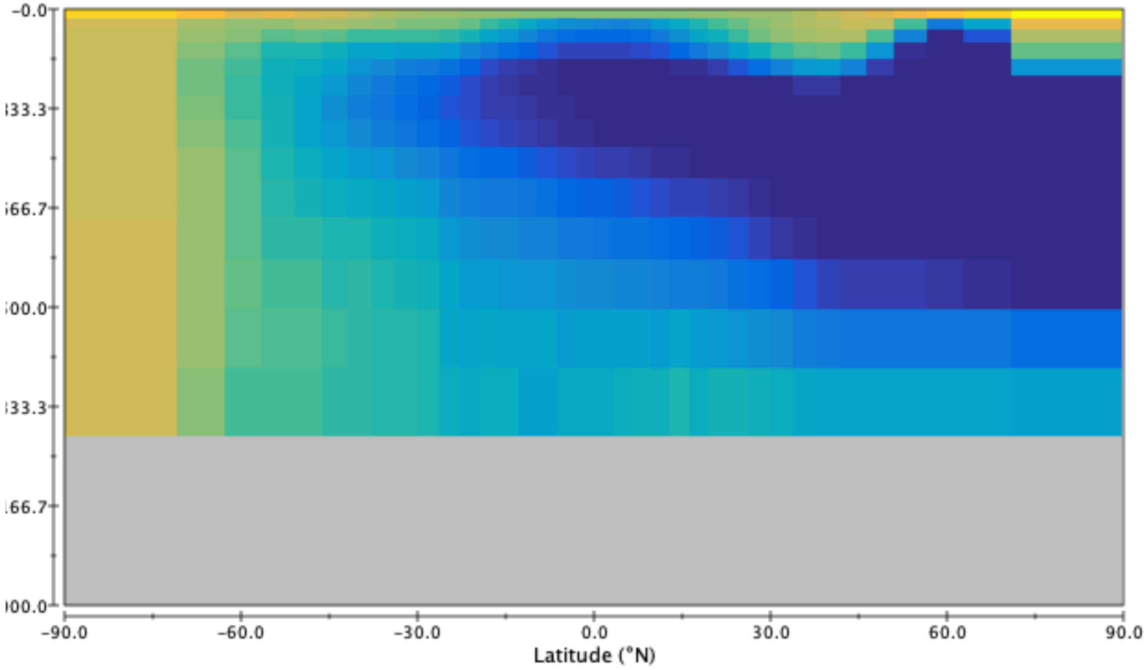
奥陶纪生物大辐射与全球海洋氧化还原状态变化

- Example Ordovician marine O_2 profiles: 16 x CO_2, 0.4 x O_2, 0.5 x PO_4

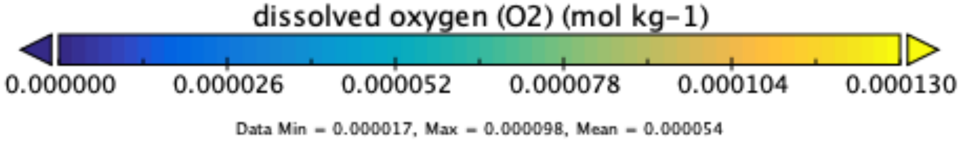
Deep ocean floor O_2



Water column O_2 vs latitude

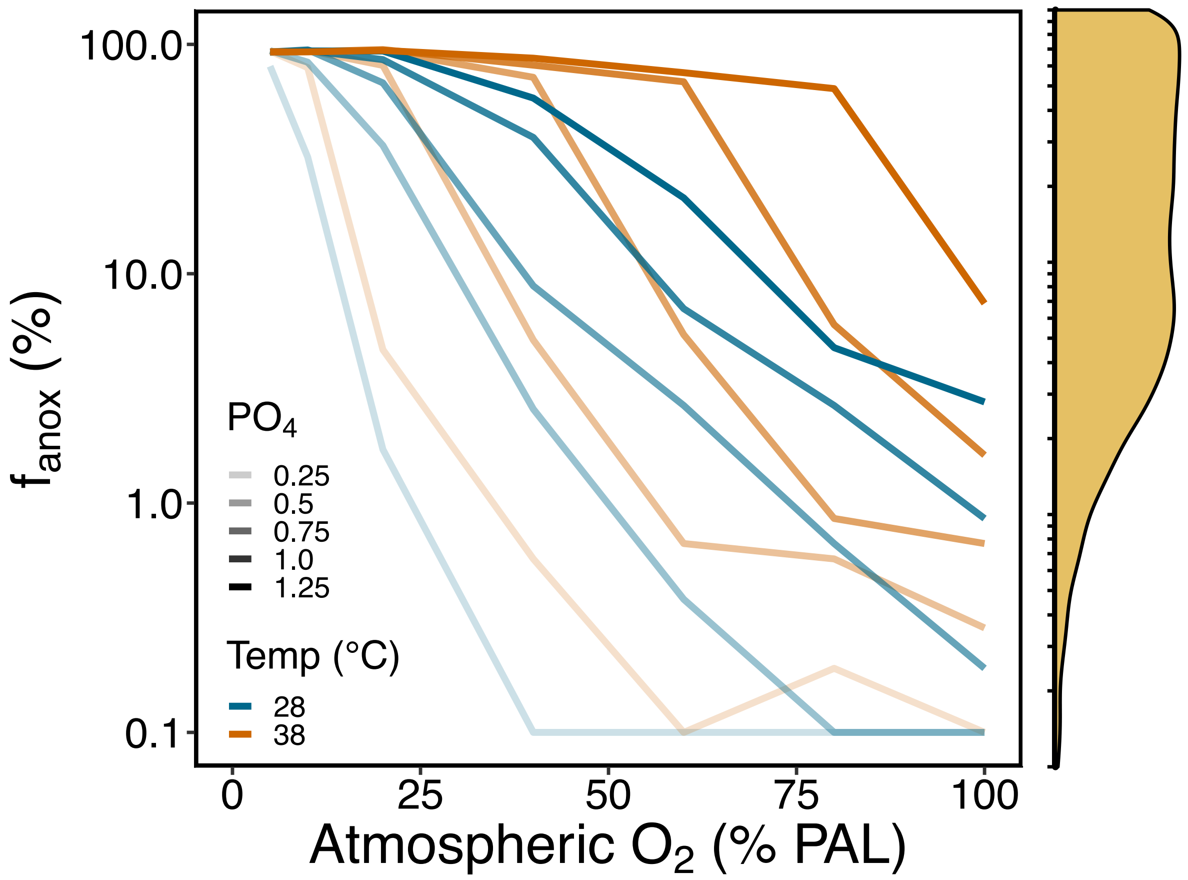


Dissolved O_2 (mol kg^{-1})



奥陶纪生物大辐射与全球海洋氧化还原状态变化

- Summarizing 70 cGENIE simulations – compared to uranium f_{anox} estimates

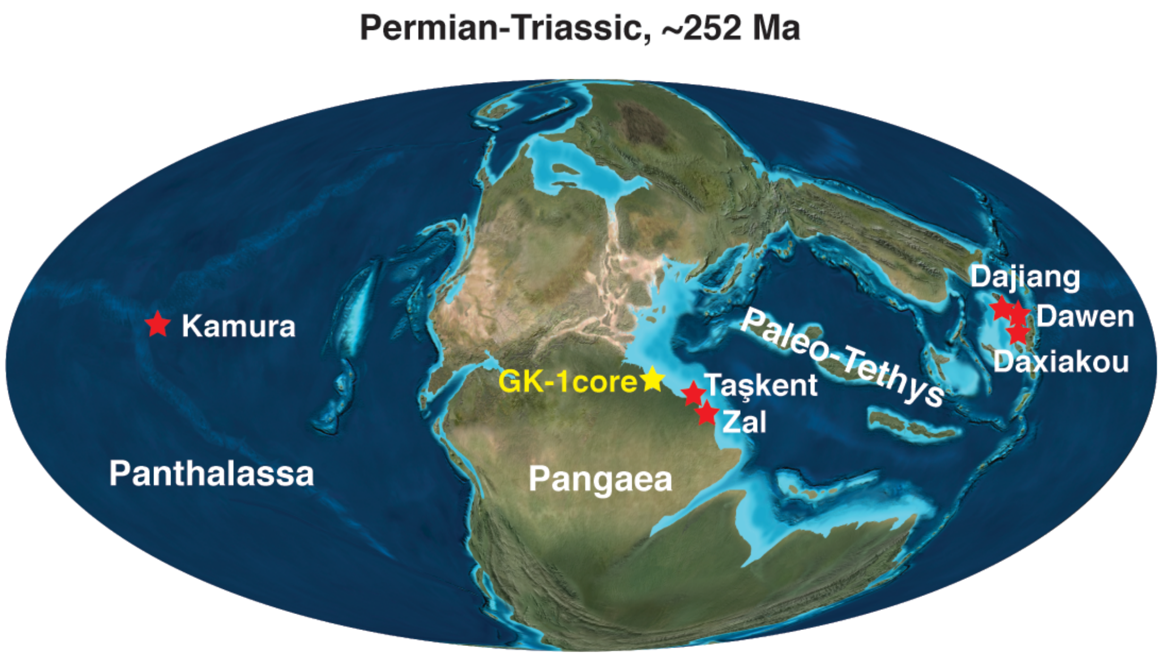


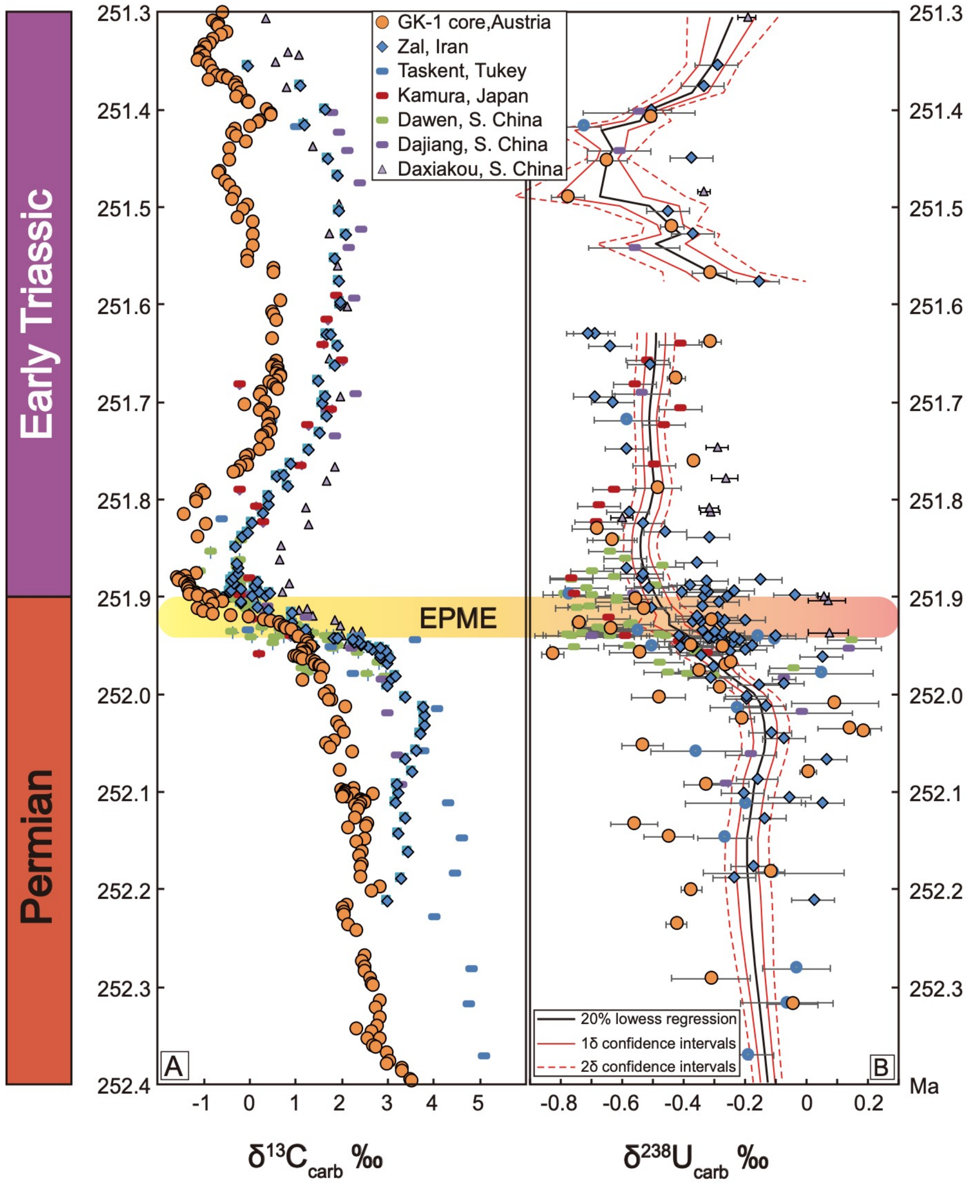
There must have been a corresponding increase in global marine productivity to counterbalance the expected effects of bottom-water oxygenation and maintain an unchanged seafloor redox landscape.

Zhang et al., in review

二叠纪末生物大灭绝与海洋缺氧

A global compilation of δ^{238}U data from measurements across the PTB.





Zhang et al., 2020b, GCA

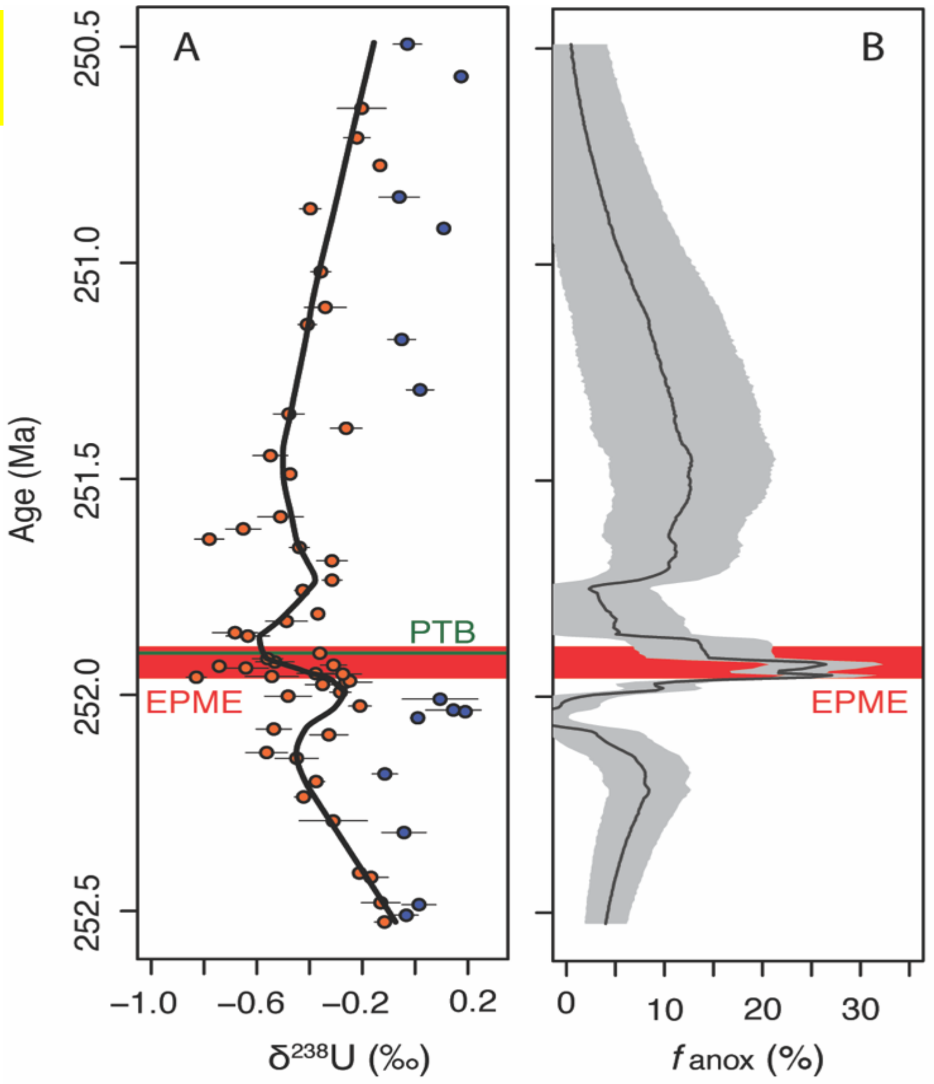
二叠纪末生物大灭绝与海洋缺氧

A simple dynamic model (coupled with a simplified Monte Carlo framework)

$$\frac{d(N_{sw} \cdot \delta^{238}U_{sw})}{dt} = F_{input} \cdot \delta^{238}U_{input} - F_{anoxic} \cdot \delta^{238}U_{anoxic} - F_{suboxic} \cdot \delta^{238}U_{suboxic} - F_{oxic} \cdot \delta^{238}U_{oxic}$$

A. $\delta^{238}U$ data with LOWESS smoothing fit.
B. B. Model estimates of anoxic seafloor area (f_{anox}) across the Permian-Triassic boundary.

The first anoxic episode lasted for ~60 kyr while anoxic seafloor area expanded to cover >18% of the entire seafloor, coeval with the main EPME horizon, agreeing with marine anoxia as a proximate kill mechanism for the EPME.

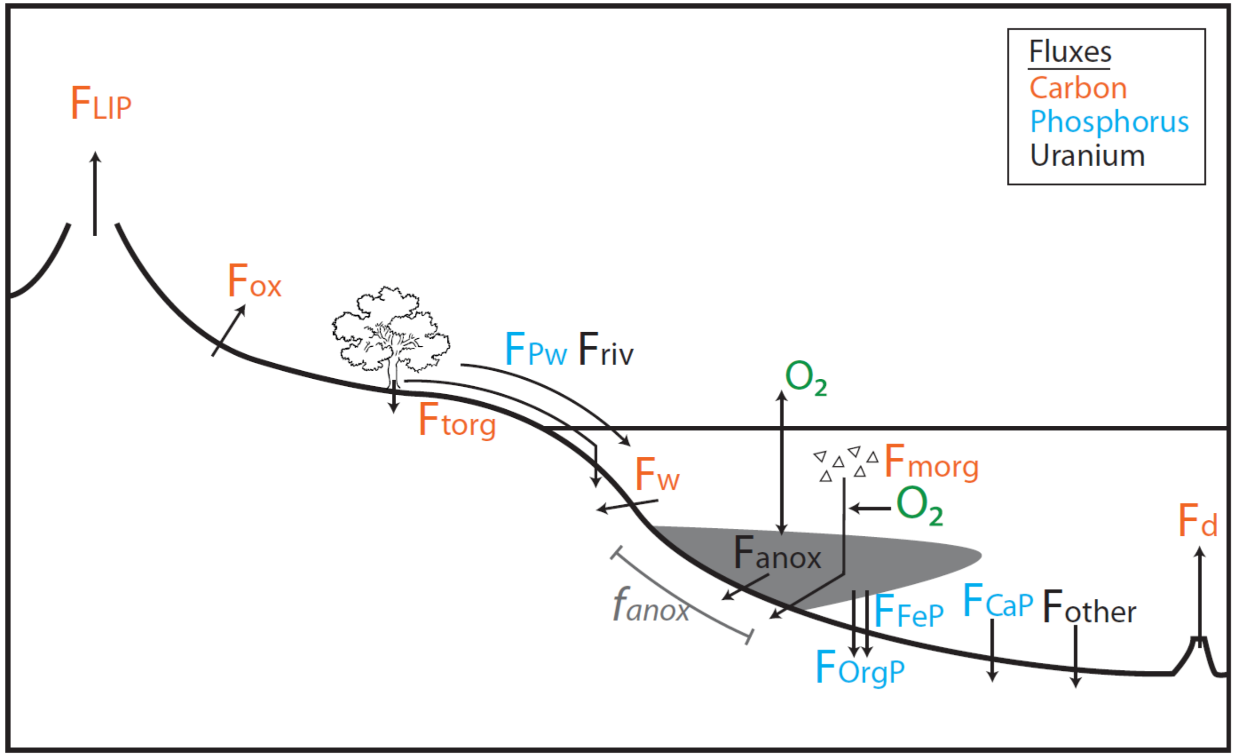


Zhang et al., 2020b, GCA

U同位素与生物地球化学模型COPSE结合

Biogeochemical model of coupled marine C-P-U cycles

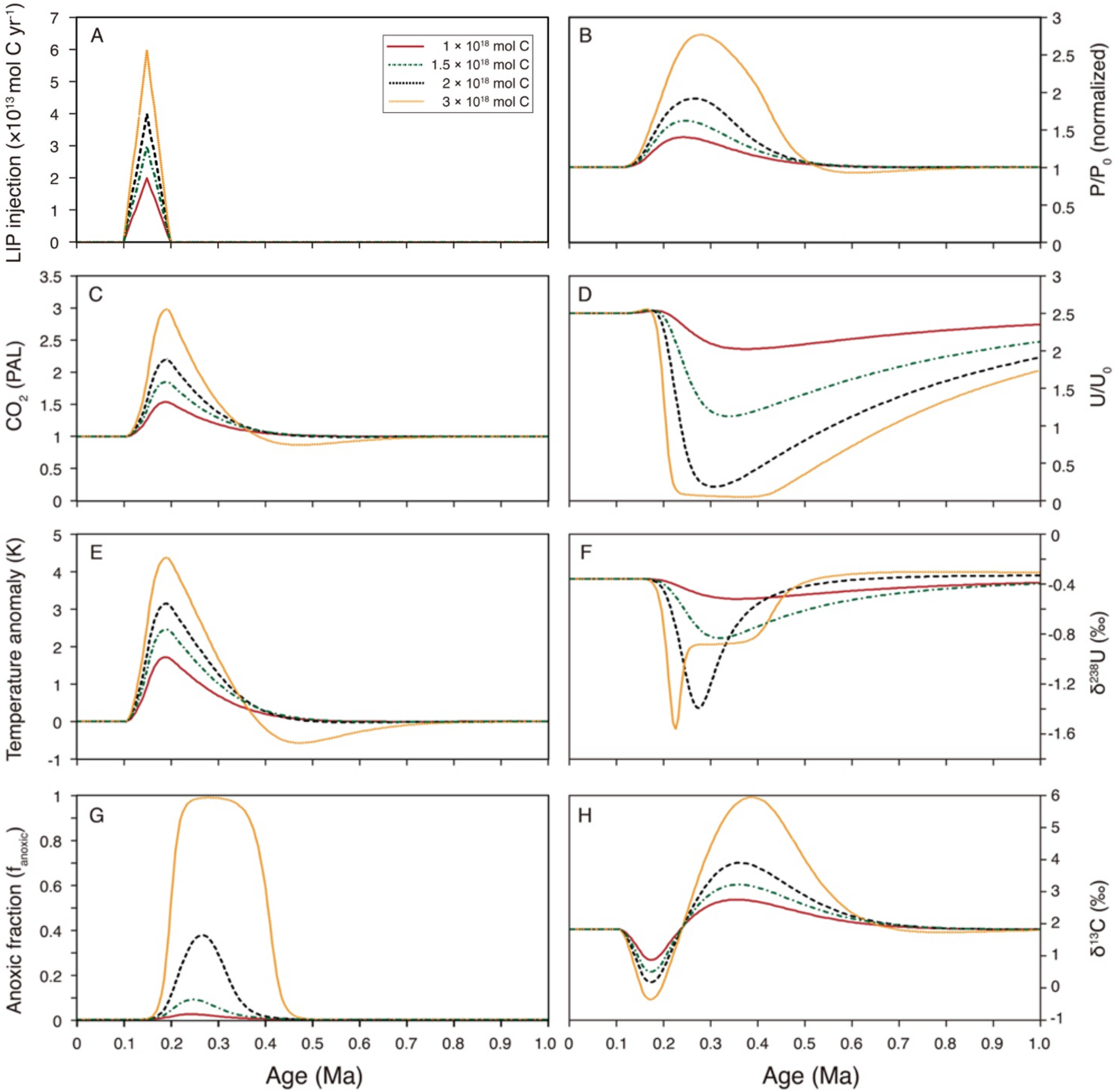
Variable/Process	Equation	Units
Differential equations		
Ocean-atmosphere C	$dA/dt = F_d - F_w + F_{ox} - F_{morg} - F_{torg} + F_{LIP}$	mol C yr^{-1}
Ocean P balance	$dP/dt = F_{Pw} - F_{OrgP} - F_{FeP} - F_{CaP}$	mol P yr^{-1}
Ocean U balance	$dU/dt = F_{riv} - F_{anoxic} - F_{other}$	mol U yr^{-1}
C isotope balance	$d\delta_A/dt = (F_{in} \times (\delta_{in} - \delta_A) + F_{LIP} \times (\delta_{LIP} - \delta_A) - F_{org} \times (-\Delta))/A$	‰ yr^{-1}
U isotope balance	$d\delta_U/dt = (F_{riv} \times (\delta_{riv} - \delta_U) - F_{anoxic} \times \Delta_{anoxic} - F_{other} \times \Delta_{other})/U$	‰ yr^{-1}
Key variables		
Atmospheric CO_2	$CO_2 = (A/A_0)^2$	PAL
Global temperature	$\Delta T = k_{CO2} \times \ln(CO_2) - k_{SL} \times (age/570)$	K, *age* (Ma)
Plant CO_2 response	$f(CO_2) = 2 \times CO_2/(1+CO_2)$	-
Weathering kinetics	$f(T) = \exp(0.09 \times \Delta T)$	-
Ocean anoxic fraction	$f_{anoxic} = 1/(1+e^{-kanox \times (ku \times (P/P0) - pO2)})$	-, pO_2 (PAL)
Carbon fluxes		
Silicate weathering	$F_w = k_w \times E \times W \times V \times f(CO_2) \times f(T)$	mol C yr^{-1}
Carbonate degassing	$F_d = k_d \times D$	mol C yr^{-1}
C_{org} oxidation	$F_{ox} = k_{ox}$	mol C yr^{-1}
Carbonate weathering	$F_{cw} = k_{carb}$	mol C yr^{-1}
Aggregate C input	$F_{in} = F_d + F_{ox} + F_{cw}$	mol C yr^{-1}
Terrestrial C_{org} burial	$F_{torg} = k_{torg} \times V \times f(CO_2)$	mol C yr^{-1}
Marine C_{org} burial	$F_{morg} = k_{morg} \times (P/P_0)$	mol C yr^{-1}
Total C_{org} burial	$F_{org} = F_{morg} + F_{torg}$	mol C yr^{-1}
Phosphorus fluxes		
P weathering	$F_{Pw} = k_{Pw} \times (F_w/k_w)$	mol P yr^{-1}
Organic P burial	$F_{OrgP} = F_{morg} \times ((f_{anoxic}/CP_{anoxic}) + ((1-f_{anoxic})/CP_{oxic}))$	mol P yr^{-1}
Fe-sorbed P burial	$F_{FeP} = k_{FeP} \times (1-f_{anoxic})$	mol P yr^{-1}
Ca-bound P burial	$F_{CaP} = k_{CaP} \times (P/P_0)$	mol P yr^{-1}
Uranium fluxes		
U weathering	$F_{riv} = k_{riv} \times F_w/F_{w0}$	mol U yr^{-1}
Anoxic U sink	$F_{anoxic} = k_{anoxic} \times (U/U_0) \times f_{anoxic}/f_{anoxic0}$	mol U yr^{-1}
Other U sinks	$F_{other} = k_{other} \times (U/U_0) \times (1 - f_{anoxic})/(1 - f_{anoxic0})$	mol U yr^{-1}



Zhang et al., 2020a, GCA

U同位素与生物地球化学模型COPSE结合

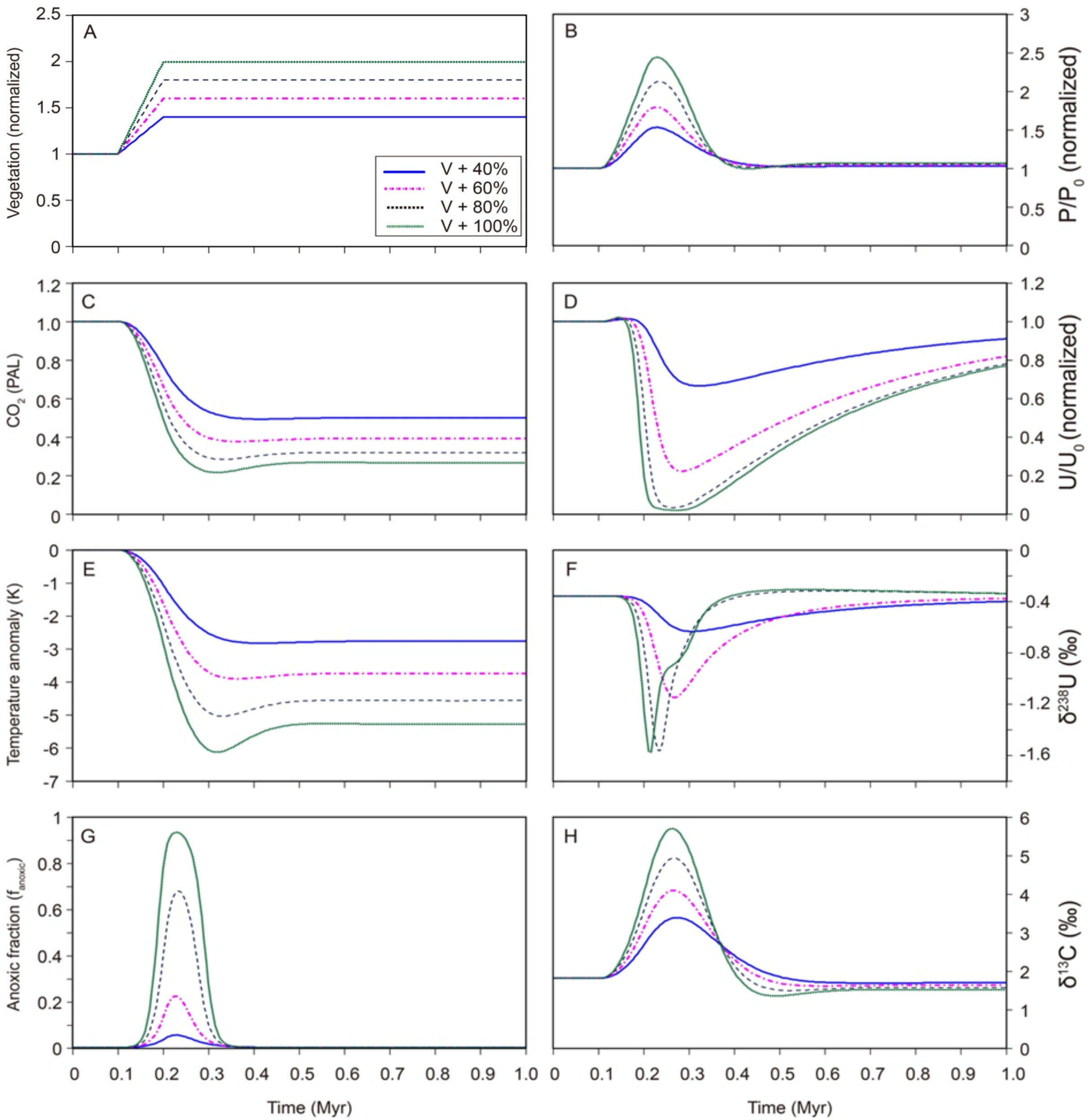
C-P-U cycle model results for cumulative carbon releases of 1 × 10^{18} mol C, 1.5 × 10^{18} mol C, 2 × 10^{18} mol C, 3 × 10^{18} mol C.



Zhang et al., 2020a, GCA

U同位素与生物地球化学模型COPSE结合

C-P-U cycle model results for increases in vegetation coverage of 40%, 60%, 80% and 100%.



Zhang et al., 2020a, GCA

谢谢大家！

敬请评判指正！