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Understanding modern kinetic isotope effect in Anjohibe Cave, in Northwestern Madagascar: a key to calibrate speleothem $\delta^{18}O$ and $\delta^{13}C$

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HORIZON 2020

MARIE CURIE ACTIONS

Background

Madagascar

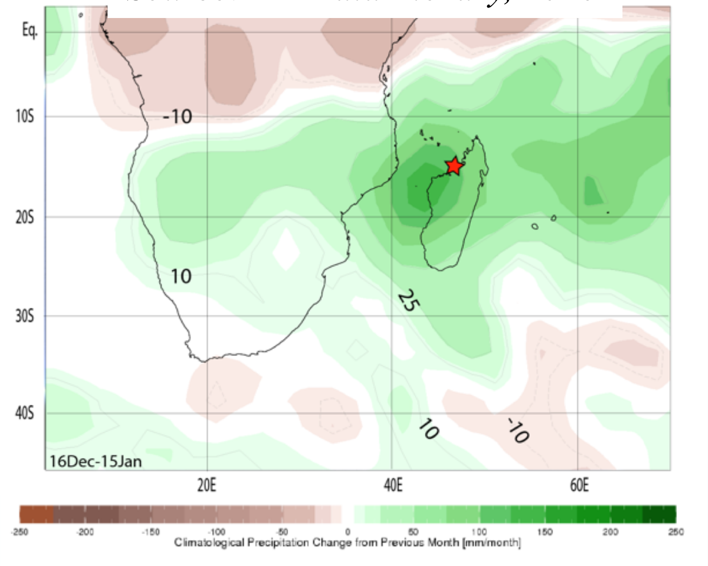
- is a natural laboratory to study paleoclimate and paleoenvironment.

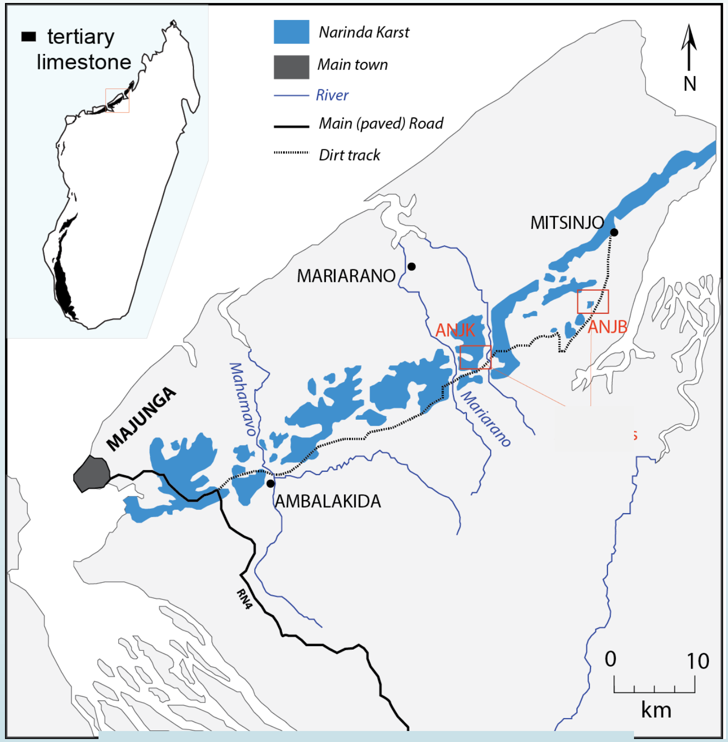
- is seasonally visited by the Intertropical Convergence Zone (ITCZ) and experiences monsoon during austral summers.

- hosts caves where speleothems can be found.

Madagascar holds a key position in the Indian Ocean to fill gaps in paleoclimate reconstruction in the Southern Hemisphere (where paleoclimate data are still scarce).

Source: IRI Data Library, 2016





Source: Voarintsoa et al., 2017b.

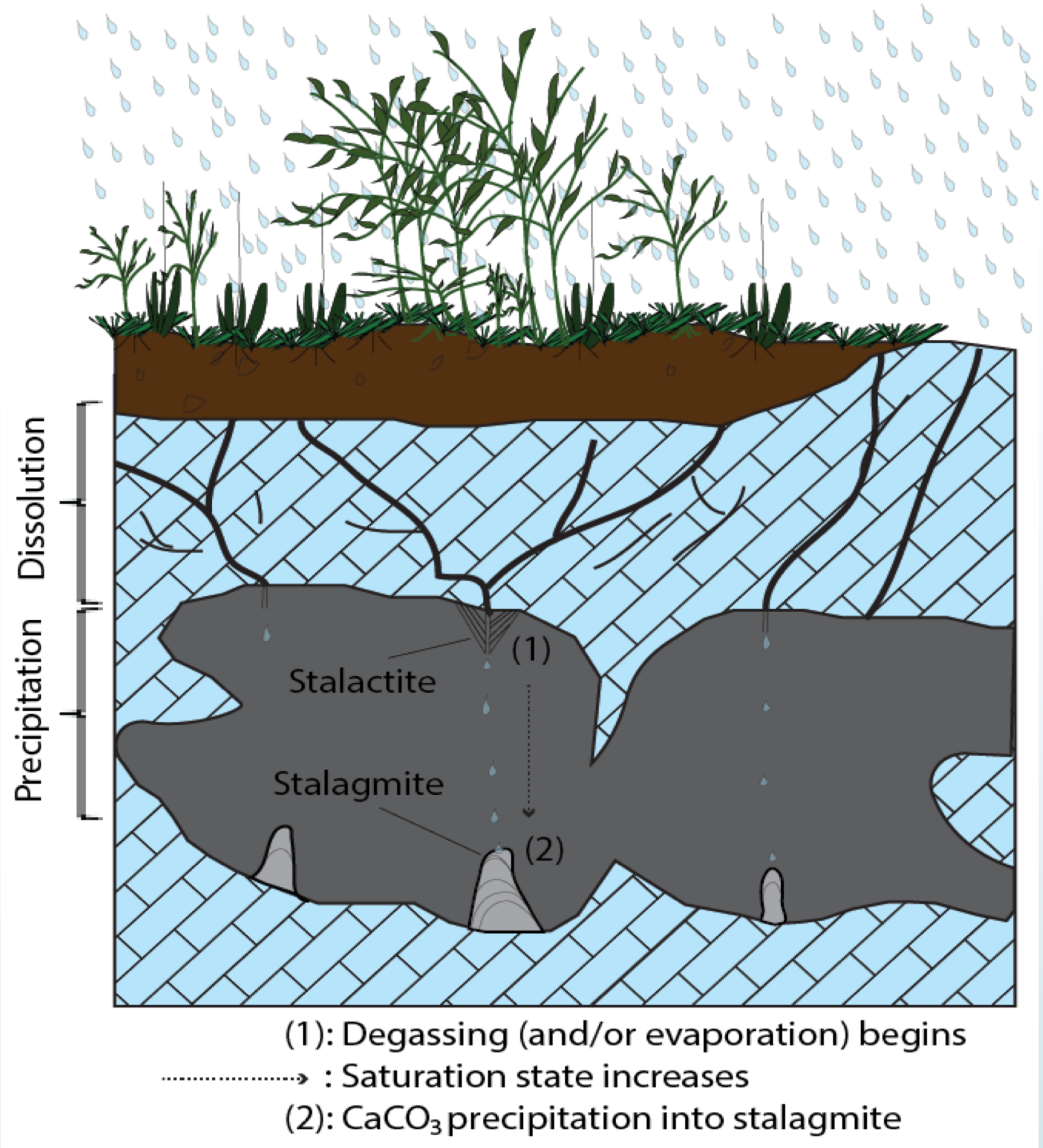
Background

Speleothems are secondary cave deposits

$$Ca^{2+}(aq) + 2HCO_3^-(aq) \underset{\text{Dissolution}}{\overset{\text{Precipitation}}{\rightleftharpoons}} CaCO_3(s) + CO_2(g) + H_2O(l)$$

The precipitated carbonate preserves various geochemical signatures that reflect environmental conditions at the time of stalagmite deposition.

*To produce reliable proxies, **"equilibrium"** was required but studies show that all cave carbonates precipitate out of isotopic equilibrium (e.g., Mickler et al., 2006; Daëron et al., 2019).*



Voarintsoa, 2017, PhD Thesis

$CO_2 + H_2O$

$\downarrow\uparrow$

H_2CO_3

$+$

$CaCO_3$

$\downarrow\uparrow$

$Ca^{2+} + 2HCO_3^-$

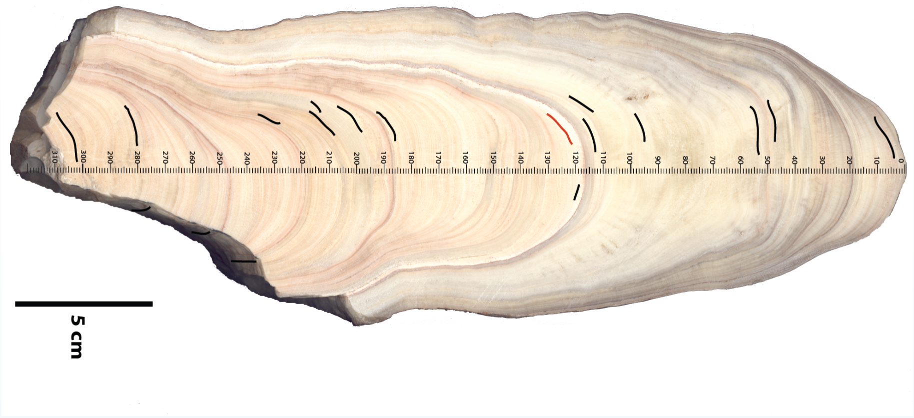
$\downarrow\uparrow$

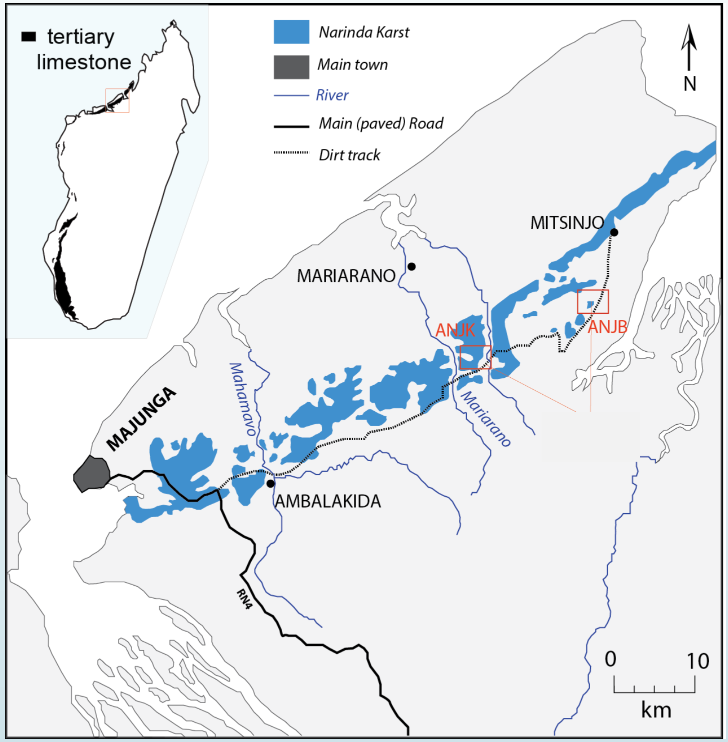
CO_2
$+$
H_2O
$+$
$\mathbf{CaCO_3}$

Background

Madagascar & speleothems revealed

- distinct early, mid, and late Holocene climatic regimes that were linked to the latitudinal migration of the ITCZ, and the monsoonal responses associated with the migration (Voarintsoa et al., 2017b)
- evidence of the African Humid Period and rapid climate changes during the Holocene (Wang et al., 2019)
- shift in $\delta^{13}C_C$ starting ca. AD 800 that was attributed to anthropogenic activities (Burns et al., 2016, Voarintsoa et al., 2017a, Scroxton et al., 2017, Wang et al., 2019)





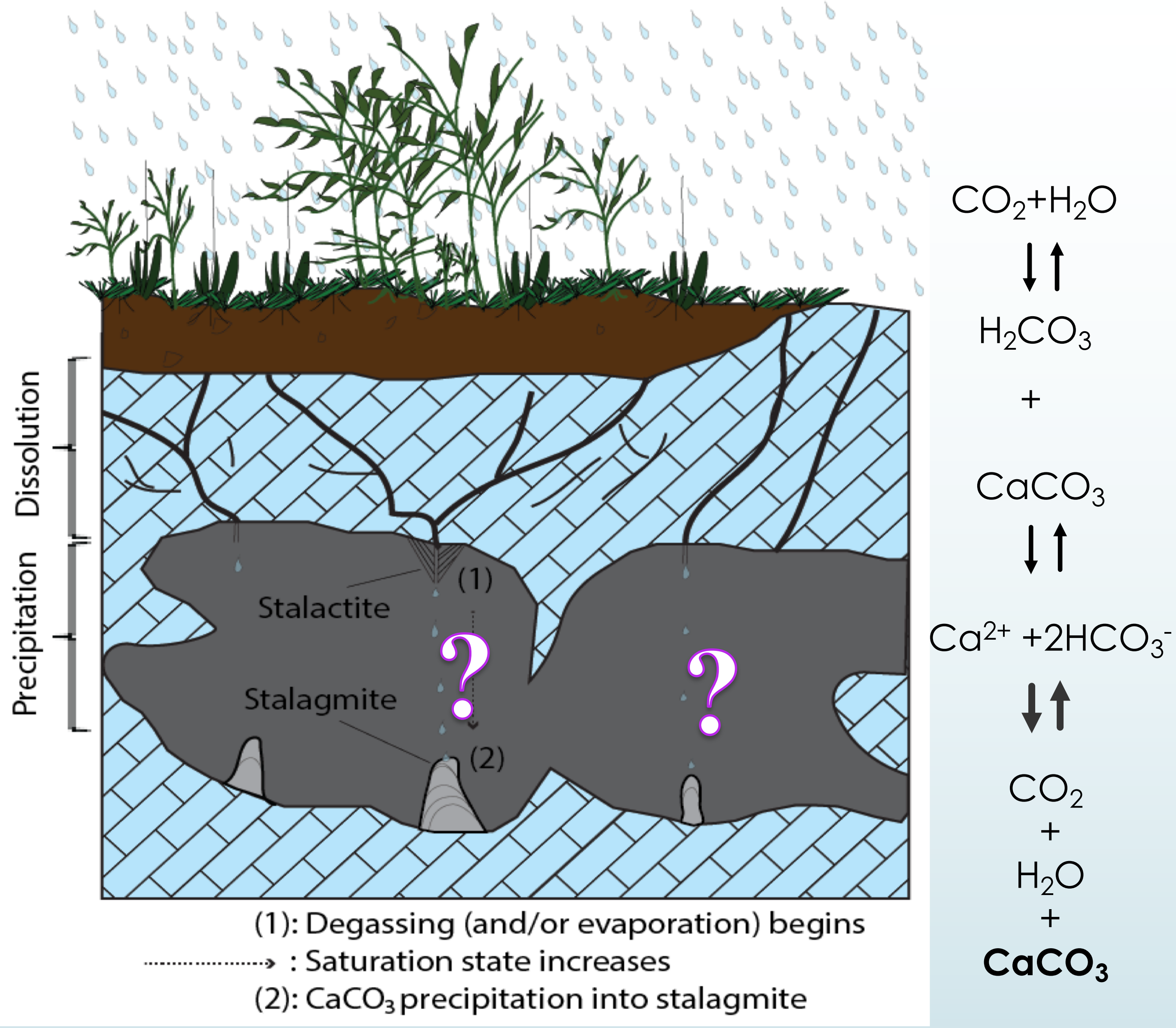
(Source: Voarintsoa et al., 2017b)

Knowledge gaps

Although information from these speleothems is unquestionably significant, there are still ***gaps in isotopic proxies interpretation****, mainly in linking* ***modern environments*** *where these speleothems grew and the signals they preserve.*

? $$^{18}\alpha = \frac{\delta^{18}O_c + 1000}{\delta^{18}O_w + 1000}$$

? $$^{13}\alpha = \frac{\delta^{13}C_c + 1000}{\delta^{13}C_{DIC} + 1000}$$



Voarintsoa, 2017, PhD Thesis

Objectives

Understand C and O isotopic fractionation in Anjohibe Cave

↓

Compare data with laboratory and/or theoretical studies

↓

- Assess the oxygen isotopic fractionation factor in a global context
- Assess carbon isotopic variations as a function of various cave parameters

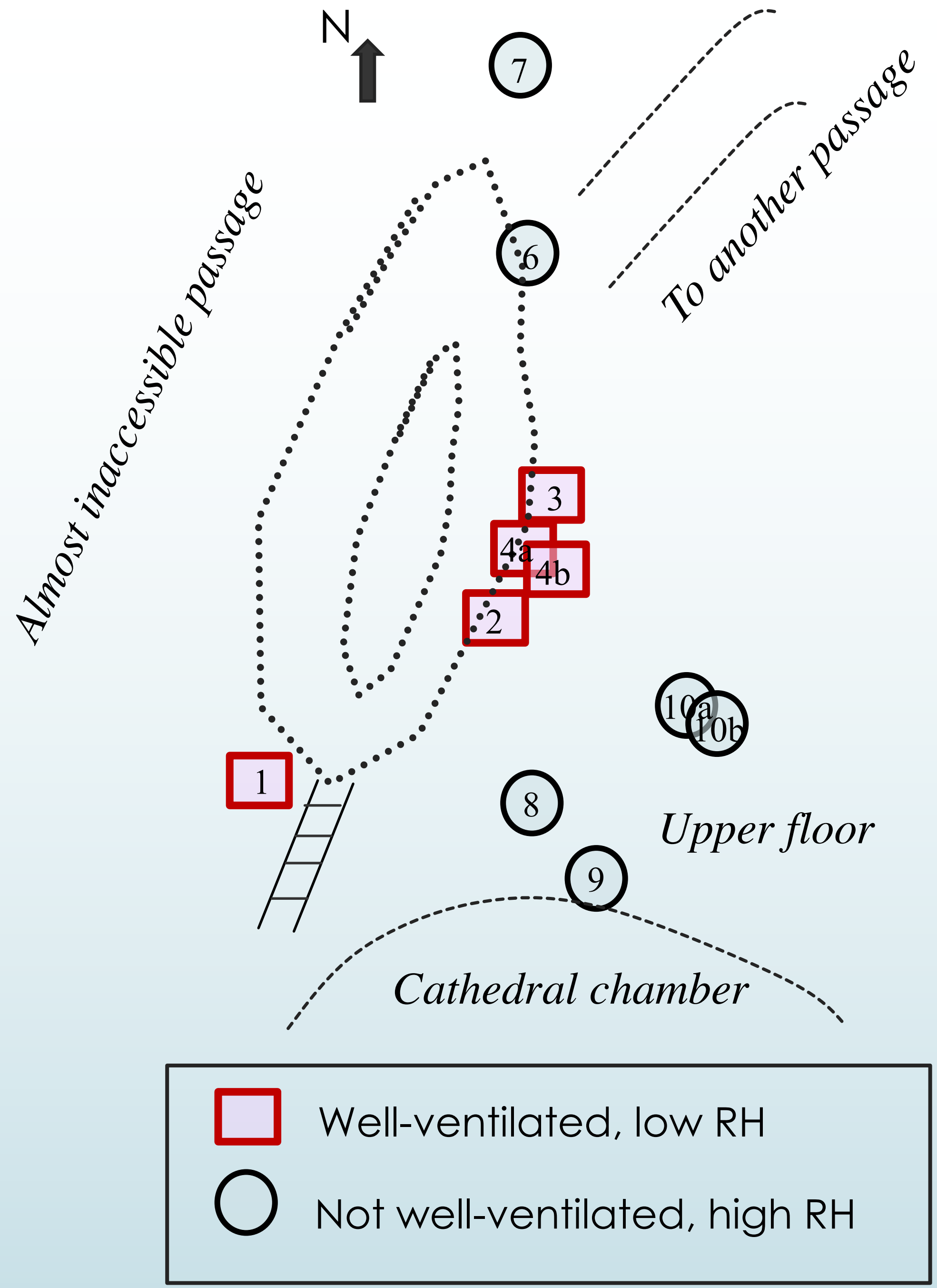
Methods

- Measuring the $\delta^{18}O_c$ and $\delta^{13}C_c$ values of modern speleothems,
- Measuring the temperature of the drip water,
- Measuring the $\delta^{18}O_w$ and the $\delta^{13}C_{DIC}$ of the feeding drip water

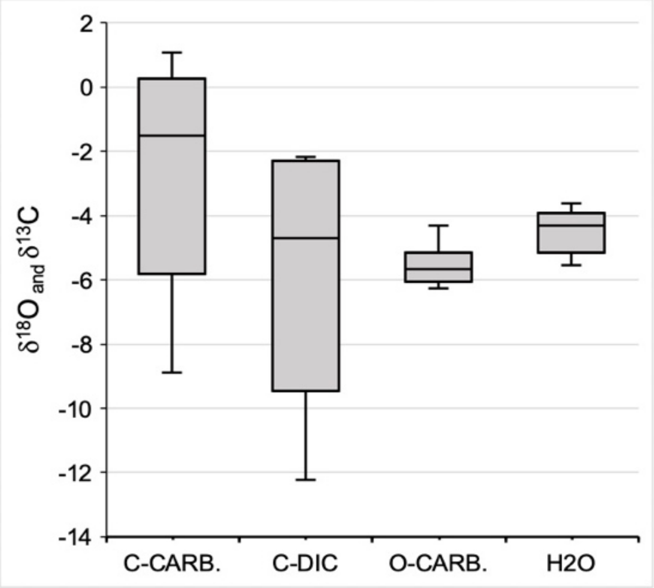
from eleven stations in the cave.

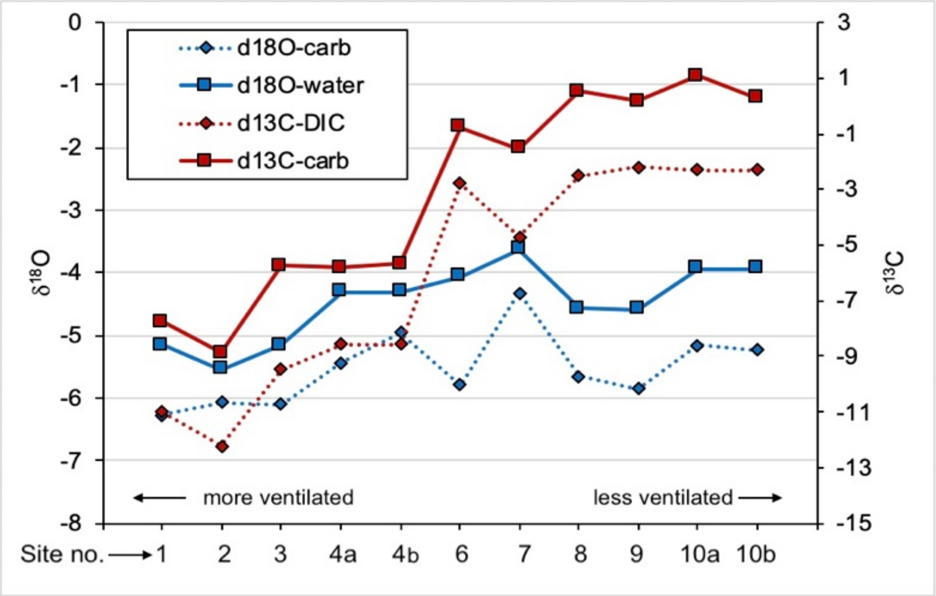
- measuring other physico-chemical parameters in the cave
  - pCO_2, Relative Humidity (RH), air T
  - pH, Electric Conductivity, Total Dissolved Solids
  - Elemental analyses (Ca, Mg, …)

DIC= Dissolved Inorganic Carbon



Overall observations





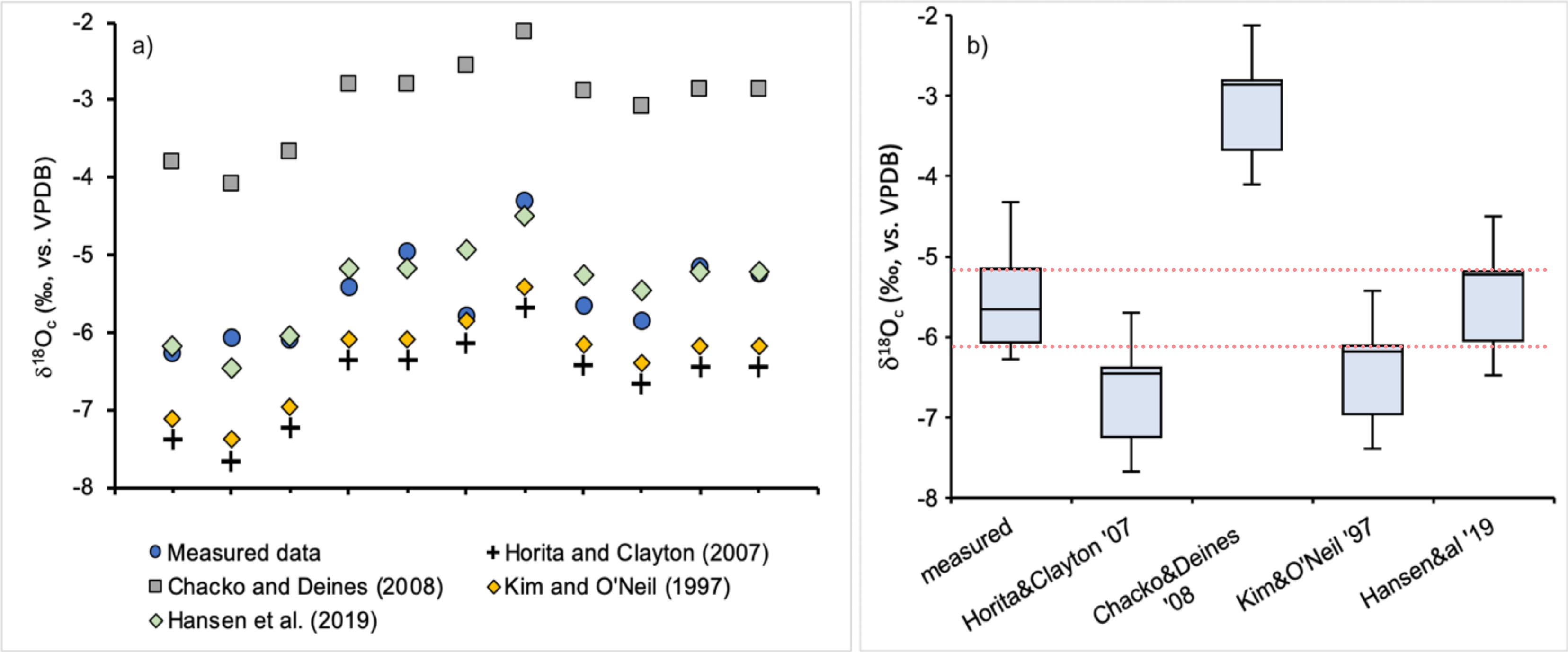
Great variability for $\delta^{13}C$

- $\delta^{13}C_C$ from–8.9 to +1.1 ‰, vs. VPDB
- $\delta^{13}C_{DIC}$ from –12.2 to –2.2‰, vs. VPDB
- This results in an isotopic difference of almost **10 ‰**

Small variability for $\delta^{18}O$

- mean $\delta^{18}O_C$ –5.53±0.60‰, vs. VPDB
- mean $\delta^{18}O_W$ –4.47±0.61‰, vs. SMOW
- This results in an isotopic difference of almost **1.2 ‰**

Predicted vs. measured $\delta^{18}O_c$

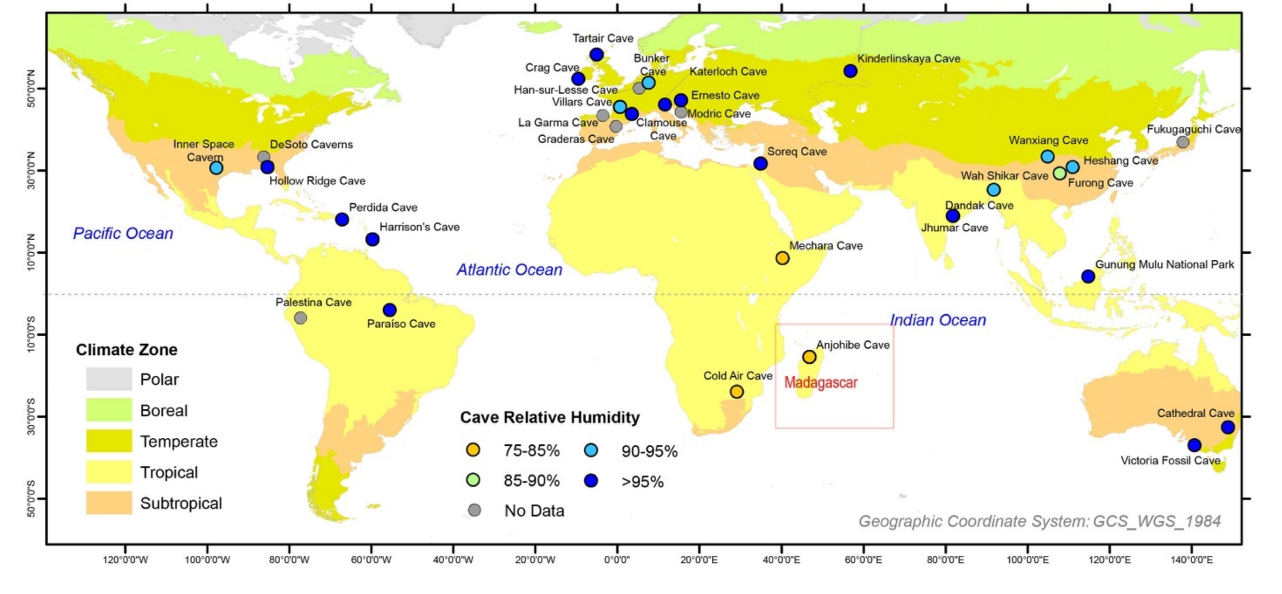


Predicted $\delta^{18}O_c$ mean values:

- **–6.63±0.58‰** (Horita and Clayton, 2007)
- **–3.06±0.58‰** (Chacko and Deines, 2008)
- **–6.35±0.58‰** (Kim an d O'Neil, 1997)
- **–5.43±0.58‰** (Hansen et al., 2019)

Our samples **–5.53±0.60‰**

- *The measured values are comparable with the predicted values using the isotopic fractionation curves of Hansen et al. (2019), which is based on cave-analog laboratory experiment.*



Global context

- The oxygen isotope fractionation factors from Madagascar **fit within the global fractionation** data as a function of temperature

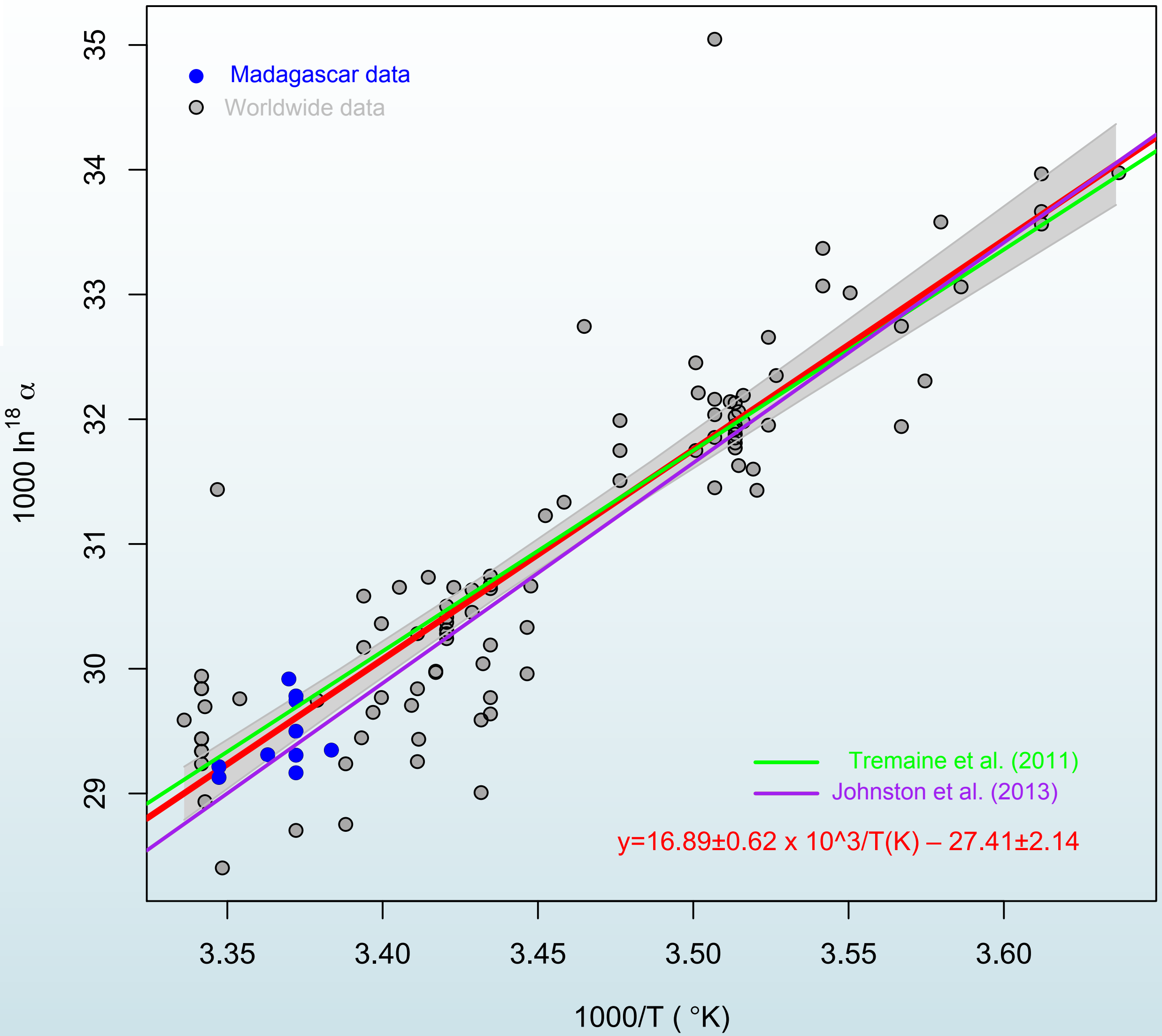
$$1000 \ln {}^{18}\alpha = 16.89 \pm 0.62\ (10^3/T(°K)) - 27.41 \pm 2.14$$

Tremaine et al. (2011)

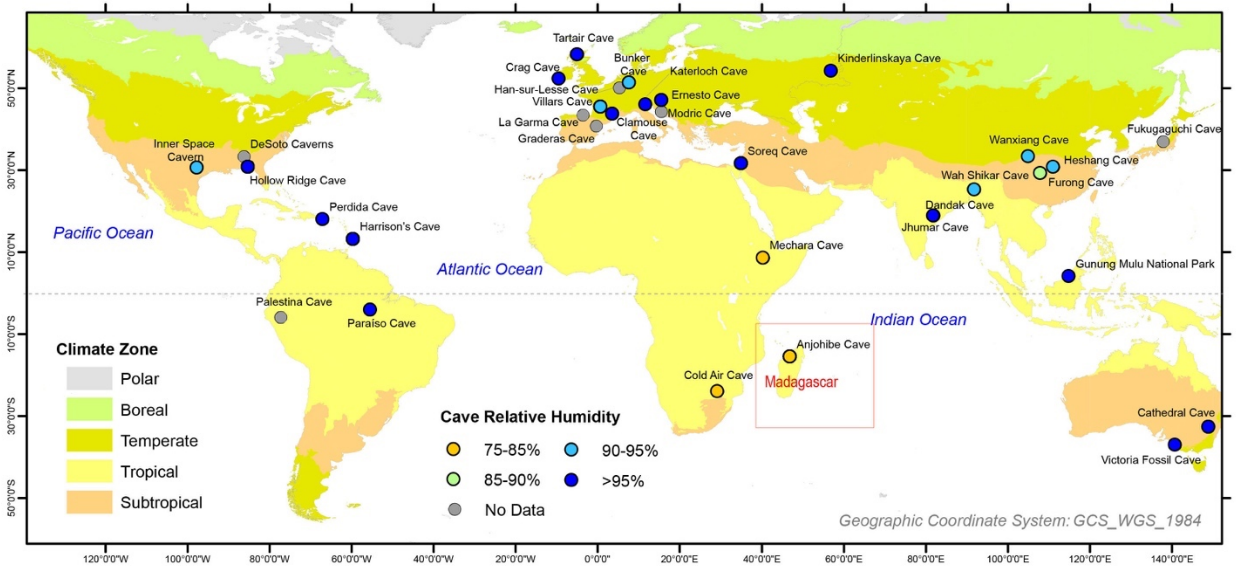
$1000 \ln {}^{18}\alpha = 16.1\ (10^3/T(°K)) - 24.6$

Johnston et al. (2013)

$1000 \ln {}^{18}\alpha = 17.66\ (10^3/T(°K)) - 30.16$



We really need to rethink about our approach about isotopic equilibrium in caves !!!!

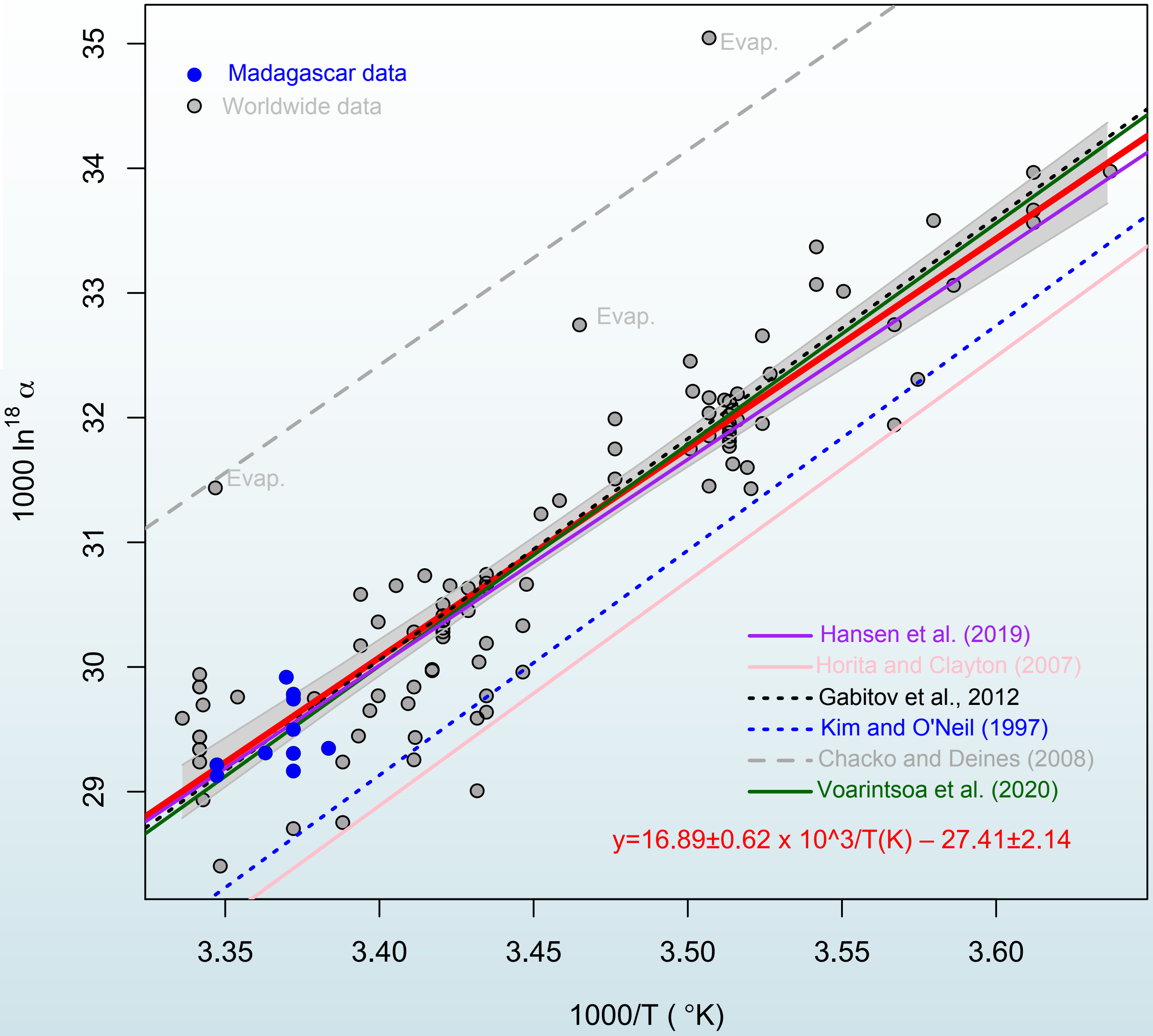


Global &other context

- The fractionation factors from Madagascar **fit within the global fractionation** data as a function of temperature

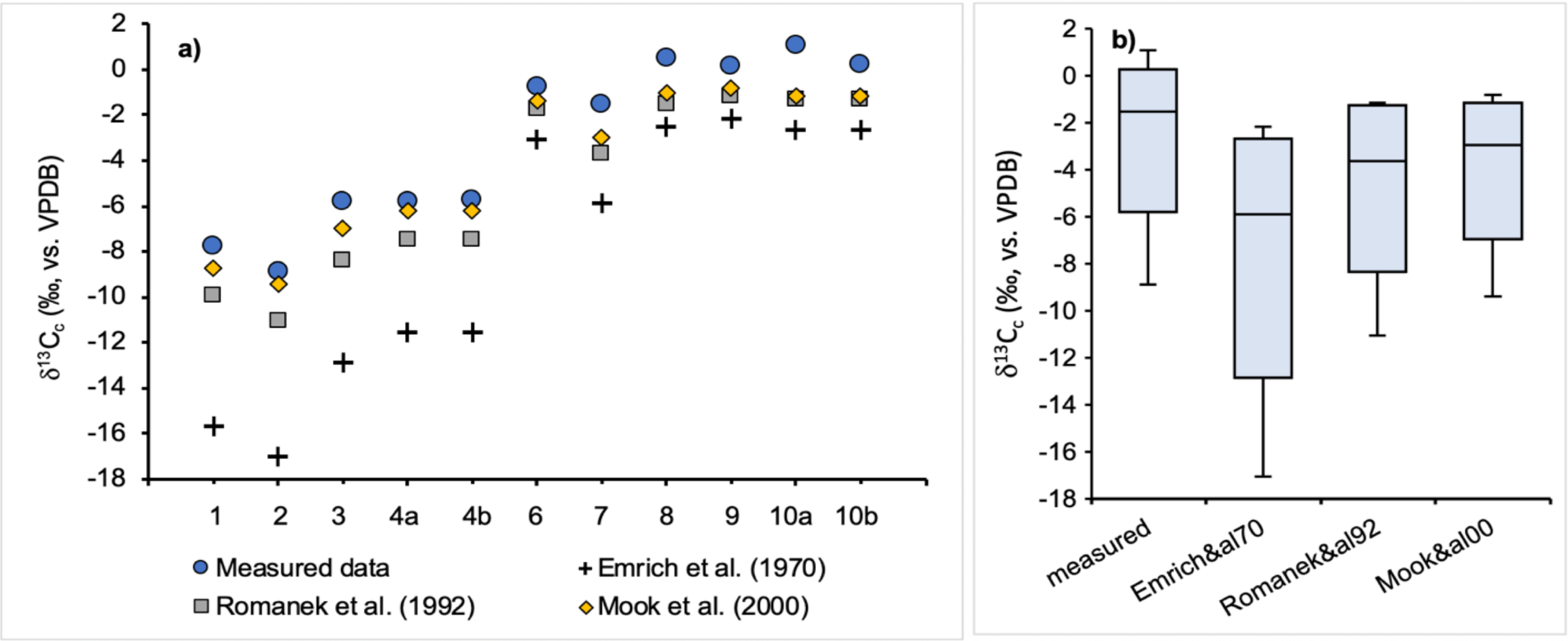
$$1000 \ln {}^{18}\alpha = 16.89 \pm 0.62\ (10^3/T(°K)) - 27.41 \pm 2.14$$

- But the isotopic fractionation curves shift away from curve derived from the lab experiments and theoretical studies, except for Hansen et al. (2019), a cave-analog experiment.



We really need to rethink about our approach about isotopic equilibrium in caves !!!!

Predicted vs. measured $\delta^{13}C_c$



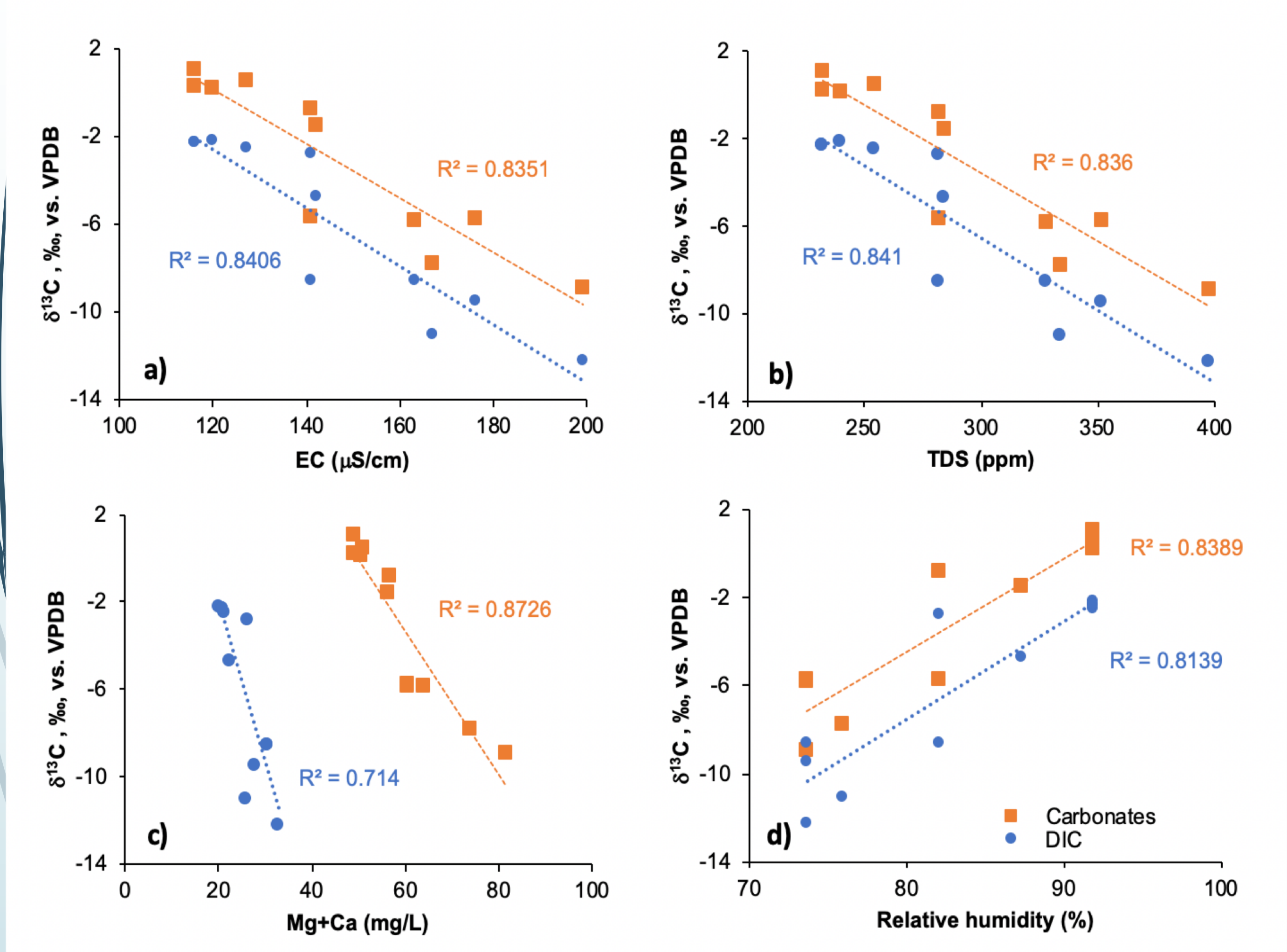
Predicted $\delta^{13}C_c$ mean values:

- **–7.98±5.82‰** (Emrich et al., 1970)
- **–4.98±3.89‰** (Romanek et al., 1992)
- **–4.18±3.36‰** (Mook, 2000),

Our samples **–3.11±3.70‰**

- *The measured values are closer to the prediction of Romanek et al. (1992) and Mook (2000) although the measured values are slightly higher.*
- *Isotopic fractionation factors are weakly temperature dependent* ($^{13}\varepsilon_{CacO3-DIC} = -0.0005\ (10^6/T^2) + 0.0082$)

$\delta^{13}C$ and other cave parameters



There is a strong inverse relationship between

- *$\delta^{13}C$ and Electric Conductivity (EC),*
- *$\delta^{13}C$ and Total Dissolved Solids (TDS),*
- *$\delta^{13}C$ and [Mg+Ca]*

There is a strong positive relationship between

- *$\delta^{13}C$ and Relative Humidity (indicator of cave ventilation)*

- Potentially a strong influence of prior carbonate precipitation (PCP) or simply fast carbonate precipitation on $\delta^{13}C$.
- Nature of the bedrock dissolution (open vs. closed conditions).

(refer to the CaveCalc model of Owen et al. (2018) and the extended ISOLUTION model of Fohlmeister et al. (2020), that is originally from Deininger et al. (2012) and Deininger and Scholz (2019)

Conclusions

The oxygen isotope fractionation factors from Madagascar **fit within the global fractionation** data as a function of temperature.

This global fractionation agrees well with that of Hansen et al. (2019).

- *We really need to rethink about our approach about isotopic equilibrium test in caves !!!!*
- ***Running a test for consistency*** *of the isotopic fractionation factors relative to the global cave isotopic fractionation curves is* ***more crucial****.*

The carbon isotope fractionation factors from Madagascar **is still difficult** to assess given the limited worldwide dataset on $\delta^{13}C_c$ and $\delta^{13}C_{DIC}$.

Only a weak temperature dependence observed.

- *Potential influence of fast carbonates precipitation and prior carbonate precipitation (PCP) on the $\delta^{13}C_{DIC}$ and hence the $\delta^{13}C_c$*
- *Potential influence of the open vs. closed bedrock dissolution on he $\delta^{13}C_{DIC}$ and hence the $\delta^{13}C_c$.*

References

Burns S. J., Godfrey L. R., Faina P., McGee D., Hardt B., Ranivoharimanana L. and Randrianasy J. (2016) Rapid human-induced landscape transformation in Madagascar at the end of the first millennium of the Common Era. Quaternary Sci Rev 134, 92-99.

Chacko T. and Deines P. (2008) Theoretical calculation of oxygen isotope fractionation factors in carbonate systems. Geochim Cosmochim Ac 72, 3642–3660.

Daëron M., Drysdale R. N., Peral M., Huyghe D., Blamart D., Coplen T. B., Lartaud F. and Zanchetta G. (2019) Most Earth-surface calcites precipitate out of isotopic equilibrium. Nat Comm. 10, 1–7.

Deininger M., Fohlmeister J., Scholz D. and Mangini A. (2012) Isotope disequilibrium effects: The influence of evaporation and ventilation effects on the carbon and oxygen isotope composition of speleothems–A model approach. Geochim Cosmochim Ac 96, 57–79.

Deininger, M., Scholz, D. (2019) ISOLUTION 1.0: an ISOtope evoLUTION model describing the stable oxygen (δ18O) and carbon (δ13C) isotope values of speleothems. International Journal of Speleology 48, 3.

Emrich K., Ehhalt D. and Vogel J. (1970) Carbon isotope fractionation during the precipitation of calcium carbonate. Earth Planet Sc Lett 8, 363–371.

Fohlmeister, J., Voarintsoa, N.R.G., Lechleitner, F.A., Boyd, M., Brandtstätter, S., Jacobson, M.J., L. Oster, J., 2020. Main controls on the stable carbon isotope composition of speleothems. Geochim Cosmochim Ac 279, 67-87.

Gabitov R. I., Watson E. B. and Sadekov A. (2012) Oxygen isotope fractionation between calcite and fluid as a function of growth rate and temperature: An in situ study. Chem Geol 306-307, 92–102.

Hansen M., Scholz D., Schöne B. R. and Spötl C. (2019) Simulating speleothem growth in the laboratory: Determination of the stable isotope fractionation ($\delta^{13}C$ and $\delta^{18}O$) between H_2O, DIC and $CaCO_3$. Chem Geol 509, 20–44.

Horita J. and Clayton R.N. (2007) Comment on the studies of oxygen isotope fractionation between calcium carbonates and water at low temperatures by Zhou and Zheng (2003; 2005). Geochim Cosmochim Ac 71, 3131–3135.

Johnston V., Borsato A., Spötl C., Frisia S. and Miorandi R. (2013) Stable isotopes in caves over altitudinal gradients: fractionation behaviour and inferences for speleothem sensitivity to climate change. Clim Past 9, 99–118.

Kim S.-T. and O'Neil J. R. (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim Cosmochim Ac 61, 3461–3475.

Mickler P. J., Stern L. A. and Banner J. L. (2006) Large kinetic isotope effects in modern speleothems. GSA Bulletin 118, 65–81.

Mook W. G. (2000) Volume 1: Introduction – theory, methods, review. In: Environmental Isotopes in the Hydrological Cycle. Principles and Applications.

Owen R., Day C. C. and Henderson G. M. (2018) CaveCalc: A new model for speleothem chemistry & isotopes. Computers and Geosciences 119, 115–122.

Romanek C. S., Grossman E. L., and Morse J. W. (1992) Carbon Isotopic Fractionation in Synthetic Aragonite and Calcite - Effects of Temperature and Precipitation Rate. Geochim Cosmochim Ac 56, 419–430.

Scroxton N., Burns S. J., McGee D., Hardt B., Godfrey L. R., Ranivoharimanana L. and Faina, P. (2017) Hemispherically in-phase precipitation variability over the last 1700 years in a Madagascar speleothem record. Quaternary Sci Rev 164, 25–36.

Tremaine D. M., Froelich P. N. and Wang Y. (2011) Speleothem calcite farmed in situ: Modern calibration of $\delta^{18}O$ and $\delta^{13}C$ paleoclimate proxies in a continuously-monitored natural cave system. Geochim Cosmochim Ac 75, 4929–4950.

Voarintsoa N.R.G. (2017) Investigating stalagmites from NE Namibia and NW Madagascar as a key to better understand local paleoenvironmental changes and implications for inter-tropical convergence zone (ITCZ) dynamics. PhD Thesis. University of Georgia.

Voarintsoa N. R. G., Wang L. X., Railsback L. B., Brook G. A., Liang F. Y., Cheng H. and Edwards R. L. (2017a) Multiple proxy analyses of a U/Th-dated stalagmite to reconstruct paleoenvironmental changes in northwestern Madagascar between 370 CE and 1300 CE. Palaeogeogr Palaeoclim Palaeocl 469, 138–155.

Voarintsoa N. R. G., Railsback L.B., Brook G. A., Wang L., Kathayat G., Cheng H., Li X., Edwards R. L., Rakotondrazafy A.F.M. and Madison Razanatseheno, M. O. (2017b) Three distinct Holocene intervals of stalagmite deposition and nondeposition revealed in NW Madagascar, and their paleoclimate implications. Clim. Past 13, 1771–1790.

Voarintsoa N. R. G., Barkan E., Bergel S., Vieten R., Affek H. P. (2020) Triple oxygen isotope fractionation between $CaCO_3$ and H_2O in inorganically precipitated calcite and aragonite. Chem Geol 539, 119500.

Wang L., Brook G. A., Burney D. A., Voarintsoa N. R. G., Liang F., Cheng H. and Edwards R. L. (2019) The African Humid Period, rapid climate change events, the timing of human colonization, and megafaunal extinctions in Madagascar during the Holocene: Evidence from a 2m Anjohibe Cave stalagmite. Quaternary Sci Rev 210, 136-153.

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