PALEO-DRIP RATES FROM TRACE METAL CONCENTRATIONS IN STALAGMITES

an inverse modeling problem with data uncertainties

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Summary

- The rate at which water drips from the cave ceiling onto the top of a stalagmite, i.e. the drip rate, is related to effective precipitation — the amount of rainfall absorbed at the surface
- Each drop of water that hits the stalagmite contains trace elements (Ni, Co, Cu, etc) trapped in Organic Metal Complexes (OMCs), which decay exponentially releasing the trace metals into the aqueous phase
- The released metal ions deposit into the stalagmite in a concentration dependent partitioning process
- Measuring trace elements along the depth of the stalagmite allow us to reconstruct the drip rate by inverting the relation between the time taken for the decay of OMCs and the trace metal concentrations
- We derive a new drip rate model and estimate model parameters using theoretical values, heuristic estimates based on monitoring data, along with meteorological data from a nearby weather station
- Our results captures long term trends in effective rainfall, corroborating existing knowledge about the weakening of monsoon during the Holocene
- However, we find that the '8.2 kyrs event' — described as a cold and dry period in the literature — did not result in a decrease in effective rainfall at Heshang

Outline of this report

- Drip rates as proxy for effective rainfall
  [a short background sketch]
- Using trace metals to estimate drip rates
  [a schematic sketch of our model]
- Relating trace element concentration in stalagmite to drip rate
  [the math underlying the model]
- Taking care of data uncertainties
  [estimating drip rate probabilities from the model]
- Calibrating the model for Heshang cave in south China
  [parameter estimation, heuristic choices, and least squares optimization]
- Results
  [reconstructed effective rainfall at Yichang and Holocene drip rate at Heshang]

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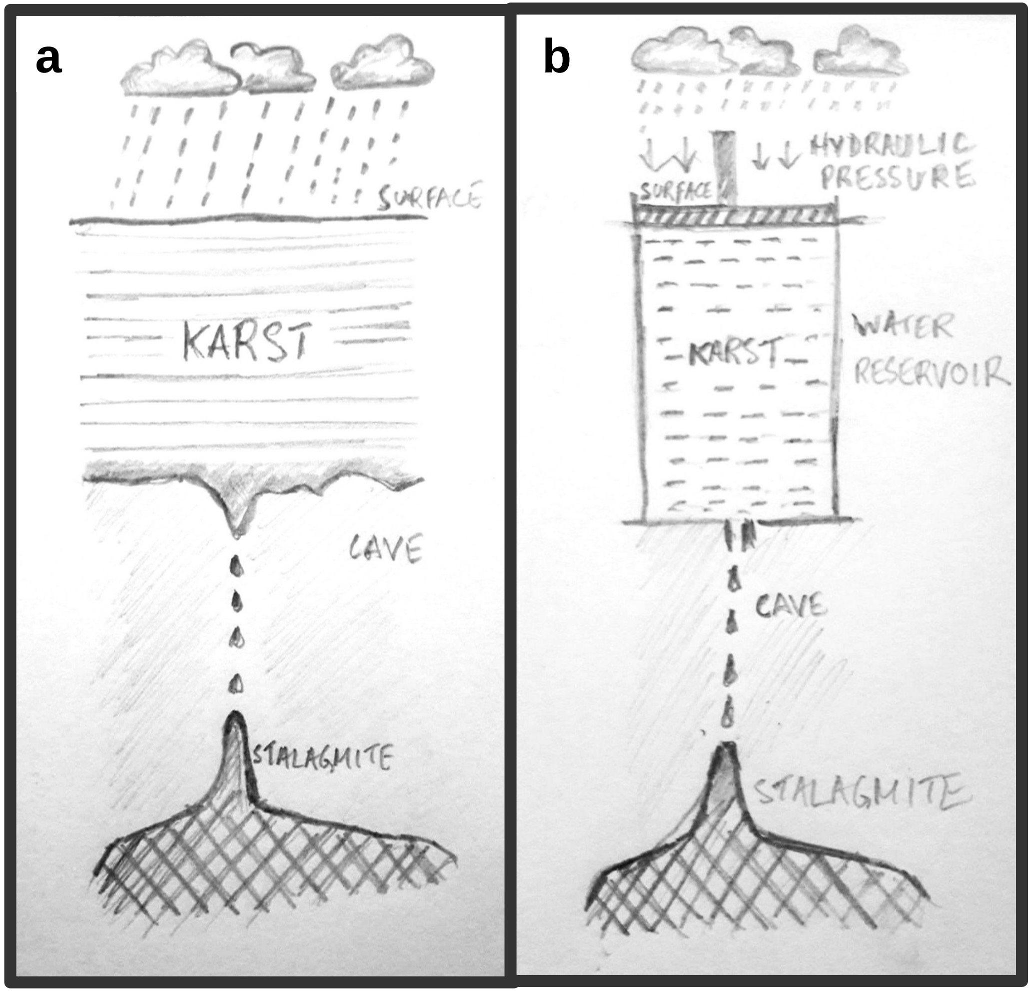
Drip rates as proxy for effective rainfall

- **Drip rates** are defined as the number of drops that fall on on the top of the stalagmite
- We assume the karst (as seen in **a**) to be a water reservoir (as seen in **b**), where the amount of rainfall absorbed at the surface (i.e. 'effective rainfall') exerts an 'instantaneous' hydraulic pressure at the drip point on the roof of the cave
- Higher effective rainfall is thus assumed to result in faster drip rates and vice versa
- Drip rates are therefore **a potential quantitative proxy** for effective rainfall



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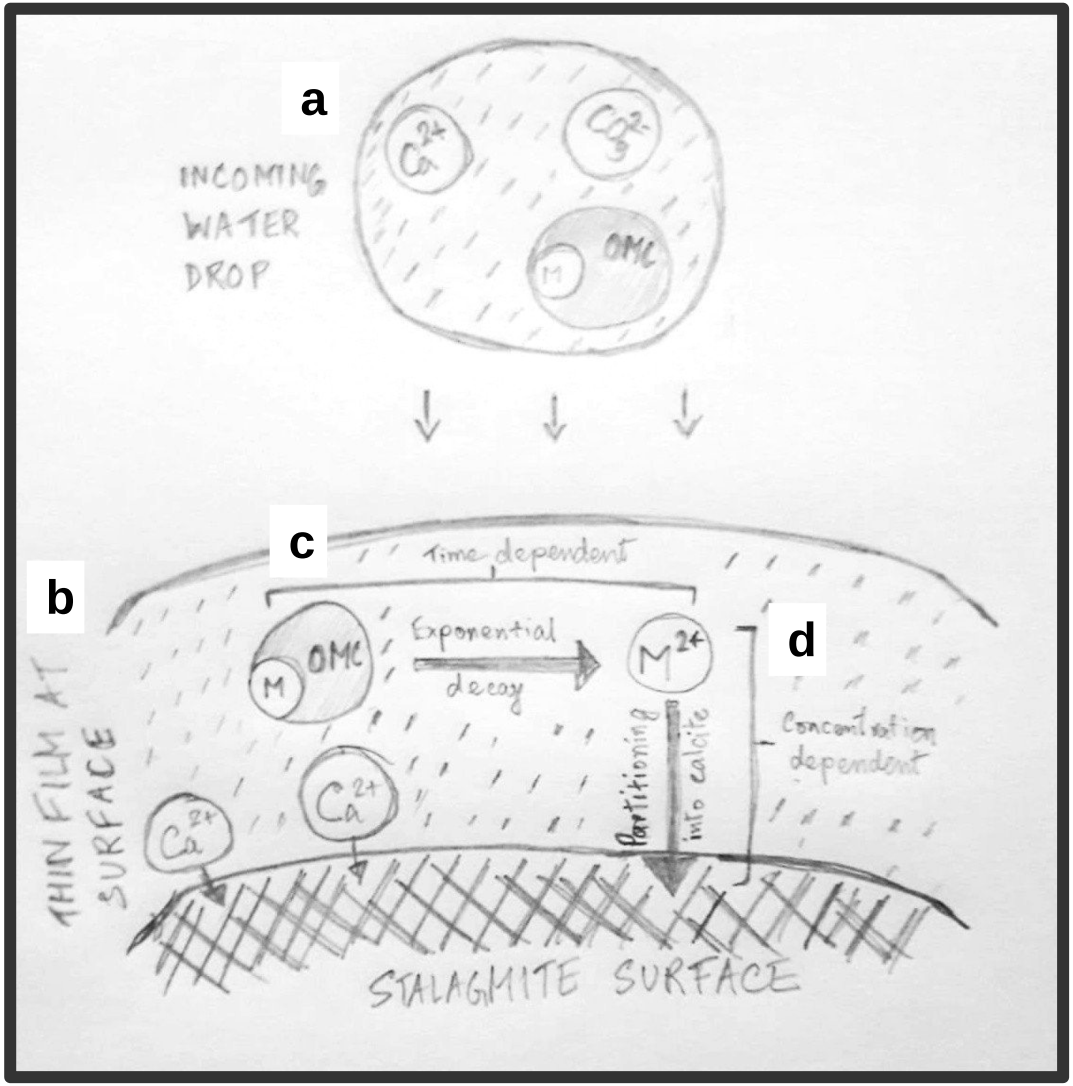
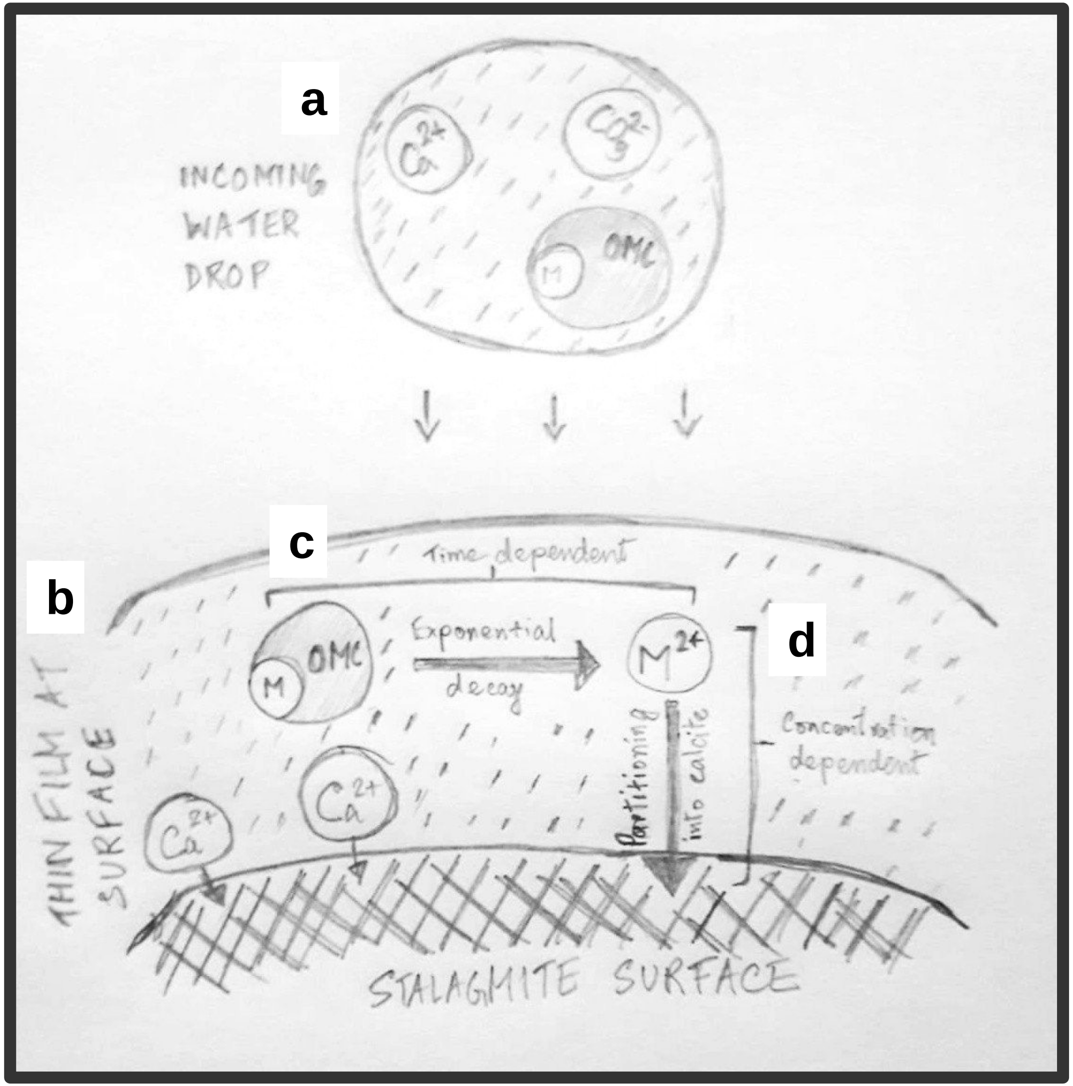
Using trace metals to estimate drip rates

- Incoming water drops contain $CaCO_3$ and trace metal ions trapped in organic metal complexes (OMCs) (shown in **a**) [1]
- Each water drop forms a thin film (shown in **b**) at the surface of the stalagmite which is replaced by the next drop
- Inside the thin film, two processes are relevant:
    - The OMCs release the trapped trace metal M^{2+} ions in a time dependent, exponential decay process (shown in **c**)
    - The released M^{2+} ions deposit into the calcite of the stalagmite in a concentration driven, partitioning process (shown in **d**)



Using trace metals to estimate drip rates

- Measuring the M^{2+} concentration in the stalagmite can thus allow as to infer the time available for its decay from OMCs, which in turn is the time between two incoming drops
- The time interval between two incoming drops is an estimate of the drip rate



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Relating trace element concentration in stalagmite to drip rate

- The partitioning process is governed by a **partitioning coefficient K_p**
- K_p is defined as a ratio of ratios, and is a theoretically estimable constant particular to each trace element (Co, Ni, Cu, etc)
- K_p is the relative concentration of the trace element (X) to that of calcium (Y) in the stalagmite ($_{st}$) to that in the aqueous thin film of water ($_{aq}$)
- Using this notation,
  - $\mathbf{X_{st}}$ ($\mathbf{X_{aq}}$) denotes trace element concentration in stalagmite (aqueous phase)
  - $\mathbf{Y_{st}}$ ($\mathbf{Y_{aq}}$) denotes calcium concentration in stalagmite (aqueous phase)

$$K_p = \frac{X_{st}/Y_{st}}{X_{aq}/Y_{aq}}$$

Relating trace element concentration in stalagmite to drip rate

- Replacing X_{aq} with the avaliable trace metal concentration X^{t}_{aq} as a result of the exponential decay of the OMCs, we can relate the concentration of trace element in the stalagmite $\mathbf{X_{st}}$ and the driprate **V**
- Each OMC decays with a slightly different decay constant $\mathbf{K_{d}}$, and the population of $\mathbf{K_{d}}$'s in the thin film are assumed to follow a lognormal distribution
- Defining $K = \ln(K_d)$, we use the expected value of decayed OMCs below based on the mean K_μ and standard deviation K_σ of the lognormal distribution based on observed data

$$X_{st} = K_p \frac{Y_{st} X^{t}_{aq}}{Y_{aq}} \left(1 - \int \frac{1}{K_\sigma \sqrt{2\pi}} \exp\left(- \frac{(K-K_\mu)^2}{2K_\sigma^2} \right) \exp\left(- \frac{e^{K}}{V} \right) dK \right)$$

trace element in stalagmite

driprate

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Taking care of data uncertainties

- Following the framework laid out in [2], we estimate the posterior probability distributions **$\rho(v|t)$** of the driprate V at each time point of the past
- Assuming the relation between X_{st} and V to be of the form $X_{st} = h(V)$, we can write down the probability density function (PDF) for the driprate given the quantity **$\rho(X_{st}|t) = \rho(h(v)|t)$** as shown below
- Here, we use ‘ to denote the derivative with respect to v

$$\rho(v|t) = \rho(h(v)|t)\, h'(v)$$

Taking care of data uncertainties

- Since we use two trace elements Ni and Co in our analysis, we can get different driprate estimates due to uncertainties in the data as well as our inability to estimate model parameters precisely
- We combine the posterior driprate PDF **$\rho^{Ni}(v|t)$** obtained from Ni to that obtained from Co, **$\rho^{Co}(v|t)$**
- Multiplying the two posterior probabilities from Ni and Co assumes that we consider both sources of information to be unreliable on their own
- We do not add the two probabilities from Ni and Co as this would implicitly assumer that we consider both trace elements to be perfect recorders of driprate, which is an impossibility in real-world scenarios

$$\rho^{comb}(v|t) = \rho^{Ni}(v|t) \times \rho^{Co}(v|t)$$

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Calibrating the model for Heshang cave in south China

- Kp is theoretically defined using median cave temperature from monitoring data
- Concentration of calcium in the stalagmite (calcite) Y_{st} is a fixed value
- Aqueous concentrations X^t_{aq} and Y_{aq} are assigned heuristically from monitoring data
- The lognormal parameters K_μ and K_σ are estimated in a calibration step

from theory

fixed value

from monitoring

calibration

$$X_{St} = K_p \frac{Y_{St} X^t_{aq}}{Y_{aq}} \left(1 - \int \frac{1}{K_\sigma \sqrt{2\pi}} \exp\left(-\frac{(K-K_\mu)^2}{2K_\sigma^2}\right) \exp\left(-\frac{e^K}{V}\right) dK\right)$$

trace element in stalagmite

driprate

Calibrating the model for Heshang cave in south China

- **We use:**
  - Meteorological data from nearby weather station data at Yichang from 1953 to 2011
  - Monitoring data from the Heshang cave which covers the period from 2005 to 2016
- **We estimate:**
  - Effective rainfall (ER)[1] on a yearly resolution for Yichang
  - ER for Heshang cave from monitoring data
- **We then estimate the following linear relations using regression:**
  - A linear relation L_1 between driprate (from monitoring) at Heshang to ER at Heshang
  - A linear relation L_2 between the ER at Heshang and the ER at Yichang
  - A linear relation L_3 based on the esimated parameters that define L_1 and L_2
- **We are thus able to formulate a model that relates the drip rate at Heshang to the ER at Yichang cave**

[1] Defined as the ratio of average precipitation to average temperature

Calibrating the model for Heshang cave in south China

- **In order to estimate the parameters K_μ and K_σ, we minimize the least squares distance between**
  - the ER series at Yichang obtained from the median driprate time series at Heshang, and
  - the observed ER series at Yichang
- **The median driprate time series at Heshang is estimated from the posterior PDFs $\rho^{comb}(v|t)$**
- **Since we have two sources, Ni and Co, we minimize the sum of four different least squares (LSQ):**
  - the LSQ residual obtained by using only Ni as a source
  - the LSQ residual obtained by using only Co as a source
  - the LSQ residual obtained by using both Ni and Co as sources, and
  - the LSQ between the ER series obtained from Ni and the ER series obtained from Co
- **The parameters K_μ and K_σ for both Ni and Co are estimated together,** in the same optimization process that minimizes the above mentioned sum of residuals
- **The optimization is done using the Nelder-Mead algorithm**, as implemented in scipy.optimize.minimize

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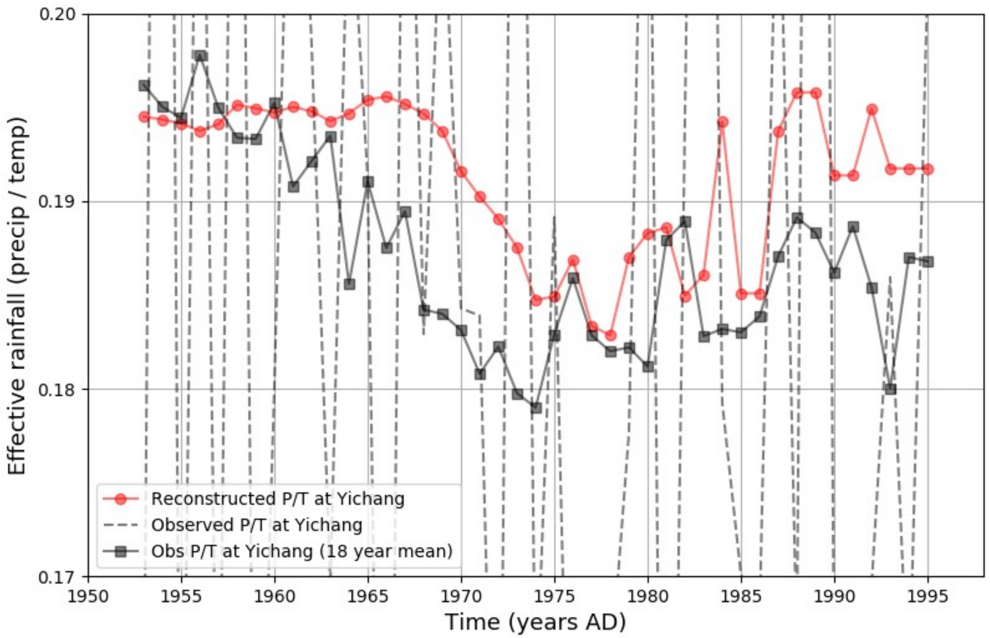
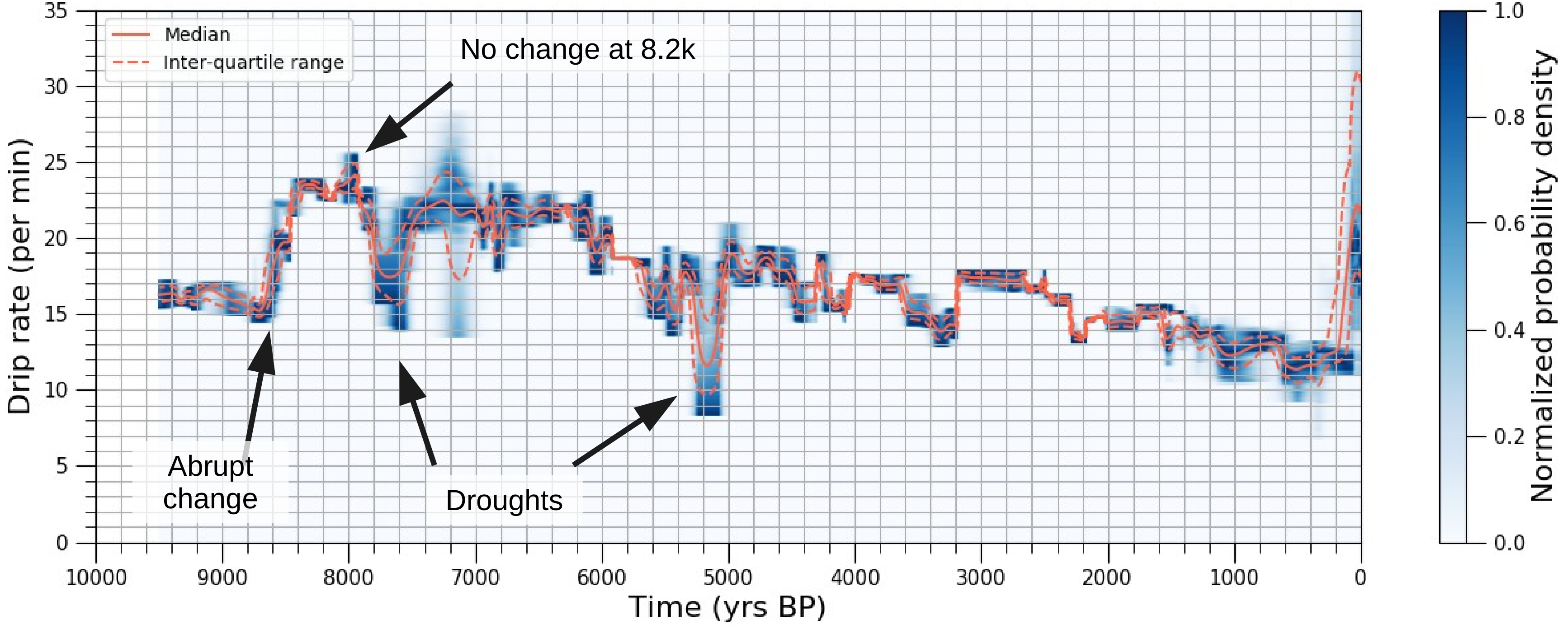
Results: Calibration to ER at Yichang

- Reconstructed ER series (labelled here as P/T) at Yichang (in red) based on the median driprate series modeled at Heshang shows **good agreement with long term trends** (in black) during the calibration period
- The **variability at subdecadal scales is not captured** in the driprate-based reconstruction
- This could be due to:
  - Uncertainties in the data yet unaccounted for
  - Finite size of the drill holes from which trace element samples are taken
- Still, long term hydrological variability is successfully recovered from the driprates
- **The reconstruction is quantitative!** *(Note that reconstruction and observed data are on the same vertical axis)*



Results: Estimated driprate record at Heshang cave for the Holocene

- Overall weakening of monsoon in Holocene due to weakening solar insolation
- The monsoon entered the Holocene Optimum ca. 8.8–8.6 kyrs BP via an abrupt change
- Severe droughts ca. 7.8–7.6 kyrs BP and 5.3–5.1 kyrs BP
- The ‘8.2k event’ cold event did not result in weaker effective rainfall at Heshang



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[2] Goswami, B., Heitzig, J., Rehfeld, K., Marwan, N., Anoop, A., Prasad, S., & Kurths, J. (2014). Estimation of sedimentary proxy records together with associated uncertainty. *Nonlinear Processes in Geophysics*, **21**, 1093-1111.