

Open system dating of corals recrystallized to calcite

The age estimation model is based on a simple geological/geochemical evolution of the reef from the time of its primary deposition through submarine diagenesis by marine groundwater, subsequent recrystallization in freshwater coastal aquifer and uplift to the present day level. The evolution of the U-Th system along this track is depicted in Fig. 1 of the manuscript. The primary deposition age of the coral is estimated by combining two close system ages: The age of coral deposition and the age of recrystallization to calcite.

Below we describe the procedure used to estimate these two ages:

The model assumes a reef terrace uplift history consisting of four consecutive steps (Fig. 2):

1. The terrace rocks are saturated with marine groundwater with high $^{234}\text{U}/^{238}\text{U}$ ratio. This early submarine diagenesis enriched the reef aragonite corals with U, elevating also their $^{234}\text{U}/^{238}\text{U}$ ratio (see Lazar et al., 2004).
2. While submerged, before reaching the fresh groundwater aquifer, the pores of the terrace aragonite corals were saturated with marine groundwater (forming a submarine saline groundwater aquifer) behaving as U-Th close system.
3. Terrace uplift into the zone of coastal freshwater aquifer (after crossing the salinewater/freshwater interface). During a short period compared to the age of terrace deposition, the terrace system opened and the aragonite corals were recrystallized to calcite, losing as a result substantial amounts of U while retaining virtually all radiogenic Th.
4. Further subaerial uplift to the present day elevation of the terrace. During that final step, the recrystallized (calcite) reef corals behaved as close U-Th system.

The closed system equations used here are the regular activity equations for ^{238}U (A_{238}), ^{234}U (A_{234}) and ^{230}Th (A_{230}), equations (1), (2) and (3), respectively:

$$A_{238} = ^{238}\text{U} = A_{238}^0 \cdot e^{-\lambda_{238} \cdot t} \quad (\text{DRE1})$$

$$A_{234} = ^{234}\text{U} = A_{238}^0 \cdot \frac{\lambda_{234}}{\lambda_{234} - \lambda_{238}} \cdot (e^{-\lambda_{238} \cdot t} - e^{-\lambda_{234} \cdot t}) + A_{234}^0 \cdot e^{-\lambda_{234} \cdot t} \quad (\text{DRE2})$$

$$A_{230} = ^{230}\text{Th} = A_{238}^0 \cdot \lambda_{230} \cdot \lambda_{234} \cdot \left(\frac{1}{(\lambda_{234} - \lambda_{238}) \cdot (\lambda_{230} - \lambda_{238})} \cdot e^{-\lambda_{238} \cdot t} - \frac{1}{(\lambda_{234} - \lambda_{238}) \cdot (\lambda_{230} - \lambda_{234})} \cdot e^{-\lambda_{234} \cdot t} + \frac{1}{(\lambda_{230} - \lambda_{238}) \cdot (\lambda_{230} - \lambda_{234})} \cdot e^{-\lambda_{230} \cdot t} \right) + A_{234}^0 \cdot \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \cdot (e^{-\lambda_{234} \cdot t} - e^{-\lambda_{230} \cdot t}) + A_{230}^0 \cdot e^{-\lambda_{230} \cdot t} \quad (\text{DRE3})$$

or in terms of isotope activity ratios:

$$\frac{A_{234}}{A_{238}} = \frac{^{234}\text{U}}{^{238}\text{U}} = (1 - e^{-\lambda_{234} \cdot t}) + \frac{A_{234}^0}{A_{238}^0} \cdot e^{-\lambda_{234} \cdot t} \quad (\text{DRE4})$$

$$\frac{A_{230}}{A_{238}} = \frac{^{230}\text{Th}}{^{238}\text{U}} = \left(1 - \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \cdot e^{-\lambda_{234} \cdot t} + \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}} \cdot e^{-\lambda_{230} \cdot t} \right) + \frac{A_{234}^0}{A_{238}^0} \cdot \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \cdot (e^{-\lambda_{234} \cdot t} - e^{-\lambda_{230} \cdot t}) + \frac{A_{230}^0}{A_{238}^0} \cdot e^{-\lambda_{230} \cdot t}$$

where A_{23i}^0 denotes the activity at time zero of one of the three isotopes; the character $i=8, 4, 0$ for the isotopes ^{238}U , ^{234}U and ^{230}Th , respectively; and λ_{23i} denotes the activity constant of one of the three isotopes.

Description of the simultaneous iterations used for calculating ages of terrace deposition and age of recrystallization:

The age of the recrystallized reef terrace TR4 (DR Fig. 1) is estimated by simultaneous iterations of the two close systems discussed above:

1. Backward calculation of the U-Th isotopic composition of the calcite reef terrace TR4 at any time in the past by running equations DRE1-DRE3 backwards (starting at $t=0$ in the direction $t \leq 0$) with A_{23i}^0 substituted by the present day (the measured) nuclide activities. The absolute value of the negative time obtained at the end of the iteration (The criterion for stopping the two simultaneous iterations is given below in section “*The criterion for ending the iterations*”) is Δt_2 which is the period that the calcite reef terrace has been subaerial (from the time it emerged above the freshwater level up to its present position as elevated terrace; Δt_2 is the time interval of step #4 above).

2. Forward calculation of the U-Th isotopic composition of a “hypothetical” aragonite reef terrace that during early submarine diagenesis gained U and increased its $^{234}\text{U}/^{238}\text{U}$ ratio. This is conducted by running forwards (starting at $t=0$ in the direction $t \geq 0$) equations DRE1-DRE3 for the starting conditions of the “hypothetical” aragonite reef terrace. The time obtained at the end of the iteration (The criterion for stopping the two simultaneous iterations is given below in section “*The criterion for ending the iterations*”) is Δt_1 , which is the period during which the reef terrace was uplifted while still submarine, before reaching the fresh groundwater aquifer (Δt_1 is the time interval of step #2 above). The A_{23i}^0 of the nuclides for this calculation was estimated from the range of ^{238}U , ^{234}U activities and the $^{234}\text{U}/^{238}\text{U}$ activity ratios in last interglacial (LIG) elevated aragonite reef terrace (Scholz et al., 2004). The procedure for A_{23i}^0 is detailed below, in the section “*Estimating the possible range of A_{234}^0 and A_{238}^0 and the A_{234}^0/A_{238}^0 ratios of a “hypothetical” aragonite reef terrace at the end of early submarine diagenesis*”.

The estimated age of deposition, t , for reef terrace TR4 is therefore $t = \Delta t_1 + \Delta t_2$.

Estimating the possible range of A_{234}^0 and A_{238}^0 and the A_{234}^0/A_{238}^0 ratios of a “hypothetical” aragonite reef terrace at the end of early submarine diagenesis:

The corals used here were sampled from the last interglacial (LIG) elevated reef terrace at Aqaba (Jordan) and from the Holocene reef there (data from ref 16) and from the Holocene reef of Tur-Yam at Eilat (Israel). The data for the elevated LIG reef terrace TR2 (dated to ~120 ka BP) and the Holocene reefs (dated to ~3 ka BP and ~6 ka BP for the Aqaba and Eilat corals, respectively) show that the $^{234}\text{U}/^{238}\text{U}$ activity ratio increases with the activity of ^{238}U (DR Fig. 2). Corals from the aragonite LIG reef terrace TR2 gained during early diagenesis (while terrace was still submerged), substantial amounts of ^{238}U and ^{234}U as compared to the Holocene corals (Supp. Figs. 3a,b). The Holocene corals have rather intermediate U concentration, much higher than the calcite corals of TR4 but lower than the aragonite corals of the Aqaba LIG reef (DR Figs. 3a-e). These corals show either U gain with normal marine $^{234}\text{U}/^{238}\text{U}$ activity ratio (Tur-Yam coral in Supp. Fig. 3a,b) or both U gain and increase in the $^{234}\text{U}/^{238}\text{U}$ activity ratio (Aqaba coral in DR Fig. 3a,b). This suggests that already during very early submarine diagenesis aragonite corals gained U with elevated $^{234}\text{U}/^{238}\text{U}$ ratio. The reef terrace was probably affected by marine groundwater with high U and $^{234}\text{U}/^{238}\text{U}$ ratio due to interaction with the nearby granites (Lazar et al., 2004). The initial $^{234}\text{U}/^{238}\text{U}$ ratio and ^{238}U content of the “hypothetical” reef terrace was estimated by calculating the composition of the corals of the 120 ka BP old LIG aragonite reef terrace TR 2 at 100 ka BP, when it was 20 ka old (the red green and blue +-s in Supp.

Fig. 3). The trend line of the $^{234}\text{U}/^{238}\text{U}$ ratio versus ^{238}U for that period (the range between the dashed red lines in DR Fig. 2) was used to estimate the initial $^{234}\text{U}/^{238}\text{U}$ ratio of the “hypothetical” reef. The initial range of ^{238}U of the “hypothetical” reef was taken as the ^{238}U concentration range of the LIG reef terrace TR2 at Aqaba (Scholz et al., 2004).

The criterion for ending the iterations:

The criterion for ending the two iterations for obtaining simultaneously Δt_1 and Δt_2 is based on the large difference between the U distribution coefficients ($^U K_D$) of aragonite ($^U K_{D,\text{arg}}$) and calcite ($^U K_{D,\text{cal}}$), where $^U K_{D,\text{arg}} > 1$ and $^U K_{D,\text{cal}} < 1$ (Lazar et al., 2004). This implies that when the reef terrace was uplifted through the fresh groundwater coastal aquifer and the corals recrystallized from aragonite to calcite they lost substantial amounts of U to the porewater. The recrystallization has therefore a potential to markedly increase the U concentration of the porewater. Depending on the rate of groundwater exchange in the aquifer (the effective water/rock ratio) the U concentration of porewater may increase from ambient concentration of several ppb to more than 1 ppm or by a factor of several hundreds up to a thousand. This is deduced from the ~2 ppm decrease in the U content of the calcite reef terrace as compared to the aragonite reef terrace (DR Fig. 3a-e). A release of 2 ppm U from the reef terrace rock should increase the maximum porewater concentration (in case of no groundwater flow) to ~10 ppm (assuming reef terrace bulk density of 1.8). Hence even if the effective water/rock ratio during recrystallization is one order of magnitude larger than the porosity, the porewater U concentration should increase to 1 ppm, an enrichment factor of several hundreds. This means that during recrystallization from aragonite to calcite, the $^{234}\text{U}/^{238}\text{U}$ ratio of the newly formed calcite remains essentially identical to the $^{234}\text{U}/^{238}\text{U}$ ratio of the original aragonite. The total U (practically all ^{238}U) concentration of the calcite is determined by the $^U K_{D,\text{cal}}$ and the porewater U concentration. This means that for a given hydrological conditions in the coastal aquifer (controlling the effective water/rock ratio), the ratio of U in the formed calcite to the U of the original aragonite is constant.

The recrystallization scenario assumes no Th loss, which means that the Th content in the recrystallized calcite remained essentially identical to its content in the original aragonite coral, due to the high affinity of Th to solids.

The iterations are conducted in the ^{230}Th versus ^{238}U field (DR Figs. 3c-e). The isotopic composition of each data point of reef terrace TR4 (DR Fig. 3c) was calculated backwards in time, as explained in item #1 of section “*Description of the simultaneous iterations used for calculating ages of terrace deposition and age of recrystallization*”, above. The backward calculation was conducted also on the linear trend-line (best fit) of TR4 (two data points with the highest U content were omitted from the fit; for reasoning see explanation below). The data points and the trend lines were plotted together for comparison (red +-s in DR Fig. 3d). A similar forward calculation was conducted on the “hypothetical” aragonite reef (the solid purple line at $^{230}\text{Th}=0$, in DR Fig. 3d), as explained in item #2 of section “*Description of the simultaneous iterations used for calculating ages of terrace deposition and age of recrystallization*”, above. The forward calculation yields for each time a linear line, but with different slope and intercept. The time is incremented independently for the calcite reef terrace TR4 and the “hypothetical” aragonite reef terrace yielding two trend lines, the line for the “hypothetical” reef:

$$^{238}\text{U}_{\text{arg}} = a_{0,\text{arg}} + a_{1,\text{arg}} \cdot ^{230}\text{Th}_{\text{arg}} \quad (\text{DRE6})$$

and the line for the calcite reef terrace TR4:

$$^{238}\text{U}_{\text{cal}} = a_{0,\text{cal}} + a_{1,\text{cal}} \cdot ^{230}\text{Th}_{\text{cal}} \quad (\text{DRE7})$$

where a_0 and a_1 denote the intercept and the slope, respectively. Reconstructing back the ^{238}U , ^{230}Th composition of TR4 before its recrystallization to calcite is conducted by the linear transformation which fulfils the condition imposed by the $^U K_{D,\text{cal}}$:

$$^{238}\text{U}_{\text{arg}} = F \cdot ^{238}\text{U}_{\text{cal}} \quad (\text{DRE8})$$

where F is the U depletion factor of calcite. Substituting into DRE6 and DRE7 the Th conservation condition: $^{230}\text{Th}_{\text{arg}} = ^{230}\text{Th}_{\text{cal}}$, yields the reconstruction equation:

$$a_{0,\text{arg}} + a_{1,\text{arg}} \cdot ^{230}\text{Th}_{\text{arg}} = F \cdot (a_{0,\text{cal}} + a_{1,\text{cal}} \cdot ^{230}\text{Th}_{\text{arg}}) \quad (\text{DRE9})$$

Equation DRE9 indicates that the linear trend line of the “hypothetical” reef terrace can be transformed to the trend line of the calcite reef terrace TR4 by multiplying the intercept and the slope of TR4 by F as follows: $a_{0,\text{arg}} = F \cdot (a_{0,\text{cal}})$ and $a_{1,\text{arg}} = F \cdot (a_{1,\text{cal}})$.

The calculated ages of the calcite reef terrace TR4:

The simultaneous iterations of forward calculation of the “hypothetical” aragonite reef terrace and the backward calculation of the calcite reef terrace TR4 were stopped when the aragonite to calcite intercepts ratio was equal to the aragonite to calcite slopes ratio:

$$\frac{a_{0,\text{arg}}}{a_{0,\text{cal}}} = \frac{a_{1,\text{arg}}}{a_{1,\text{cal}}} = F$$

The value of F (at the level of three significant digits) was found to be 2.54 (DR Fig. 3d). This means that the aragonite corals lost a factor of 2.54 of their U content, during recrystallization to calcite. The ages calculated by the iteration are:

1. The period, Δt_1 , which passed from the time of TR4 deposition until end of recrystallization is estimated to be 48.4 ka.
2. The period, Δt_2 , which passed from the time the terrace emerged above the freshwater level up to its present position as elevated terrace TR4 is estimated to be 141.9 ka.
3. The estimated age of TR4 deposition is therefore $48.4 + 141.9 = 190.3$ ka BP.

The ^{230}Th versus ^{234}U of the Holocene coral, LIG aragonite reef terrace (16) and calcite reef terrace TR4 (DR Figs. 3f-h) show also that their evolution through time also fall on straight lines. The ^{230}Th versus ^{234}U composition of corals from the LIG aragonite reef terrace calculated 71.6 ka backwards (blue, green, red +s and x-s in DR Figs. 3g,h) and their best fit (dashed purple lines in DR Figs. 3g,h) follows nicely the trend line of the forward calculation of the “hypothetical” aragonite reef terrace (solid purple lines in DR Figs. 3g,h). This indicates that the aragonite corals in the LIG reef terrace follow rather nicely a close system evolution with no significant gain or loss of U and Th.

The position of the sample containing the highest ^{238}U in the calcite reef terrace TR4 in the ^{230}Th versus ^{234}U field after “returning” it 141.9 ka backward (red +s in DR Figs. 3g,h) lies very close to the 48.4 ka BP trend line of the “hypothetical” aragonite reef (solid purple lines in DR Figs. g,h) calculated by a close system model (equations DRE1-DRE3). This corroborates the age of recrystallization suggesting that this coral sample retained most of its original U (and Th).

The coral sample U-Th composition and their calculated composition after their backward and forward transformations as estimated on the fields of ^{234}U versus ^{238}U , ^{230}Th versus ^{238}U and ^{230}Th versus ^{234}U (DR Fig. 3) follow a linear trend lines also on the traditional $^{234}\text{U}/^{238}\text{U}$ versus $^{230}\text{Th}/^{238}\text{U}$ field even for the calcite reef terrace TR4. It is rather reassuring that the sample with the lowest $^{230}\text{Th}/^{238}\text{U}$ in the calcite reef terrace TR4 plots almost on the 190.3 ka BP isochron, that is the open system age estimated for this terrace.

Table DR1. U-Th data for calcite corals from reef terrace TR4.

#	Sample	^{238}U nmol·g ⁻¹	^{232}Th nmol·g ⁻¹	^{230}Th pmol·g ⁻¹	$^{234}\text{U}/^{238}\text{U}$ activity	error 2σ	$^{230}\text{Th}/^{238}\text{U}$ activity	error 2σ
1	Aq B1	4.765	0.466	95.2	1.2064	0.0024	1.1935	0.0024
2	Aq B2	5.223	1.058	103.7	1.2005	0.0024	1.1860	0.0024
3	Aq B3	4.550	0.481	89.0	1.1954	0.0024	1.1678	0.0023
4	Aq B4	4.038	0.215	76.4	1.1726	0.0023	1.1289	0.0023
5	Aq B5	6.387	0.229	110.9	1.1939	0.0024	1.0367	0.0021
6	Aq B6	4.697	0.215	89.3	1.1833	0.0024	1.1352	0.0023
7	Aq B7	4.286	0.342	81.5	1.1782	0.0024	1.1357	0.0023
8	Aq B8	5.416	0.313	99.2	1.1663	0.0023	1.0941	0.0022
9	Aq B10	4.197	0.408	78.8	1.1784	0.0024	1.1207	0.0022
10	Aq B11	3.891	0.160	72.2	1.1805	0.0024	1.1078	0.0022



Figure DR1: The uplifted reef terraces at the northern Gulf of Aqaba (GOA), south to the city of Aqaba, Jordan. **a-** Satellite image showing the reef terraces and the cross-section A-A'.

b- Photograph of the different terraces along the A-A' cross-section: Terrace I (Holocene), and terraces II, III, and IV (Pleistocene). Aragonite and calcitic corals were recovered from terrace II (16), while calcitic corals are abundant in terraces III and IV. Reef terraces II and IV are named in the manuscript TR2 and TR4, respectively.

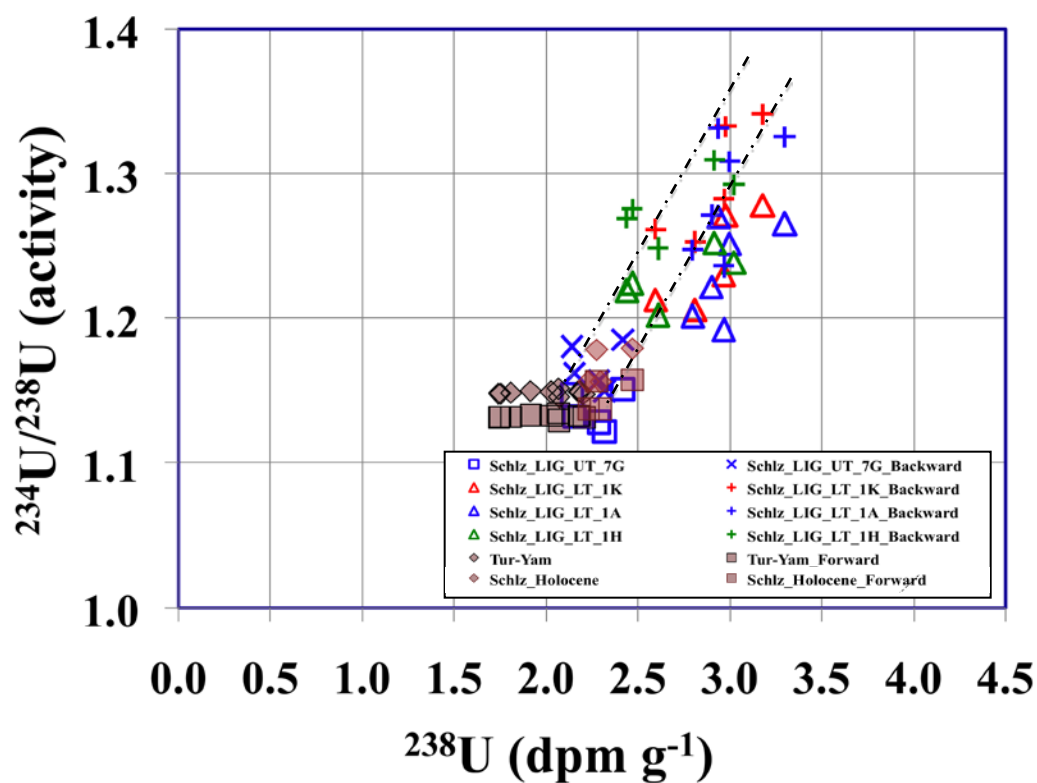


Figure DR2: The $^{234}\text{U}/^{238}\text{U}$ activity ratios versus ^{238}U activity in the GOA corals from the modern a fossil reef terraces (see text, Fig. DR1 and Table DR1).

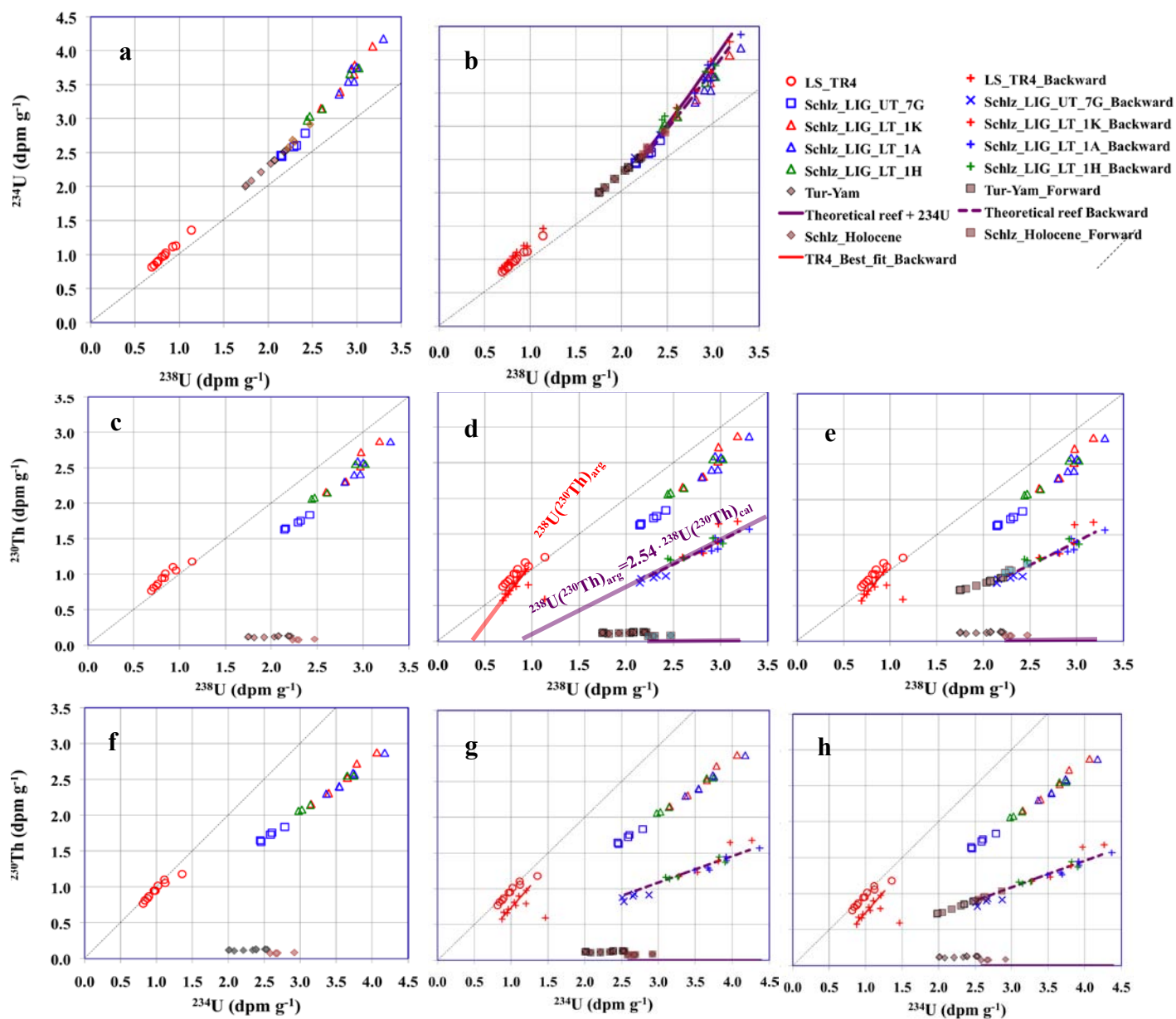
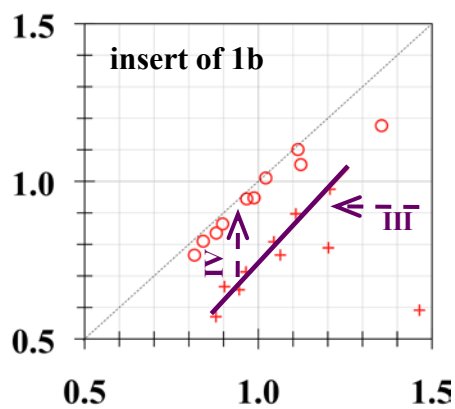
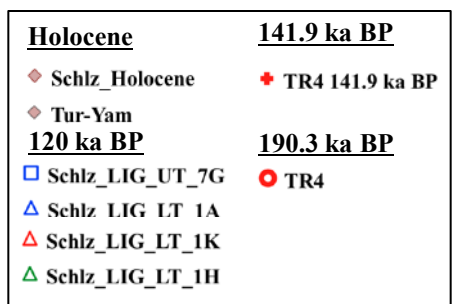
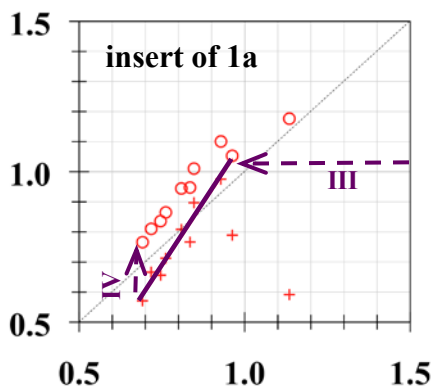


Figure DR3: Nuclide versus nuclide plots for the corals from the modern and fossil reef terraces in northern GOA (see text and DR Fig. 1). **a,b-** The ^{234}U versus ^{238}U activities; **c-e-** The ^{230}Th versus ^{238}U activities; and **f-h-** The ^{230}Th versus ^{234}U activities.



Data Repository Figure DR4