Supplementary Information (SI) for

Anoxic depositional overprinting of $^{238}\text{U}/^{235}\text{U}$ in calcite:

When do carbonates tell black shale tales?

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A. Methods

A.1 Elemental concentration analysis

The concentrations of trace metals and major cations in all the samples were determined using iCAP Q inductively coupled plasma mass spectrometry (ICP-MS) at Arizona State University (ASU). Carbonate sediments were dissolved in 1 M HNO₃ to dissolve the calcium carbonate and centrifuged at 4500 rpm to separate the insoluble solid. The dissolved fraction was digested using conc. HNO₃ + 30 % H₂O₂ while the insoluble fraction was digested following the procedure described by Chen et al. (2018). After digestion, the soluble and insoluble fractions of each sample ran through UTEVA column chemistry separately for elemental concentration and U isotopic ratio measurements. The digested samples were diluted in 0.32 M HNO₃ for concentration analysis. The measurement precision for trace elements were generally $\pm 5\%$ by ICP-MS.

The sinking particles from sediment traps were freeze-dried (Millrock BT-48 freeze dryer) and weighed to obtain the net dry masses of the samples to calculate the flux of particles in the water column at different depths. The dried samples were digested using aqua regia, and conc. HNO₃ + 30 % H₂O₂ for elemental concentration analyses.

A.2 Uranium isotope measurements

U isotopic compositions were measured using ²³³U-²³⁶U double-spike method by multicollector-inductively coupled plasma mass spectrometer (MC-ICP-MS) at ASU (Chen et al., 2016). Prior to U purification, each digested sample was mixed with double-spike U solution (IRMM-3636) to achieve a spike:sample molar ratio of 0.0363. The double-spike is used to correct for any isotope fractionation that might occur during the U purification process and sample analysis.

The protocol of U purification followed Chen et al. (2016). After rinsing the polypropylene columns (BioRad#7311550) with 10 ml 18.2 MΩ-cm deionized water, a volume of 1 ml UTEVA resin (Eichrom Technologies, LLC) was loaded on each column. The resin was then conditioned by passing through 2.5 ml 0.05 M HCl four times to remove impurities, and 0.8 ml 3 M HNO₃ three times to convert the resin to nitric form. Then the double-spiked U sample (dissolved in 3 M HNO₃) was loaded on the column and rinsed with 3 M HNO₃ (2 + 2 + 2 + 3 + 3 ml) to remove all matrix ions except U and Th. The resin was then converted to chloride form by passing through 10 M HCl (3 × 1 ml). Th was removed by a mixture of 5 M HCl and 0.05 M oxalic acid (3 × 1 ml). Then, the oxalic acid was removed by rinsing 5 M HCl (3 × 1 ml). The adsorbed U on the resin was eluted using 0.05 M HCl (1 + 1 + 1 + 2 + 2 ml). The U cuts were dried down and then heated with a mixture of 2 ml concentrated HNO₃ and 0.2 ml 30 % H₂O₂ to remove any organic residue eluted from the UTEVA resin. This process was repeated twice to ensure sample purity.

After UTEVA column chemistry, U samples dissolved in 0.32 M HNO₃ were measured MC-ICP-MS at a U concentration of ~ 50 ppb. Ion beams of ²³³U, ²³⁵U, ²³⁶U, and ²³⁸U were collected with Faraday cups connected to 10¹² Ω, 10¹² Ω, 10¹² Ω, and 10¹¹ Ω resistors, respectively. The typical voltage for ²³⁸U at a U concentration of 50 ppb was ~ 30 V. U isotopic compositions are reported in δ notation relative to the reference standard CRM-145a as follows:

$$\delta^{238}\text{U} = \left[\frac{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}}}{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{CRM-145a}}} - 1 \right] \times 1000 \quad \text{Eq. S1}$$

After UTEVA column chemistry, each sample was typically analyzed in triplicate provide adequate U was available. The precision of the U isotope measurement in this study was reported as twice the standard deviation (2 SD) of the reference standard CRM-145a or the 2 SD of triplicate

analyses of the samples, whichever was larger. The standard CRM-145a was analyzed before and after every two samples to correct for small amounts of instrument drift. The reproducibility of multiple runs of $\delta^{238}\text{U}$ for the standard CRM-145a were within ± 0.10 ‰, respectively (2 SD, N = 45). The accuracy of U isotope measurement was confirmed by multiple analyses of the secondary standard CRM-129a, which gave a value of -1.70 ± 0.08 ‰ (N = 8, 2 SD), indistinguishable from independent measurements by other laboratories (Wang et al., 2015; Jemison et al., 2016; Lau et al., 2016). Our measured value from CRM129a is lighter than $\delta^{238}\text{U}$ of one separate aliquot of CRM-129a measured at Stanford University (-1.52 ± 0.13 ‰) and the certified value of CRM-129a by New Brunswick Laboratory (-0.90 ± 0.53 ‰). This suggests that one or more batches of CRM-129a may be heterogeneous.

The blank from the UTEVA column chemistry purification step was about 0.02 ± 0.02 ng (2 SD, N = 6), which was negligible relative to the >100 ng U sample. Four aliquots of the reference standard CRM-145a were purified together with natural samples of FGL. The average value of $\delta^{238}\text{U}$ for these aliquots of CRM-145a was 0.00 ± 0.03 ‰, which was identical to the direct measurement of pure CRM-145a (0.00 ± 0.03 ‰).

A.3 Estimation of authigenic U concentration and $\delta^{238}\text{U}$ values

Uranium in the bulk sinking particles of sediment traps and sediments of FGL are assumed to consist of detrital, carbonate and authigenic fractions (Andersen et al., 2014). The detrital fraction (f_{detrital}) of U was estimated by normalization to the average shale (Tribovillard et al., 2006) using the equation:

$$f_{\text{detrital}} = \frac{(\text{U/Al})_{\text{AS}}}{(\text{U/Al})_{\text{sample}}} \quad \text{Eq. S2}$$

80 where the subscript ‘AS’ represent average shale. $(U/Al)_{AS}$ (3.37×10^{-5}) is close to the average
 81 values of U/Al in the three bedrock samples of FGL (3.48×10^{-5}). The carbonate fraction of U (f_{carb})
 82 was calculated using the equation:

$$f_{carb} = \frac{(U/Ca)_{calcite}}{(U/Ca)_{sample}} \quad \text{Eq. S3}$$

83 where $(Ca/U)_{calcite}$ (0.65×10^{-6}) is the Ca to U ratio in calcite formed at the surface water of FGL
 84 (See Table S3). As a result, authigenic U concentration (U_{auth}) and isotopic composition ($\delta^{238}U_{auth}$)
 85 are calculated as:

$$U_{auth} = U_{sample} \times (1 - f_{detrital} - f_{carb}) \quad \text{Eq. S4}$$

$$\delta^{238}U_{auth} = \frac{\delta^{238}U_{sample} - f_{detrital} \times \delta^{238}U_{detrital} - f_{carb} \times \delta^{238}U_{calcite}}{1 - f_{detrital} - f_{carb}} \quad \text{Eq. S5}$$

86 where $\delta^{238}U_{detrital}$ is -0.30 ‰ (Bedrock samples in this study), and $\delta^{238}U_{calcite}$ is -0.51 ‰ (see Table
 87 S3). U isotopic composition in carbonate sediments deposited under anoxic bottom waters was
 88 defined as:

$$\delta^{238}U_{carb} = \frac{\delta^{238}U_{sample} - f_{detrital} \times \delta^{238}U_{detrital}}{1 - f_{detrital}} \quad \text{Eq. S6}$$

89 where U in carbonate sediments include both authigenic U in the sediments due to anoxic
 90 deposition and U derived from primary calcite.

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92 **B. Estimation of fluxes of particulate authigenic U in sediment traps**

93 To quantitatively assess the contributions of the two U(VI) reduction processes (U
 94 reduction in the anoxic water column and below the sediment-water interface) to the water profile
 95 of dissolved U concentration and $\delta^{238}U$ below the chemocline, we compared the annual flux of
 96 particulate authigenic U (PAU which excludes U from detrital and calcite fractions) at the deepest

sediment trap (45.5 m) with the annual flux of authigenic U in the carbonate sediments deposited under anoxic bottom waters.

The annual flux of PAU (AF_{PAU}) at 45.5 m is calculated as:

$$AF_{PAU} = \frac{AF \times U_{PAU}}{M_U} \quad \text{Eq. S7}$$

where AF is the annual total mass flux ($348 \text{ g m}^{-2} \text{ yr}^{-1}$, Table S4) of sinking particles, U_{PAU} (= 0.32 ppm) is the U concentration of particulate authigenic U, and M_U is the molecular weight of U ($238.029 \text{ g mol}^{-1}$). Substituting these values into Eq. S7, AF_{PAU} at 45.5 m is $0.47 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$.

C. Estimation of fluxes of authigenic U in sediments deposited under anoxic conditions

The annual authigenic U flux (AF_{anox}) in the carbonate sediments deposited under anoxic bottom waters is estimated using the equation:

$$AF_{anox} = \frac{MAR \times U_{anox-auth}}{M_U} \quad \text{Eq. S8}$$

where $U_{anox-auth}$ ($\sim 2 \text{ ppm}$) is the authigenic U concentration in sediments deposited under anoxic conditions, and MAR is the annual mass accumulation rate of sediments in units of $\text{g m}^{-2} \text{ yr}^{-1}$.

MAR can be estimated using the equation:

$$MAR = LSR \times \rho \quad \text{Eq. S9}$$

where ρ and LSR are the dry density of sediments ($= 1.00 \text{ g ml}^{-1}$) and the sedimentation rate of sediments (0.7 mm/year ; Hilfinger et al., 2001). Submitting these values into Eq. S9, we can obtain the value of $700 \text{ g m}^{-2} \text{ yr}^{-1}$ for MAR.

Substituting the value of MAR ($= 700 \text{ g m}^{-2} \text{ yr}^{-1}$) into Eq. S9, we can get $AF_{anox} = 5.88 \text{ } \mu\text{mol m}^{-2} \text{ yr}^{-1}$. Thus, sinking particles in FGL contributes about 8 % of authigenic U to the carbonate sediments deposited under anoxic conditions.

116 **D. Summary of geochemical data for Fayetteville Green Lake**

117 Table S1. U concentration, $\delta^{234}\text{U}$ and $\delta^{238}\text{U}$ in water samples of Fayetteville Green Lake

Sample	Depth m	U nM	$\delta^{234}\text{U}$ ‰	2 SD ‰	$\delta^{238}\text{U}$ ‰	2 SD ‰
TM00	0	9.28	683	6	-0.54	0.10
TM01	0	9.37	679	6	-0.50	0.10
TM02	2	9.28	684	6	-0.56	0.10
TM03	4	10.54	677	6	-0.62	0.10
TM04	6	11.01	663	6	-0.56	0.10
TM05	8	11.18	665	6	-0.53	0.10
TM06	10	11.26	669	6	-0.50	0.10
TM07	12	11.30	670	6	-0.48	0.10
TM08	16	11.76	680	6	-0.52	0.10
TM09	16.5	11.60	683	6	-0.57	0.10
TM10	17	11.64	691	6	-0.57	0.10
TM11	17.5	11.68	694	6	-0.54	0.10
TM12	18	12.27	705	6	-0.53	0.10
TM13	18.5	11.47	699	6	-0.52	0.10
TM14	19.5	11.81	690	6	-0.59	0.10
TM15	20.5	11.26	696	6	-0.61	0.10
TM16	21.5	10.17	701	6	-0.62	0.10
TM17	22	9.79	709	6	-0.68	0.10
TM18	22.5	9.16	708	6	-0.71	0.10
TM19	23	8.82	721	6	-0.67	0.10
TM20	23.5	8.02	714	6	-0.72	0.10
TM21	24	7.14	713	6	-0.69	0.10
TM22	31	6.47	714	6	-0.70	0.10
TM23	33	6.34	717	6	-0.75	0.10
TM24	41	4.37	720	6	-0.83	0.10
TM25	43	4.03	721	6	-0.88	0.10
TM26	46	3.82	722	6	-0.94	0.10
TM27	48	3.57	722	6	-0.96	0.10
Inlet	0	7.60	775	6	-0.55	0.10
Outlet	0	9.58	642	6	-0.57	0.10

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Table S2. Summary of elemental concentrations and $\delta^{238}\text{U}$ in primary calcite formed in surface water and carbonate sediments deposited under anoxic bottom waters of Fayetteville Green Lake

Sample Types	Sample No.	Depth cm	Al ppm	Ca wt%	U ppm	$\delta^{238}\text{U}$ ‰	2 SD ‰	$\delta^{238}\text{U}_{\text{carb}}$ ‰
Anoxic carbonate sediments	LS01	0.25	5894	25	1.75	−0.32	0.10	−0.28
	LS03	2.25	5810	23	1.83	−0.38	0.10	−0.34
	LS05	4.25	4075	29	1.91	−0.30	0.11	−0.27
	LS07	6.25	7436	27	1.69	−0.43	0.10	−0.37
	LS09	8.25	9422	27	2.74	−0.31	0.10	−0.27
	LS11	10.5	6660	26	2.25	−0.23	0.10	−0.19
	LS13	14.5	5280	25	2.11	−0.32	0.12	−0.29
	LS15	18.5	9978	28	2.03	−0.38	0.17	−0.32
	LS17	22.5	7141	27	3.22	−0.64	0.10	−0.61
	LS19	26.5	2916	28	1.92	−0.43	0.16	−0.41
	LS21	32	422	30	4.66	−0.33	0.10	−0.33
	LS23	40	246	29	2.61	−0.28	0.10	−0.28
Bedrock	GVSHC	—	—	—	1.29	−0.28	0.14	—
	RVSHC	—	—	—	0.57	−0.24	0.10	—
	Dolomite	—	—	—	0.26	−0.31	0.10	—
Surface water primary calcite	BC01	—	32	36	0.22	−0.53	0.10	—
	BC02	—	38	35	0.29	−0.51	0.10	—
	BC03	—	20	35	0.22	−0.50	0.10	—
	BC04	—	25	36	0.37	−0.50	0.10	—
	BC05	—	22	37	0.21	−0.53	0.10	—

Note: Anoxic carbonate sediments means carbonate sediments deposited under anoxic bottom waters in Fayetteville Green Lake. $\delta^{238}\text{U}_{\text{carb}}$ was estimated using Eq. S6. Surface water primary calcite samples were collected from the uppermost layer (0 – 1.5 cm) of the bioherm using a rock hammer at Dead Man's Point, Fayetteville Green Lake.

Table S3. Summary of geochemical data in sediment traps.

Depth	AF	AF _{PAU}	Al	Ca	U	U _{PAU}	$\delta^{238}\text{U}$	$\delta^{238}\text{U}_{\text{PAU}}$
m	$\text{g m}^{-2} \text{yr}^{-1}$	$\mu\text{mol m}^{-2} \text{yr}^{-1}$	ppm	wt%	ppm	ppm	‰	‰
12.1	336	0.42	2531	31	0.59	0.30	-0.48	-0.51
19.5	434	0.58	2484	27	0.58	0.32	-0.45	-0.44
27	362	0.53	2769	29	0.63	0.35	-0.37	-0.30
45	348	0.47	2608	24	0.56	0.32	-0.28	-0.16

Note: AF is the annual total mass flux, and AF_{PAU} is the annual particulate U flux in sinking particles. U_{PAU} and $\delta^{238}\text{U}_{\text{PAU}}$ represent particulate authigenic U (PAU) concentration and isotopic composition.

Table S4. Aqueous uranium speciation in the water column of Fayetteville Green Lake and modern seawater

Depth	pH	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	UO ₂ (CO ₃) ₂ ²⁻	UO ₂ (CO ₃) ₃ ⁴⁻	Ca ₂ UO ₂ (CO ₃) ₃	CaUO ₂ (CO ₃) ₃ ²⁻	MgUO ₂ (CO ₃) ₃ ²⁻
m		mM	mM	mM	mM	mM	mM	%	%	%	%	%
Fayetteville Green Lake water column												
0	7.88	1	2.4	9.74	1.49	9.74	1.64	0.02	0.11	92.22	7.31	0.33
6	7.49	1.1	2.61	11.19	1.46	9.59	2.22	0.03	0.10	92.96	6.66	0.29
16	7.21	1.13	2.75	12.1	1.54	10.88	2.21	0.04	0.09	93.12	6.52	0.27
20	7.29	1.23	3.01	13.6	1.85	11.28	2.71	0.06	0.09	93.40	6.11	0.25
25	6.96	1.35	3.18	14.08	1.91	15.31	4.39	0.04	0.10	93.03	6.55	0.27
31	6.95	1.36	3.12	13.56	1.97	14.7	3.79	0.05	0.11	92.94	6.63	0.28
41	6.95	1.55	3.3	14.02	2.39	14.06	4.2	0.04	0.10	93.15	6.42	0.28
48	6.95	1.62	3.33	14.02	2.53	14.06	4.51	0.04	0.10	93.13	6.44	0.28
Modern seawater												
0	8.2	480	56	10	560	28	2.3	0.04	5.95	58.08	18.01	17.80

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