CaveCalcV2.0 Overview

including Carbonate Data Analyser (CDA)
facilitating speleothem paleoclimate interpretations

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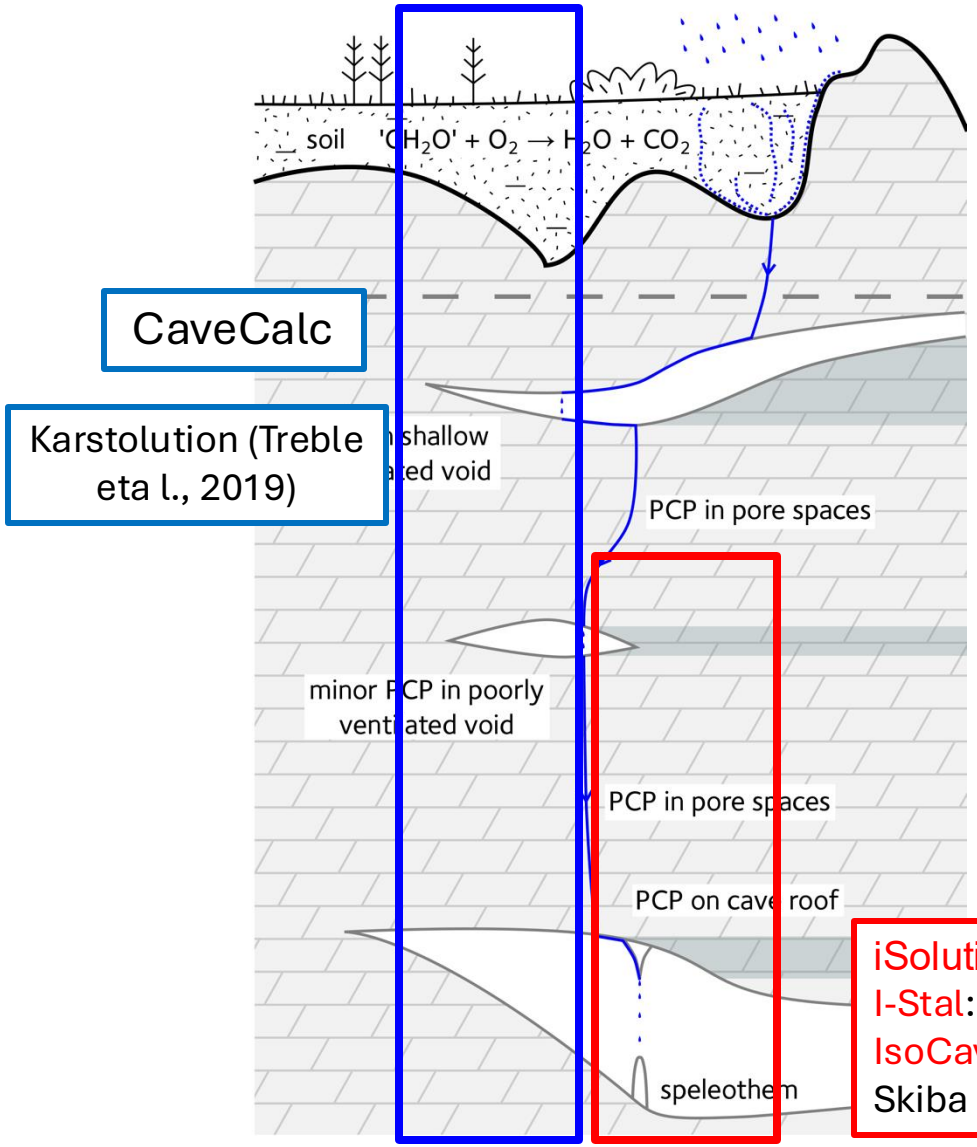
NATURAL ENVIRONMENT RESEARCH COUNCIL

CaveCalc

Research paper

CaveCalc: A new model for speleothem chemistry & isotopes

Robert Owen, Christopher C. Day, Gideon M. Henderson



CaveCalc

Karstolution (Treble eta l., 2019)

- PHREEQC-based forward modelling tool programmed in Python
- Forward modelling **from soil to analysis-speleothem**
- Incorporates soil-water equilibration, bedrock dissolution & Prior Carbonate Precipitation (PCarbP) along the flow-path
- Model the evolution of isotopes ($\delta^{13}C$, $\delta^{18}O$, $\delta^{44}Ca$) and trace-elements (Mg/Ca, Sr/Ca, Ba/Ca)

iSolution: Deininger and Scholz.
I-Stal: Stoll, Müller, Prieto
IsoCave: Guo and Zhou
Skiba & Fohlmeister

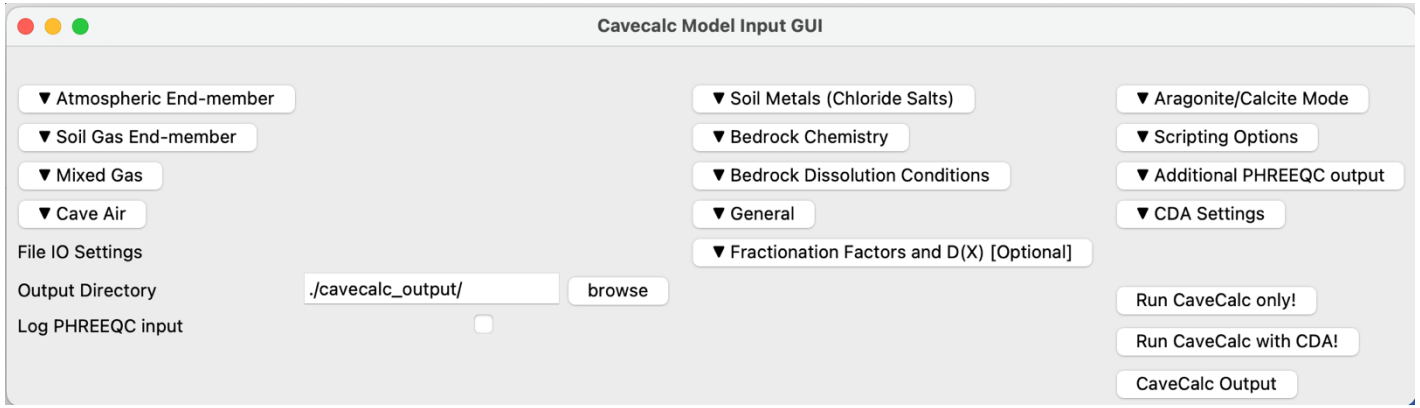
Additions to CaveCalcV2.0

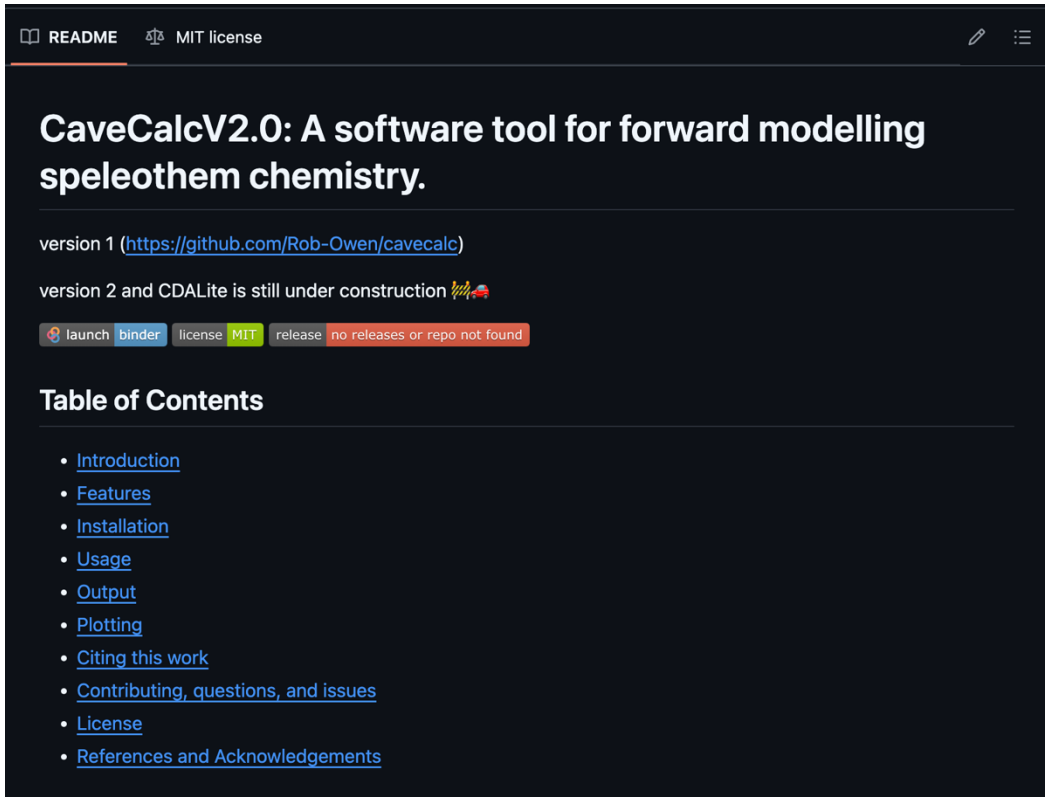
Improved installation and usability

- Easier Windows Installation

Automatic installation of the PHREEQC-COM server

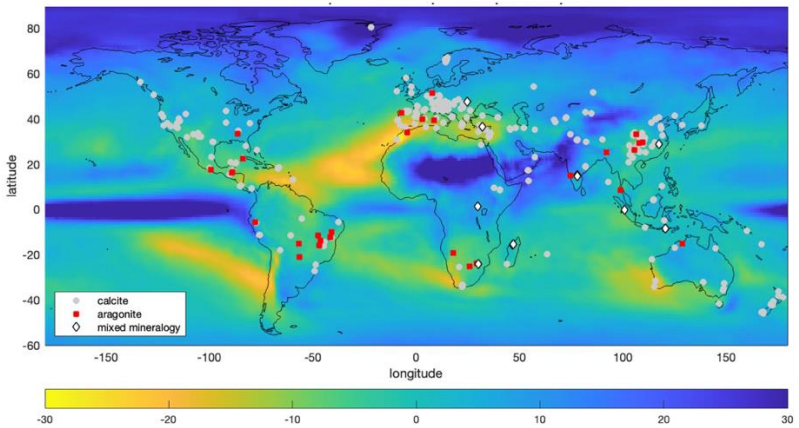
- More user-friendly Graphical User Interface (GUI)
- More detailed user manual
- Available for early testing (https://github.com/Samhollowood/CaveCalcV2.0)



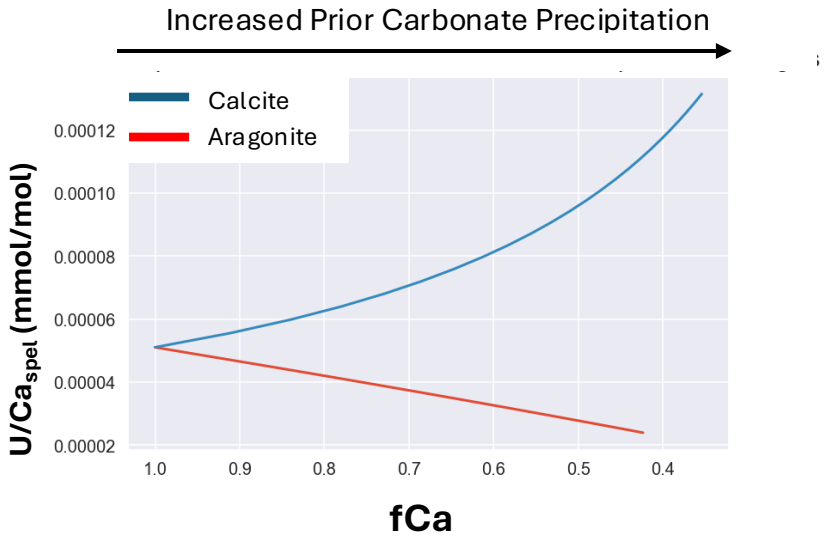


Main Additions to CaveCalcV2.0

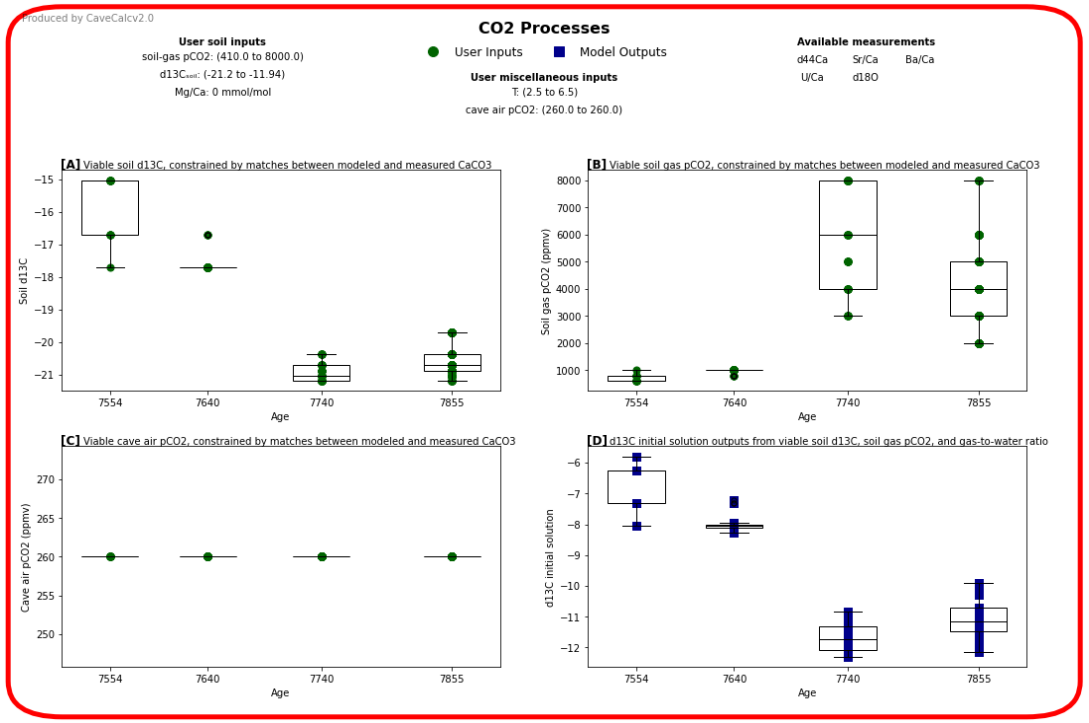
Forward-modelling of speleothem aragonite



Addition of speleothem U/Ca

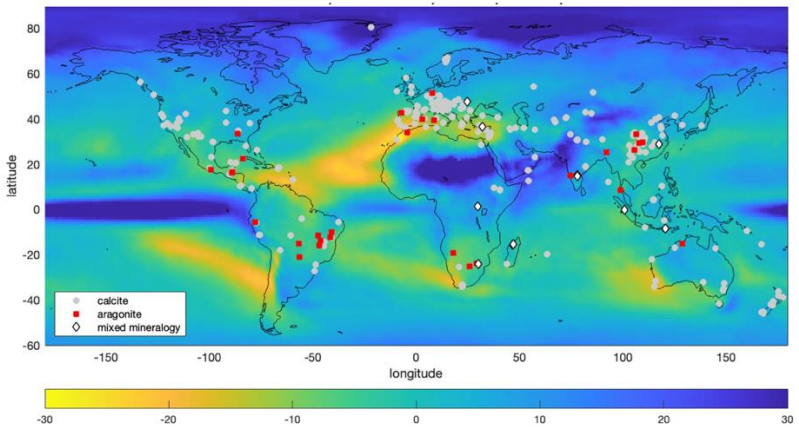


Carbonate Data Analyser (CDA) Mode



Speleothem Aragonite & U/Ca

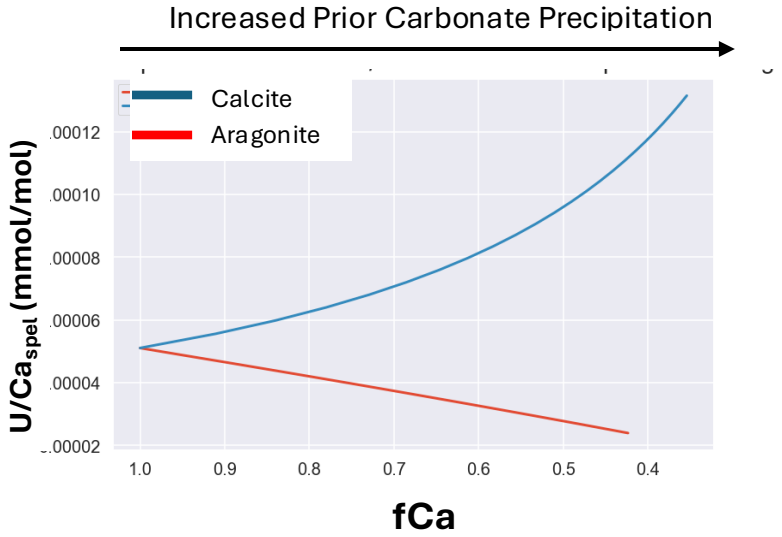
Forward-modelling of speleothem aragonite



Kaushal et al,, 2024

- ~20% of speleothems in SISALV3.0 are aragonite
- CaveCalcV2.0 can now forward-model aragonite precipitation along the flow-path.
- Allows for the assessment of Prior Aragonite Precipitation (PAP)

Addition of speleothem U/Ca



$D(U)_{calcite} < 1$ e.g., Day & Henderson, 2013

$D(U)_{aragonite} > 1$ e.g., Wassenburg et al., 2024

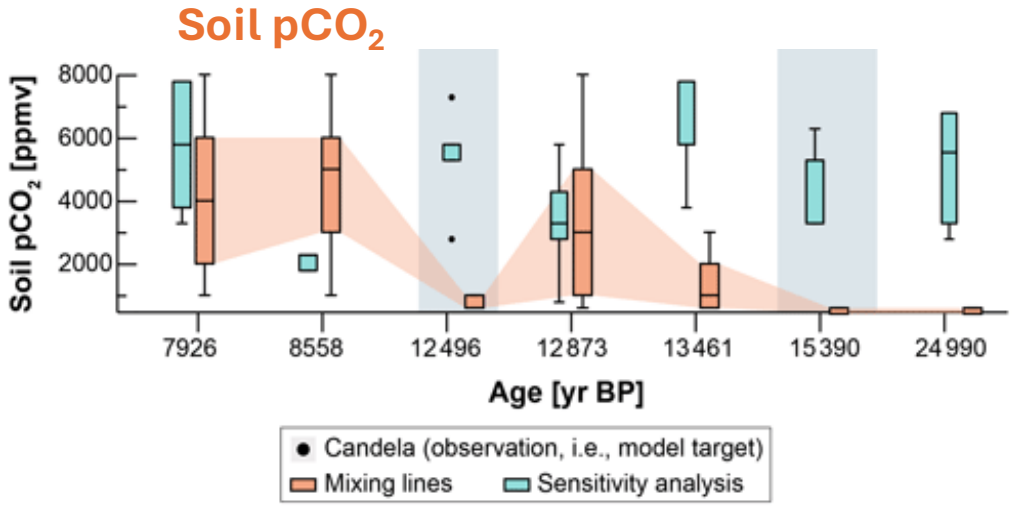
- U/Ca: helps with distinction between calcite and aragonite flow-path-precipitation

Carbonate Data Analyser (CDA)

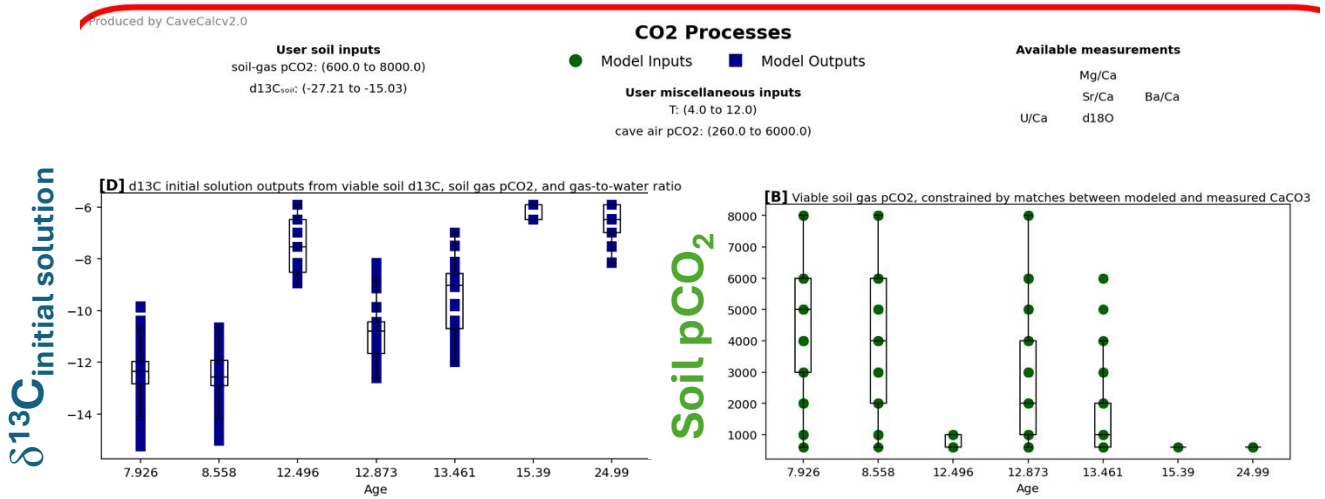
facilitating speleothem paleoclimate interpretations

- **Automates** the comparison between CaveCalcV2.0 model output and measured speleothem data
- Returns the **environmental input values (e.g soil pCO_2)** that match (within user defined tolerance) with the measured speleothem data

Internalises procedures developed in Lechleitner et al., 2021; Stoll et al, 2023



Lechleitner et al., 2021



CaveCalcV2.0 generated figures

Carbonate Data Analyser (CDA)

Operating procedure

1) Speleothem input file

Age (kaBP)	d13C (‰)	d18O (‰)	d44Ca (‰)	DCP (%)	Mg/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)	U/Ca (mmol/mol)
15	-6.0	-11.0	0.71	23	1.10	0.3	0.1	0.07
18	-5.0	-8.0	0.82	17	1.20	0.4	0.1	0.08
25	-3.2	-6.7	0.99	12	1.50	0.6	0.2	0.09

Up to 8 proxies ($\delta^{13}C$, $\delta^{18}O$, $\delta^{44}Ca$, DCP, Mg/Ca, Sr/Ca, Ba/Ca, U/Ca)

With more proxies leading to a more constrained environmental system

2) CaveCalc model inputs (environmental variables values to constrain with measured speleothems)

e.g.

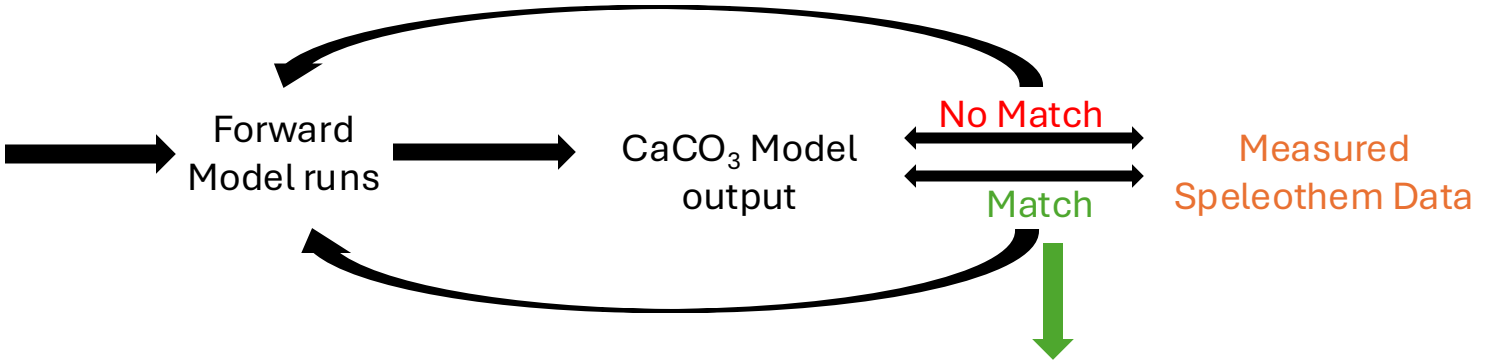
Soil-gas pCO_2 = (x_1……x_n)

Soil-CO_2 $\delta^{13}C$ = (y_1……y_n)

Soil gas volume = (z_1……z_n)

Temperature = (t_1……t_n)

Cave air pCO_2 = (c_1……c_n)



3) CDA Output file (Matched speleothem and environmental values)

Age (ka BP)	$\delta^{13}C_{CaCO3}$	CaveCalc $\delta^{13}C_{CaCO3}$	Mg/Ca_{CaCO3}	CaveCalc Mg/Ca_{CaCO3}	fCa	soil_pCO2	soil_d13C	soil_Mg	bedrock_MgCa	temperature	.....
12	-8.40	-8.56	1.80	1.81	0.92	500	-18	0	130	10	
12	-8.40	-8.39	1.80	1.90	0.88	500	-18	0	130	10	
25	-6.50	-6.92	2.90	2.88	0.58	4000	-18	0	130	10	

CDA Graphical Output Example

Summary of model inputs is provided e.g. →

Soil-gas pCO_2: 200 to 8000 ppmv

$\delta^{13}C_{soil\text{-}gas}$: -25 to -15‰

Cave air pCO_2: 260 to 1500 ppmv

Temperature: 19°C

Gas Volume (L/kg): 15 to 150 L/kg

User input file (measured speleothem)

Age [kaBP]	$\delta^{13}C$ (‰, VPDB)	$\delta^{44}Ca$ (‰, SRM 915a)	DCP (%)
Last Millennium	-4.63	-0.05	22.3
Mid-Holocene	-3.85	0.87	10

Tolerance_d13C = 0.3

Tolerance_d44Ca = 0.2

Tolerance_DCP = 1

Also available graphical outputs of:

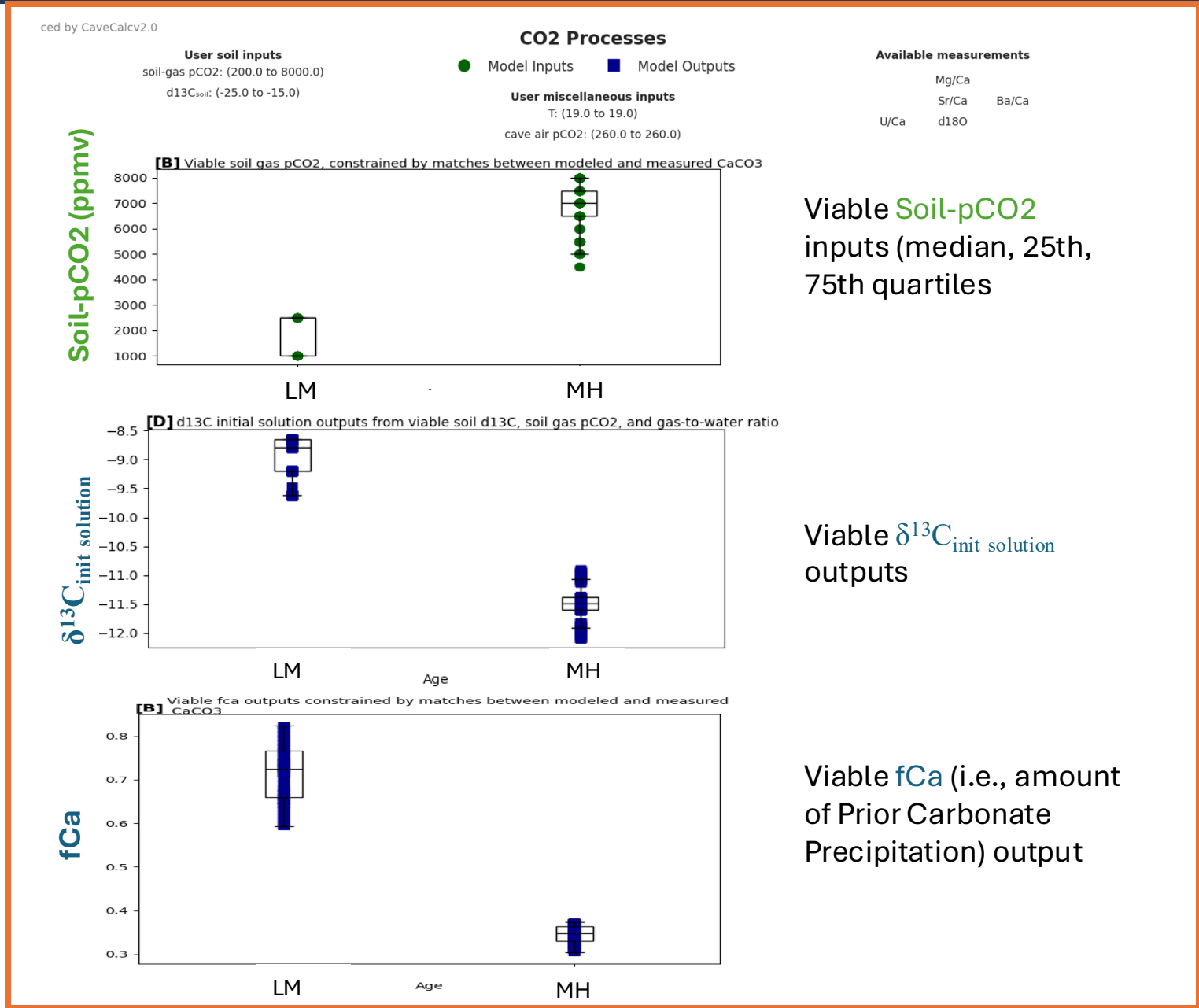
$\delta^{13}C_{soil\text{-}pCO2}$

Gas Volume (L/kg)

Initial Ca^{2+} (mmol/kgw)

Cave air pCO_2

+ many more in the .csv file



Viable Soil-pCO2 inputs (median, 25th, 75th quartiles

Viable $\delta^{13}C_{init\ solution}$ outputs

Viable fCa (i.e., amount of Prior Carbonate Precipitation) output

Thanks for listening!

https://github.com/Samhollowood/CaveCalcV2.0

SCAN ME

Any Questions please reach out at
Samuel.Hollowood@bnc.ox.ac.uk!