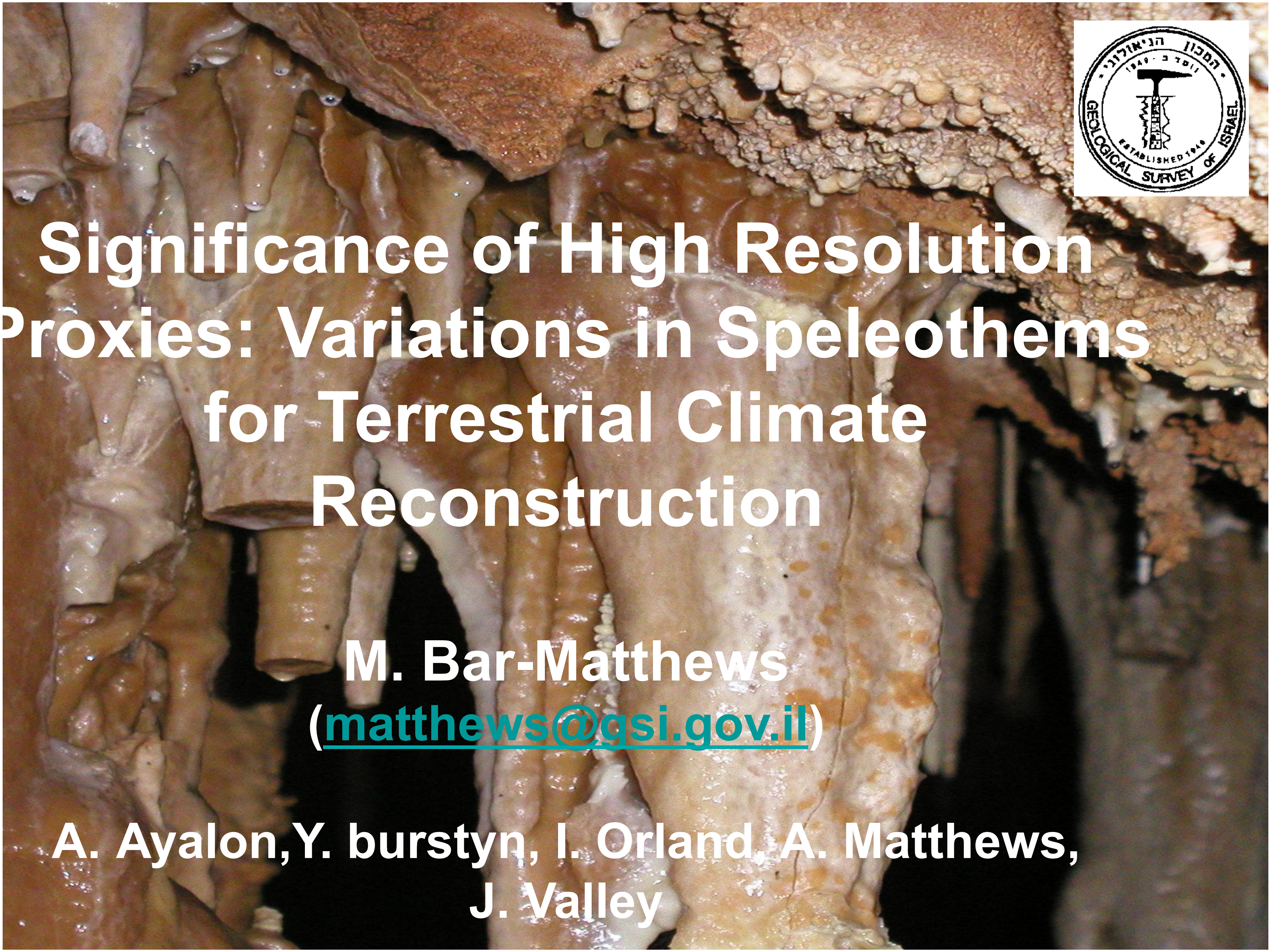

GEOLOGICAL SURVEY OF ISRAEL

Significance of High Resolution Proxies: Variations in Speleothems for Terrestrial Climate Reconstruction

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A. Ayalon,Y. burstyn, I. Orland, A. Matthews,
J. Valley

Speleothems formation as a recorder of climate signals

Speleothems are cave deposits [from Latin *spēlaeum* cave]

their formation include processes related to ocean, atmosphere, hydrosphere, soil, epikarst

1. Soil CO_2 rainwater carbonic acid:

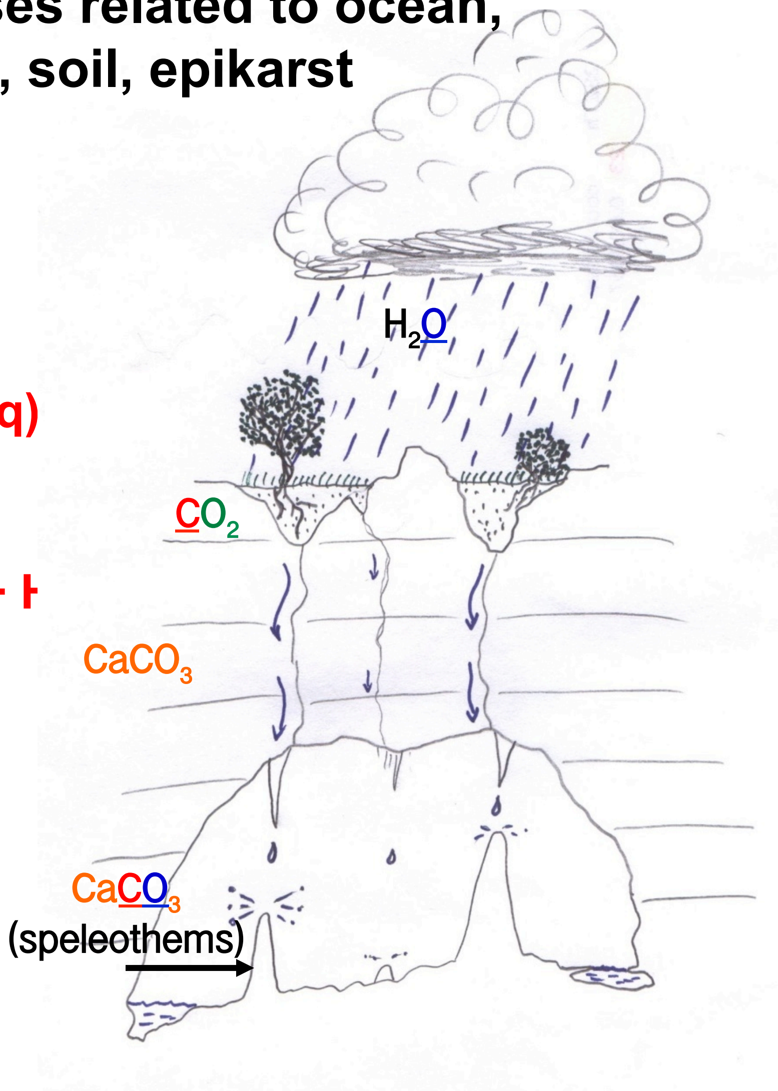
CO_2 (g) + H_2O (aq) → H_2CO_3 (aq)

2. Dissolution of the carbonate bedrock

H_2CO_3 (aq) + $CaCO_3$(s) → $2HCO_3^-$ (aq) + Ca^{2+}(aq)

3. CO_2 degassing and carbonate precipitation

$2HCO_3^-$ (aq) + Ca^{2+} (aq) → CO_2 (g) + $CaCO_3$(s) +
(aq)



Speleothems are laminated and each lamina can be dated precisely. Each lamina carry environmental information.

The $\delta^{18}O$ values of speleothems depend on:

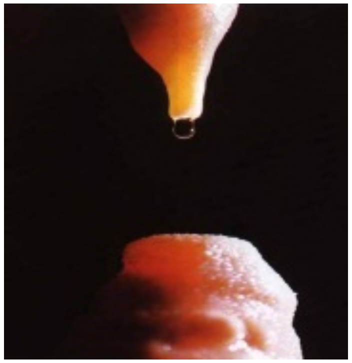
Temperature and the isotopic composition of the water from which the speleothems were deposited, which in turn depends on the isotopic composition of the source (sea surface).

rainfall amount, seasonality, and mixing processes in the unsaturated zone.

$\delta^{13}C$ values of speleothems is a proxy of:

Vegetation type;

plant stress due to water deficiency and temperature, atmospheric CO_2 concentrations, water-soil rock interaction.

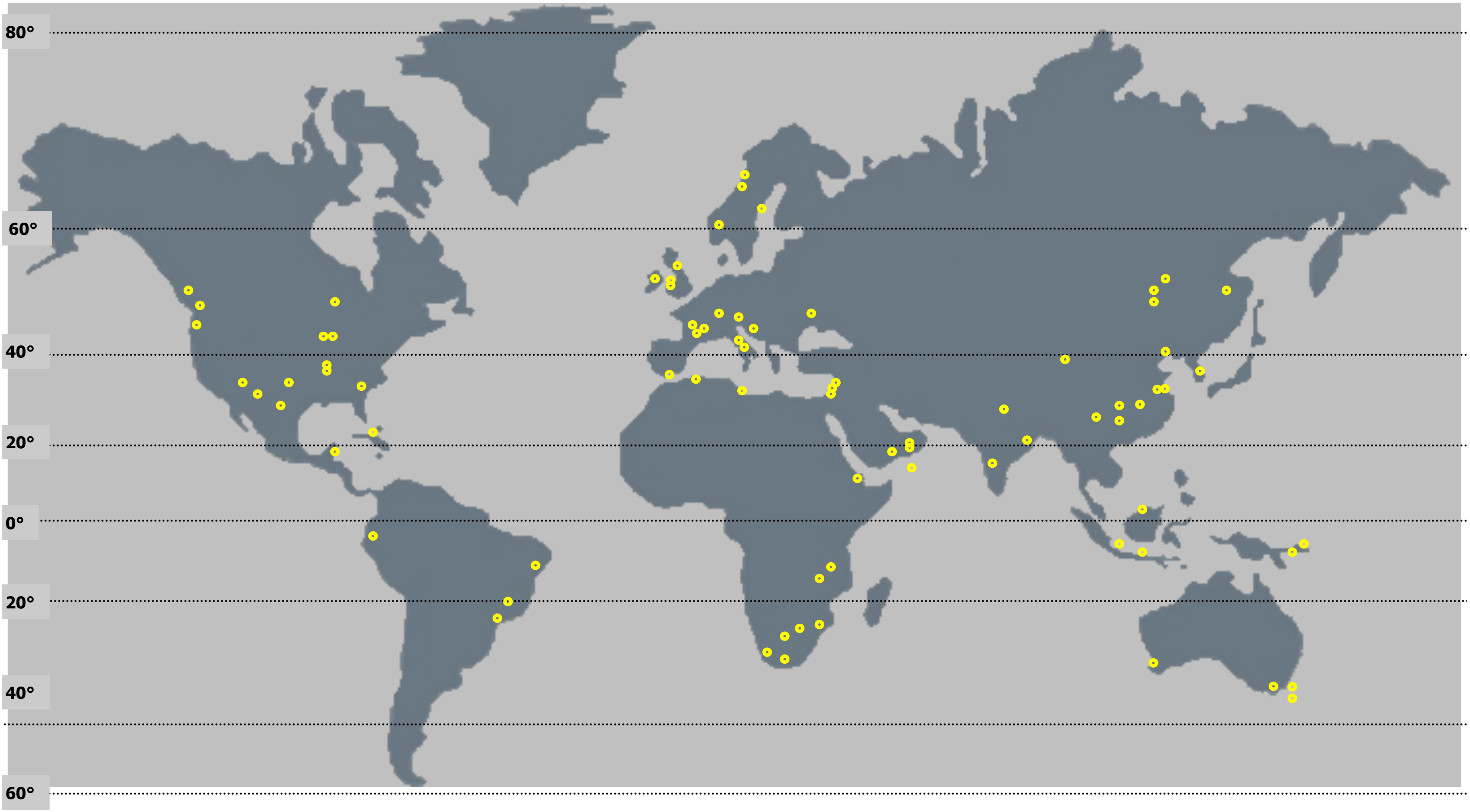


speleothems are excellent recorders for continental paleoclimate:

- Speleothems scattered over most continental areas (large scale teleconnection over distant regions).
- The environmental and paleoclimate information can be on different time scale (thousand, hundred, decades, several years, seasonality).

Their growth period and isotopic and geochemical composition reflects larger scale processes:

- rainfall source,
- storm patterns,
- ocean-land heat transfer,
- vegetation,
- soil-water-rock interactions,

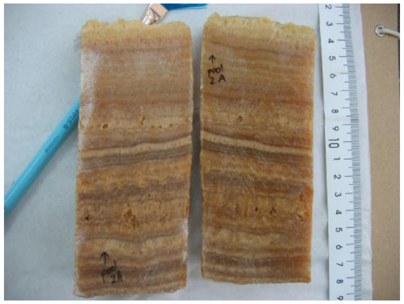

80°
60°
40°
20°
0°
20°
40°
60°

THE LARGE SCALE PICTURE:
Marine—Atmosphere-Land relationships

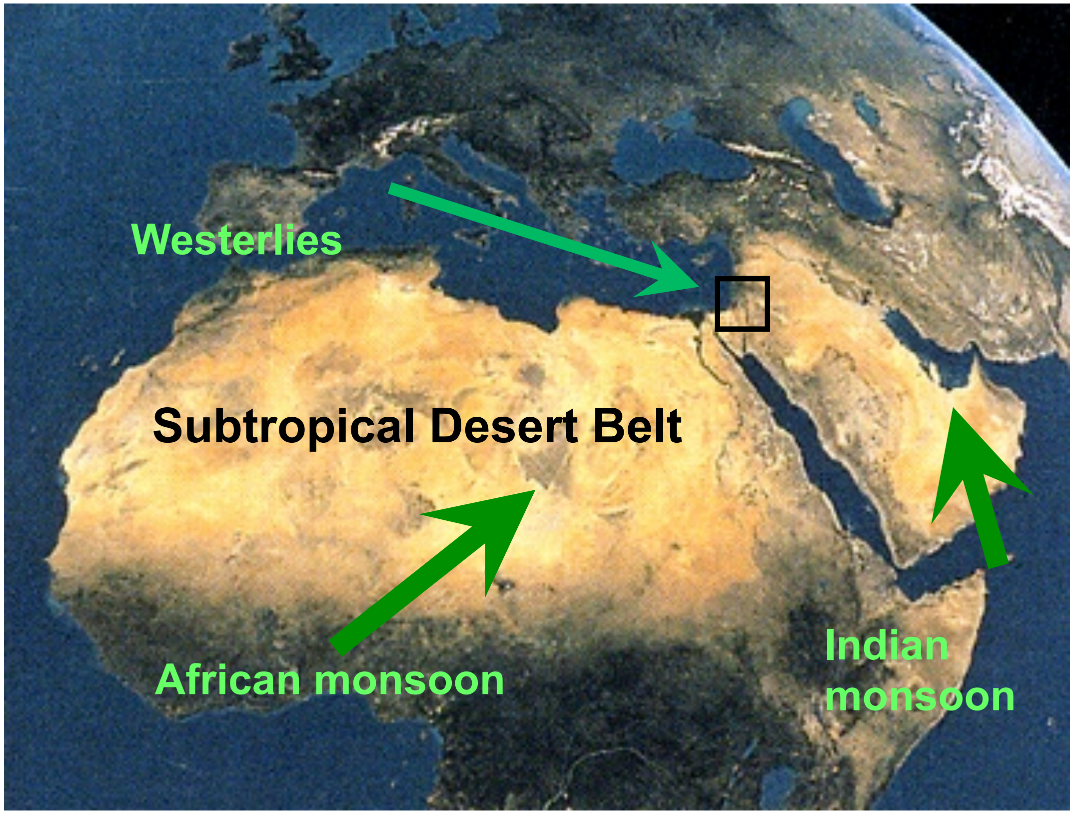
Series of abrupt climate change

marine cores

speleothems



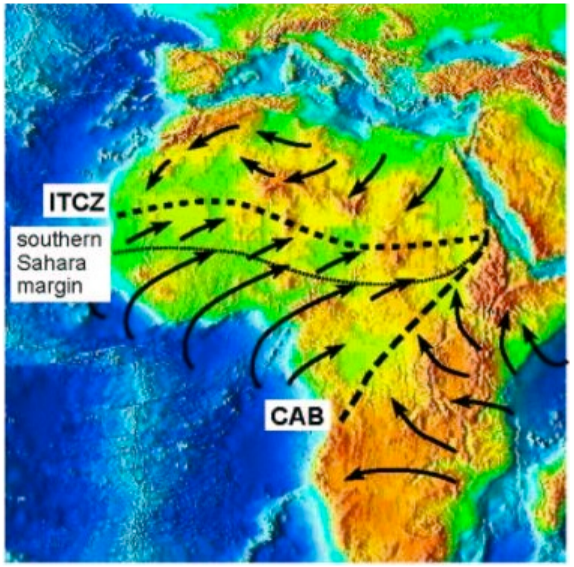
ice core



THE LARGE SCALE PICTURE:

The Middle-East and North Africa, is part of large desert belt, located at the boundary between high - to- mid latitude and tropical-subtropical climate systems. The Mediterranean Sea moderate the climate in the Eastern Mediterranean (EM).

The synoptic system in the EM. Rainfall fronts originate in the NE Atlantic Ocean, pass over Europe and extract moisture from the Mediterranean Sea.

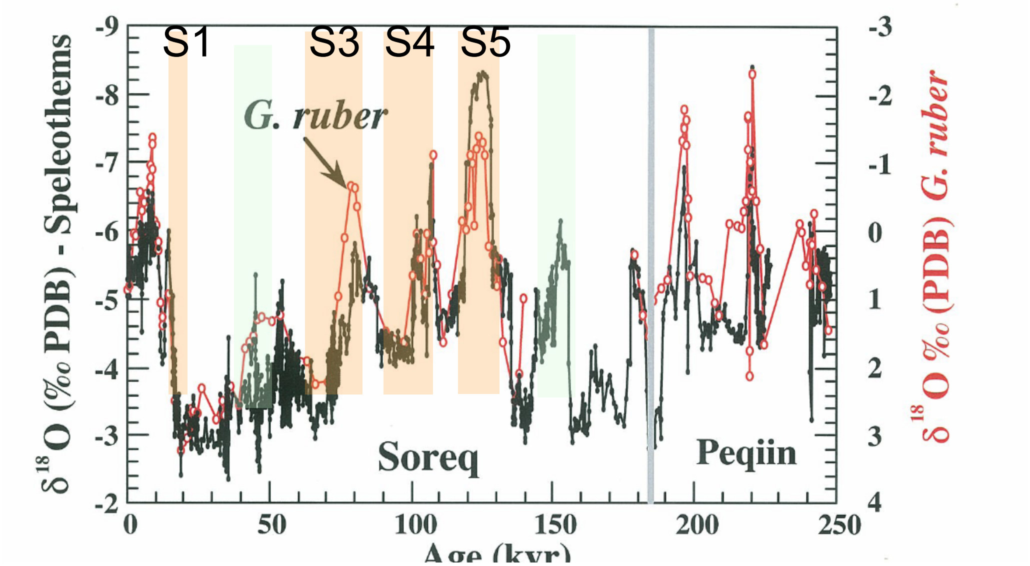


The Nile basin hydrology is connected to the Mediterranean Sea. It is linked to the intensity of the African/Asian monsoon systems that originate in the low latitudes of the Atlantic or the Indian Ocean.

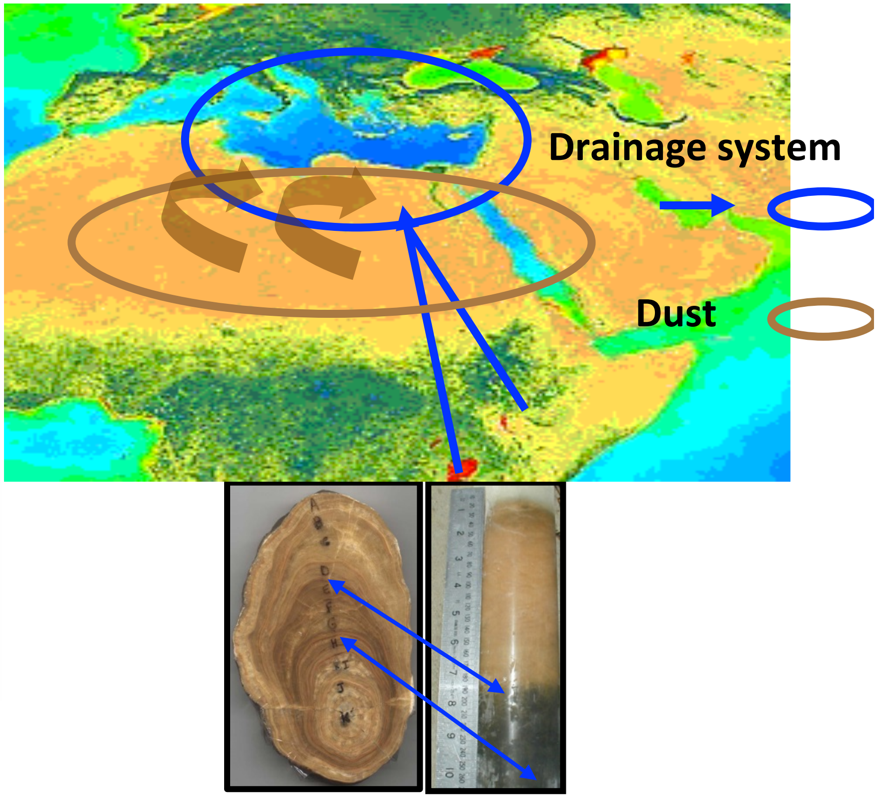
Eastern Mediterranean Speleothems: regional and global synchroneity

1. Monsoon-driven leading to increased River Nile discharge and increased river discharge from central Sahara.
2. Enhanced westerly activity, resulting in increased regional rainfall.
3. **Sapropel layers:** organic-rich marine sediments, finely laminated, devoid of benthic fauna, rich in sulphides, reflecting anoxic conditions.

- Synchronicity over the region.
- Lowest $\delta^{18}O$ speleothems coincide with sapropels.



Bar-Matthews et al., GCA 2003



How does the land record response to the duality between the Atlantic-Mediterranean system and the intensity of the African/Asian monsoon systems?

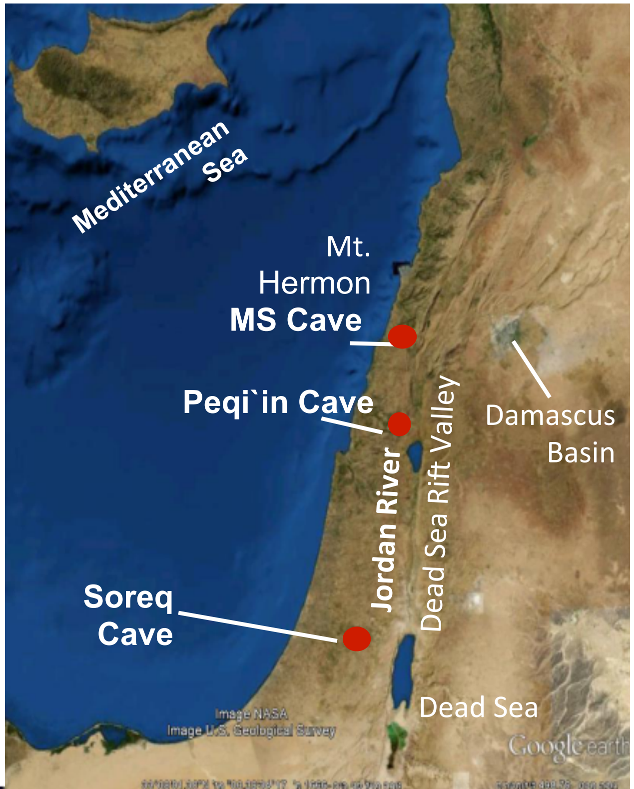
What are the human implications?

Location of caves:

From average annual precipitation of 800 mm to less than 50 mm

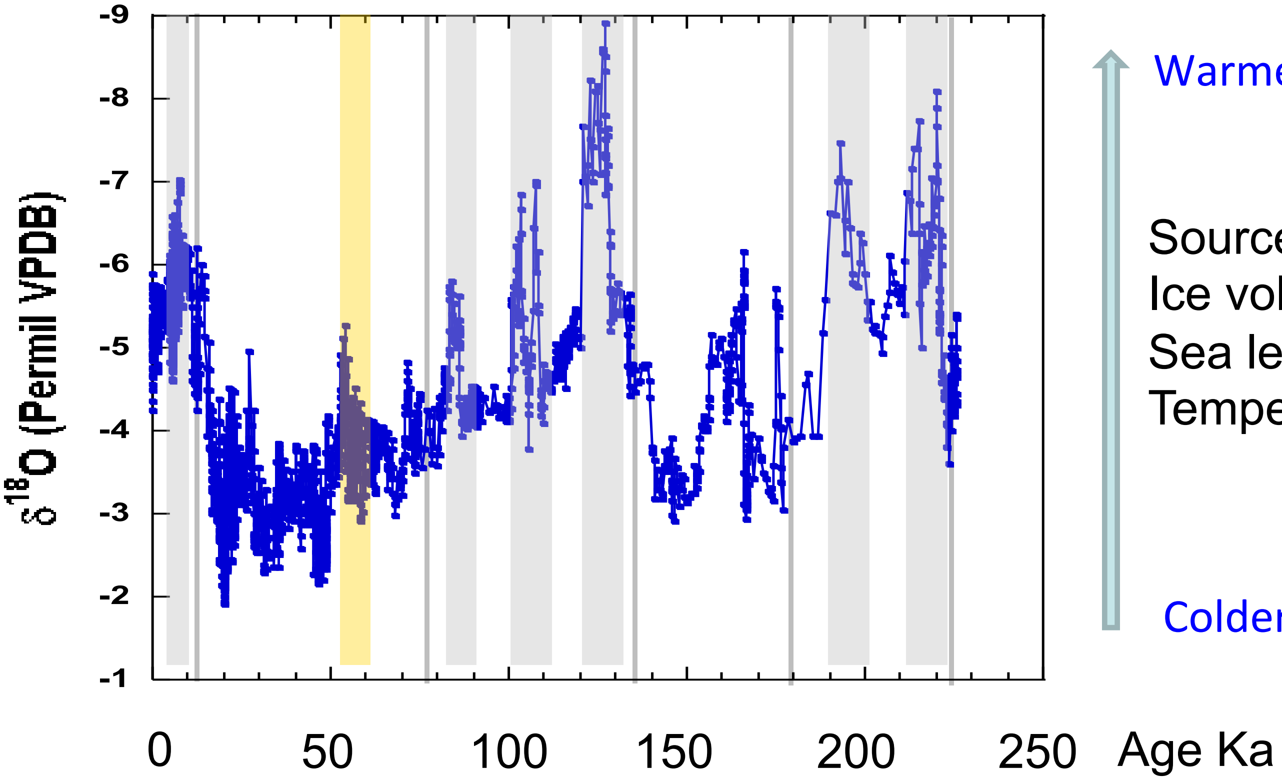
Negev Desert Caves

●



Eastern Mediterranean Speleothems – The oxygen isotopic record:

- Continuous growth through glacial/interglacial cycles;
- water was always available; annual precipitation during warm interglacials and cold glacials was higher than a limiting threshold for speleothems growth. For interglacials ~250-300 mm;
- The large isotopic fluctuations are indicative of major climatic changes (resolution ~10-100 years).

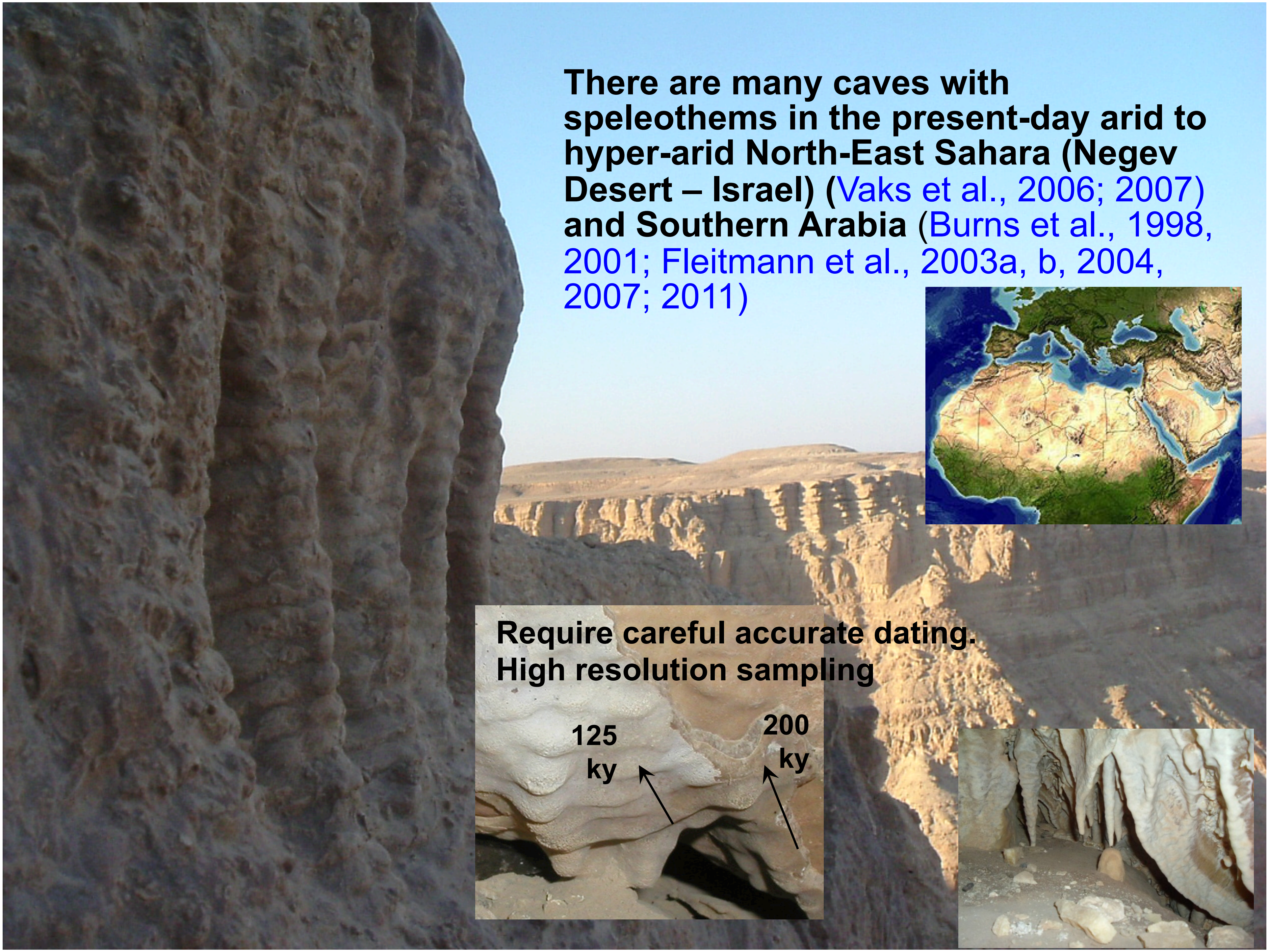


Warmer - wetter

Source
Ice volume
Sea level
Temperature   1‰ = 4°C

Colder - dryer

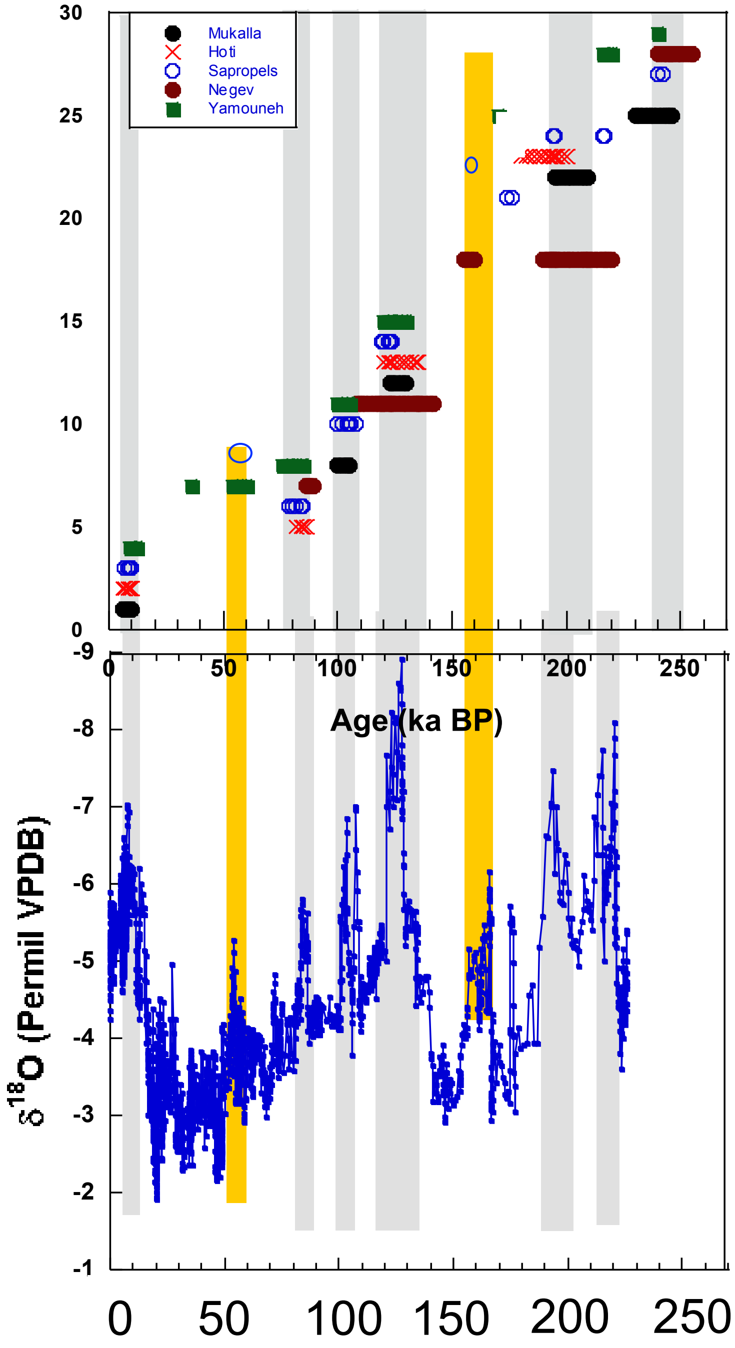
There are many caves with speleothems in the present-day arid to hyper-arid North-East Sahara (Negev Desert – Israel) (Vaks et al., 2006; 2007) **and Southern Arabia** (Burns et al., 1998, 2001; Fleitmann et al., 2003a, b, 2004, 2007; 2011)



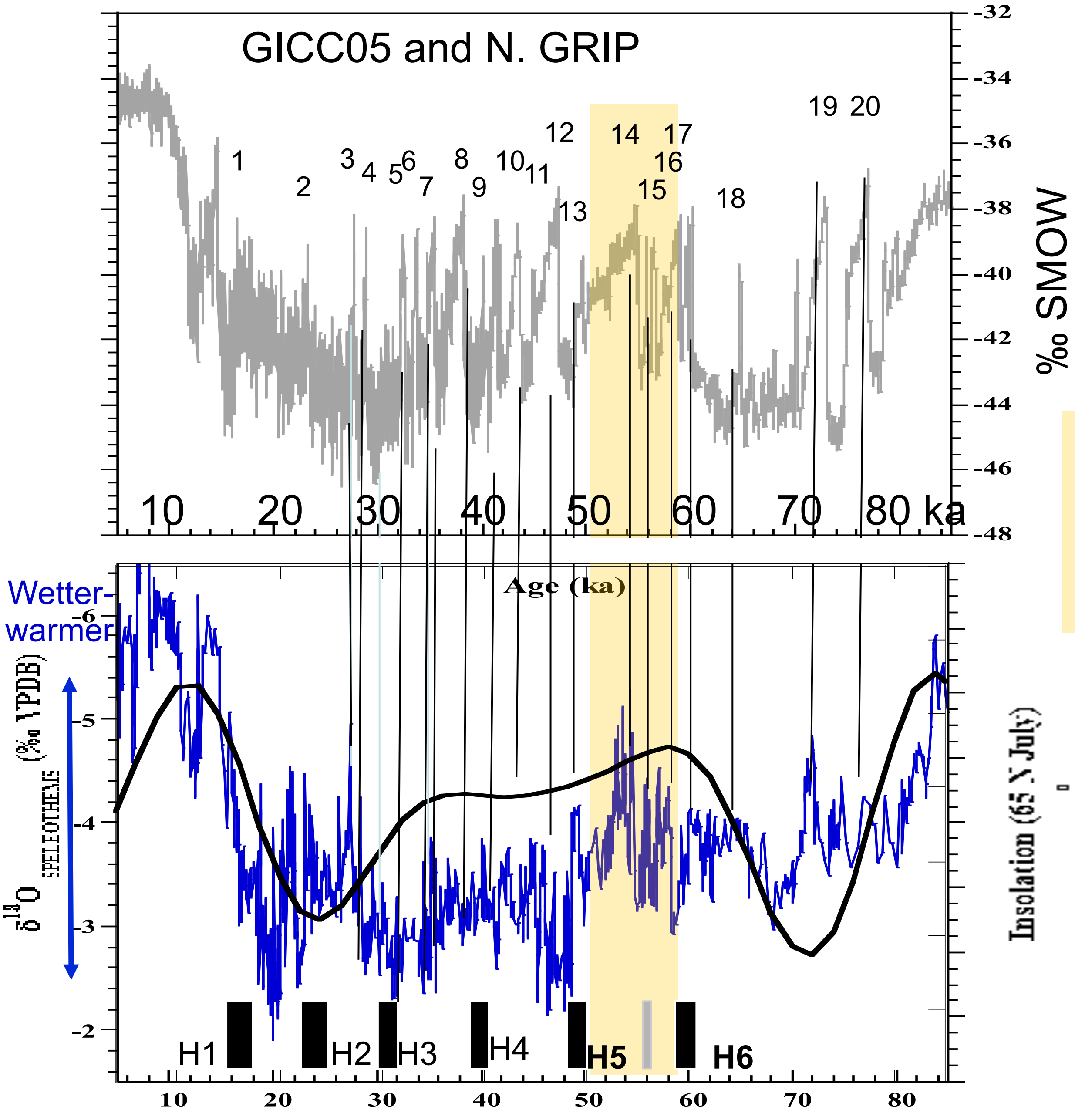
Require careful accurate dating.
High resolution sampling

Depositional periods of Southern Arabia and NE Sahara (Negev Desert, Israel) speleothems:

Mainly during peak interglacials; 250-240, 220-200, 130-120, 108-98, 87-84 ka, and early Holocene.
coinciding with periods of reducing size of the arid Sahara, i.e., periods of sapropel deposition. **There are evidence that major human and animal dispersals out of Africa occurred at these intervals and their arrival into the EM (Zuttiyeh, Qesem, Skhul-Qafzeh).**
The annual rainfall require for their deposition during interglacial is estimated at ~250-300 mm.



THE LARGE SCALE PICTURE in the EM – last glacial

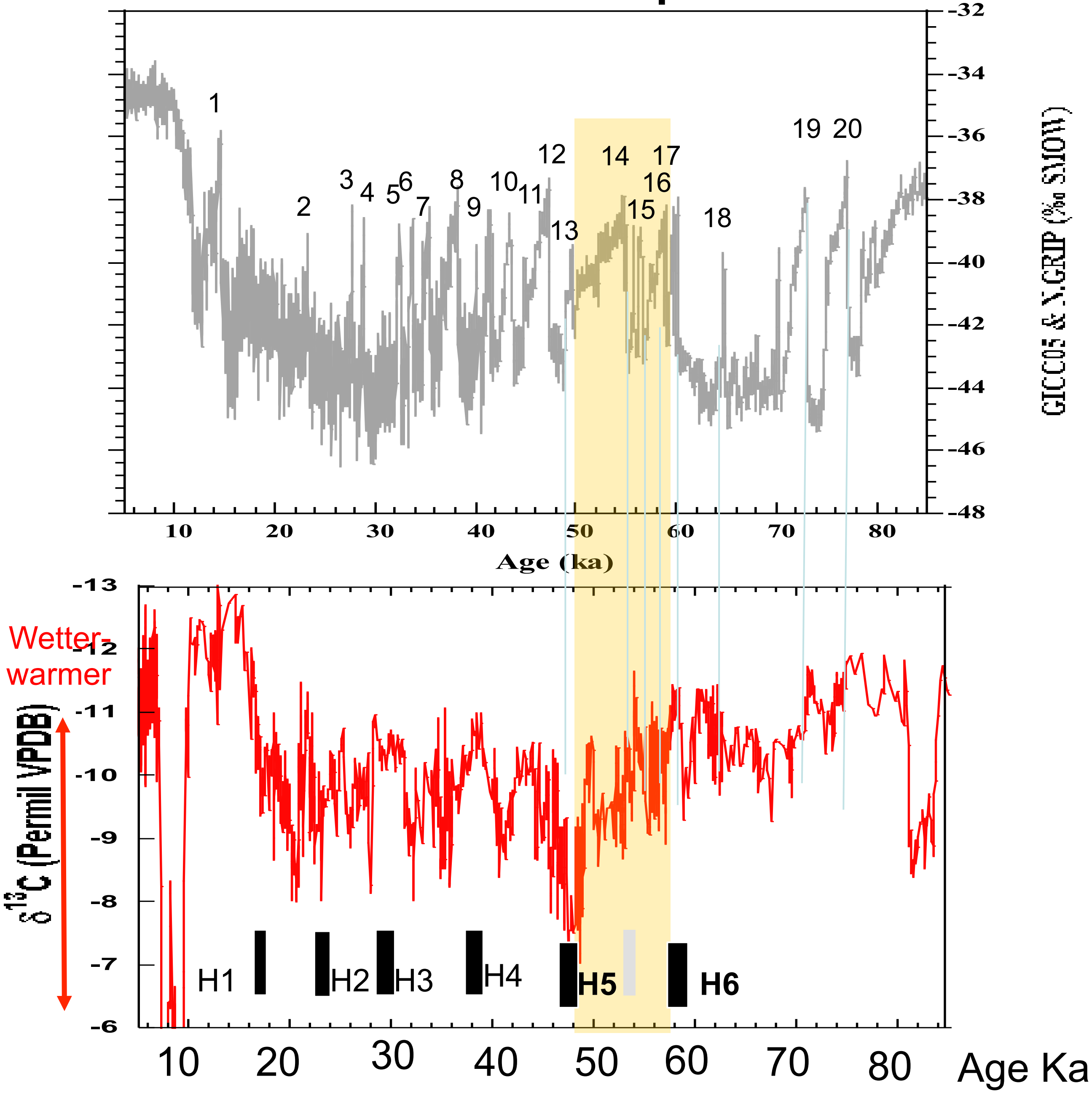


D-O and H events are recorded in EM speleothems.

The most pronounced $\delta^{18}O$ oscillations occur between H6 and H5, ~60 - 50 ka, during D-O 16 to D-0 13.

the sharpest transition to almost interglacial wet conditions is at D-O 14, at ~54 ka, followed by gradual change to full dry glacial conditions at ~50-48 ka.

D-O and H events in EM speleothems



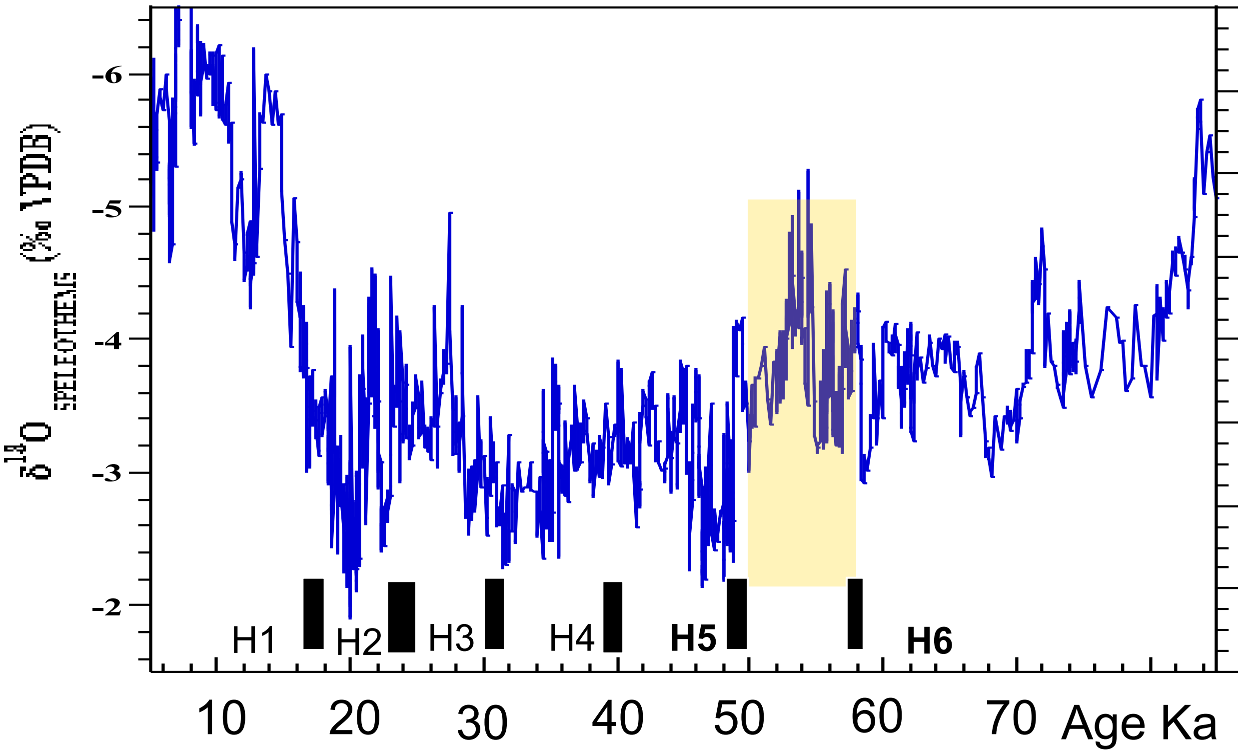
Vegetation response

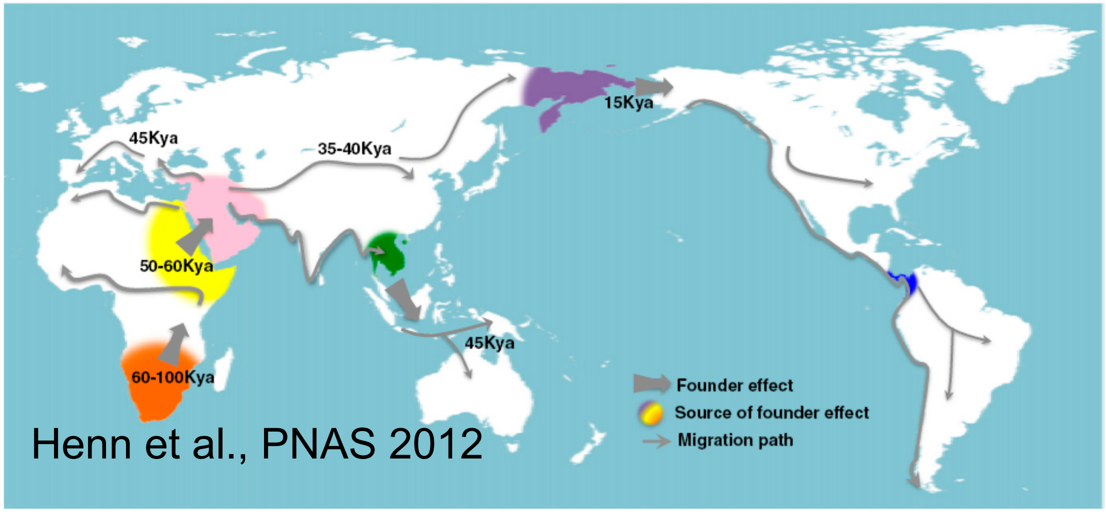
The carbon isotopic composition increase from ~60-50 ka, suggesting transition from C3 Mediterranean type vegetation to more dominant C4 type vegetation.

The Human Connection

Genetic rate of mutation data indicate **very rapid population expansion, the Great Expansion, outside Africa at ~ 60-50 ka**. In this case the expansion occurred between H6 and H5, (D-O 16 to 13). This period can be considered as **The "glacial analogue" to the extreme wet periods during the interglacials.**

Suggesting ideal **"climatic window" for modern human migration** out of Africa. (Manot Cave)





Henn et al., PNAS 2012

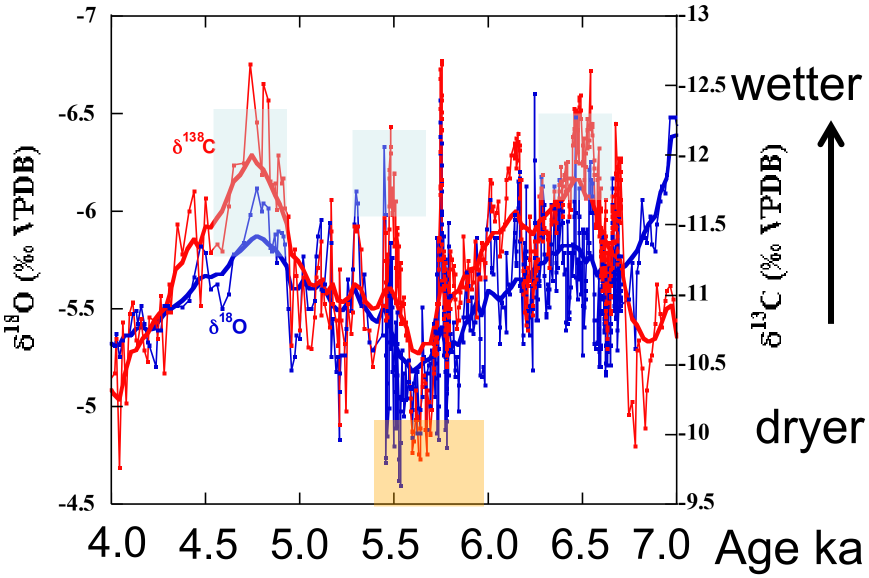
D-O type events during the Holocene and the connection to human history

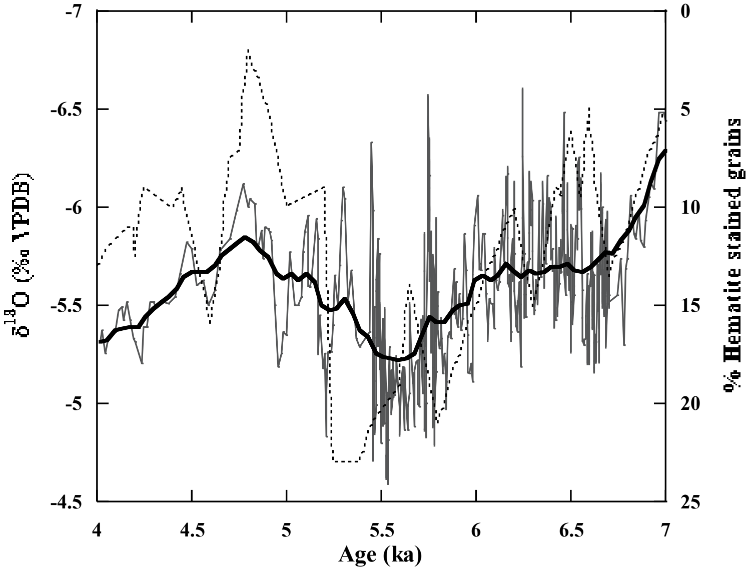
Fast growing speleothems reveal: Mid Holocene, sinusoidal isotopic cyclicity (~1500 years) reflecting changes in rainfall amount.

Droughts
~ 300-400 mm

Wet climate
~ 700-800 mm

Good match with Bond Cycles (ice-rafted debris, Bond et al.,2001) suggesting that high latitude cooling, is associated with drier EM.





Bar-Matthews & Ayalon , 2011

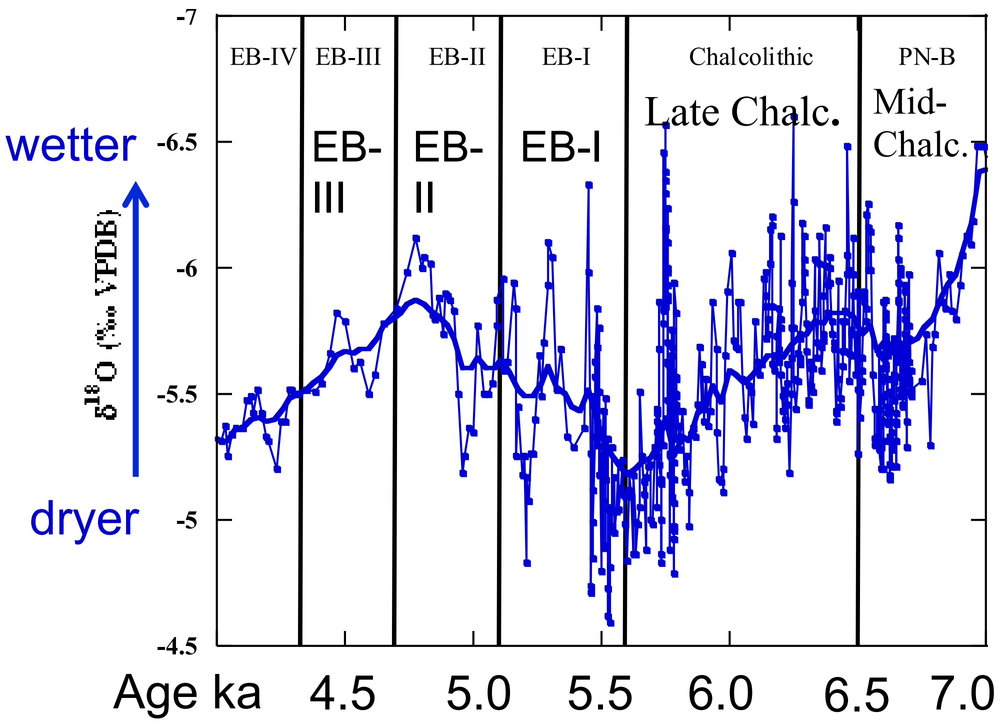
A. Frequent δ^{18}O oscillations (3-10 years resolution).

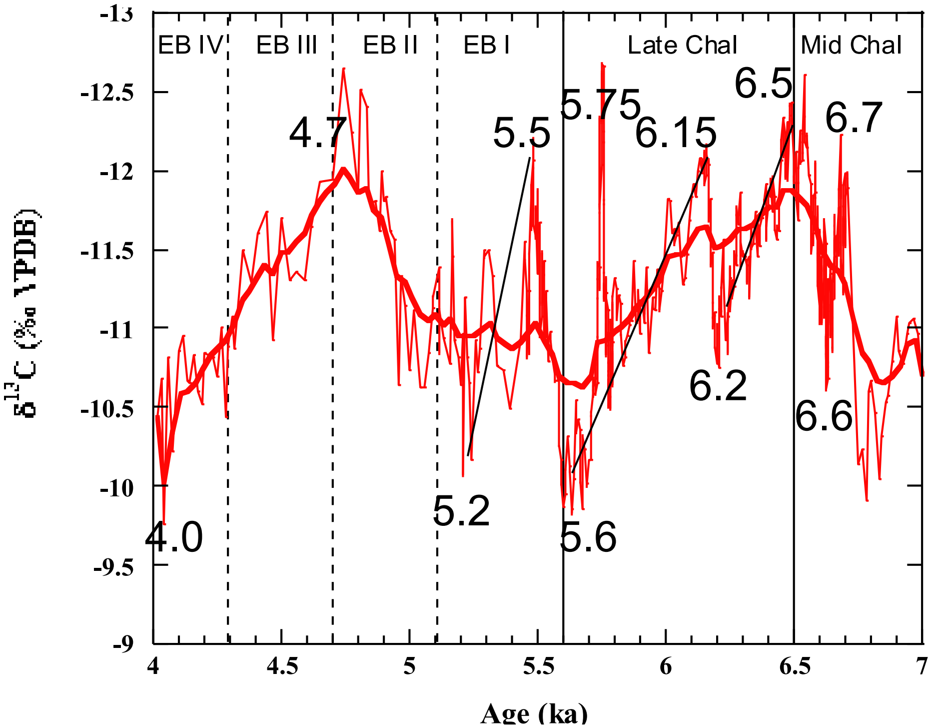
Why? What does it reflect?

B. Human connection

The transition between Mid-Chalcolithic to Late Chalcolithic, and between Early Bronze II to Early Bronze III occur at the peak of wet climate ~700 mm. Transition between Late Chalcolithic to Early Bronze I occur at the peak of dry conditions ~300 mm.

Seesaw trend and Rapid Climate Changes (RCC) **:**
Transitions to wetter conditions are fast ~100 y and to drier conditions slower >200-700 y
Are they reflected in the archeological record?



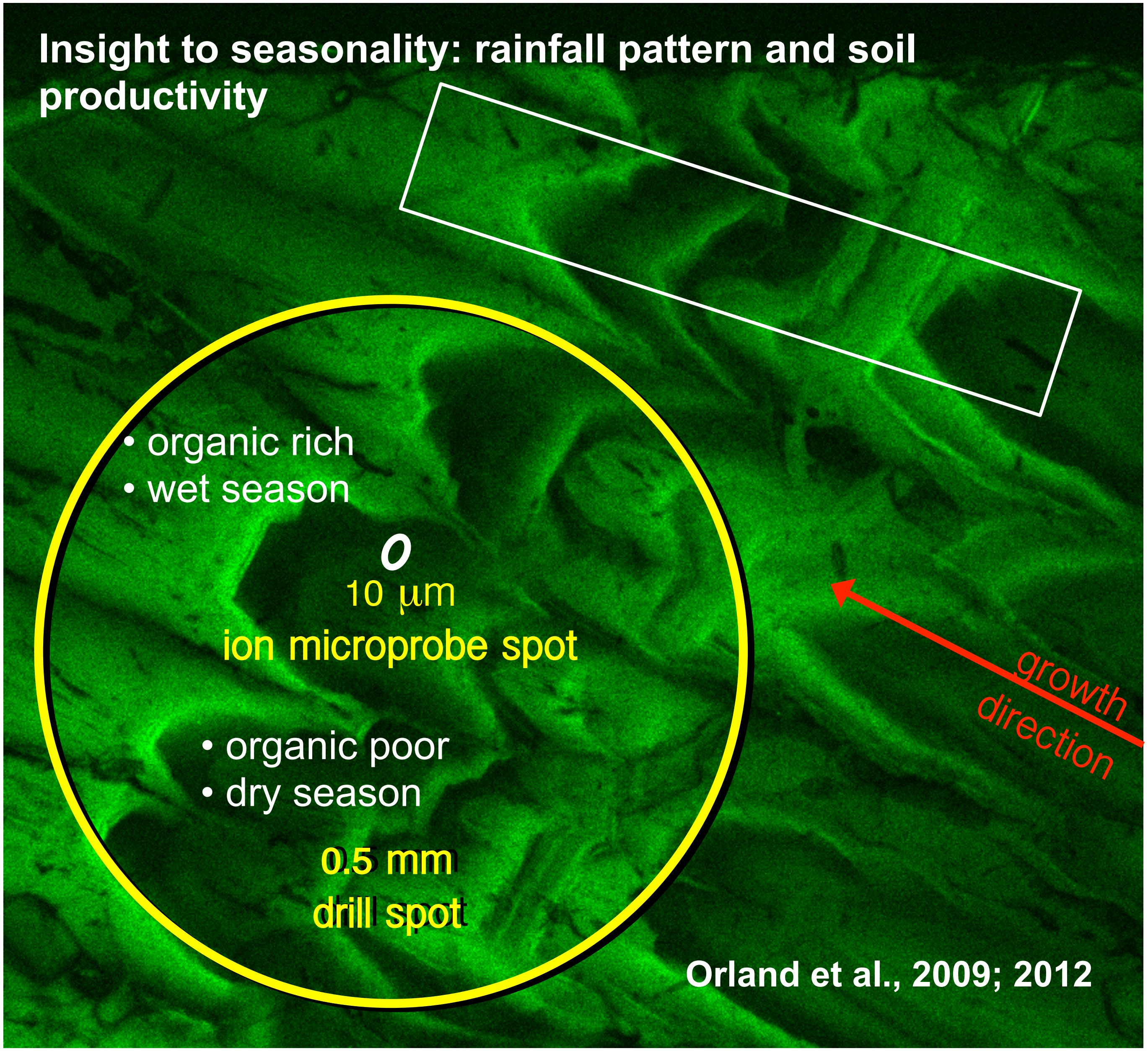


Seasonal resolution in speleothems, what can we gain?

We need to apply advanced analytical techniques for High Resolution

1) High-precision, high-spatial-resolution $\delta^{18}O$ analyses
[Ion Microprobe]

2) Imaging of annual show seasonal change
[Confocal Laser Fluorescent Microscope - CLFM]



Orland et al., 2009; 2012

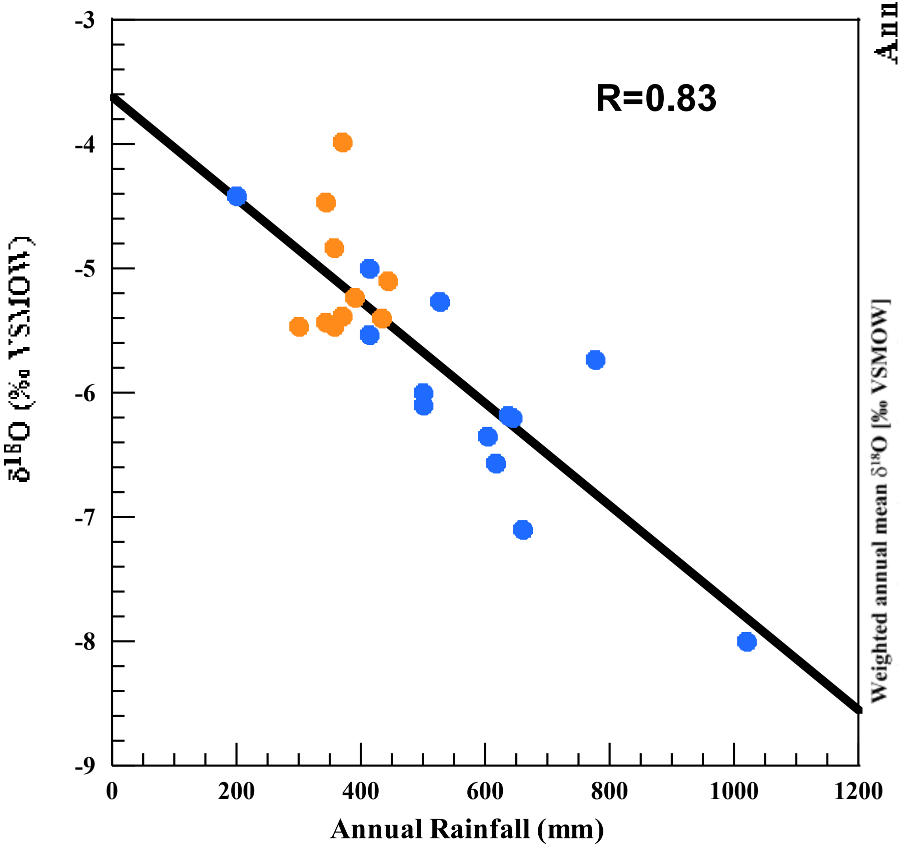
Monitoring active cave in the Eastern Mediterranean semi-arid climate help understanding how speleothems capture seasonal resolution

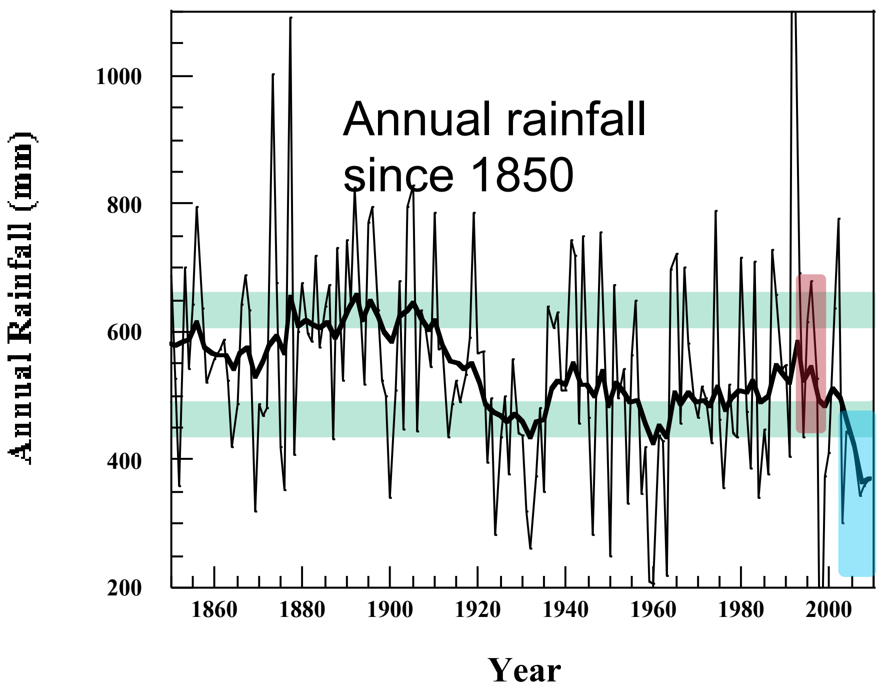
Slow drip - pore water reservoir

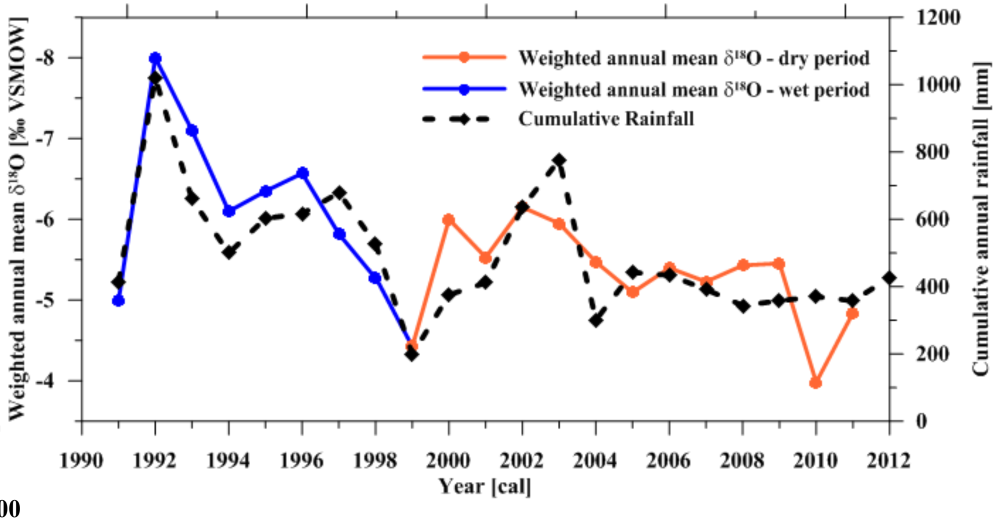
Fast drip – fast reservoir

Annual rainfall vs. $\delta^{18}O$

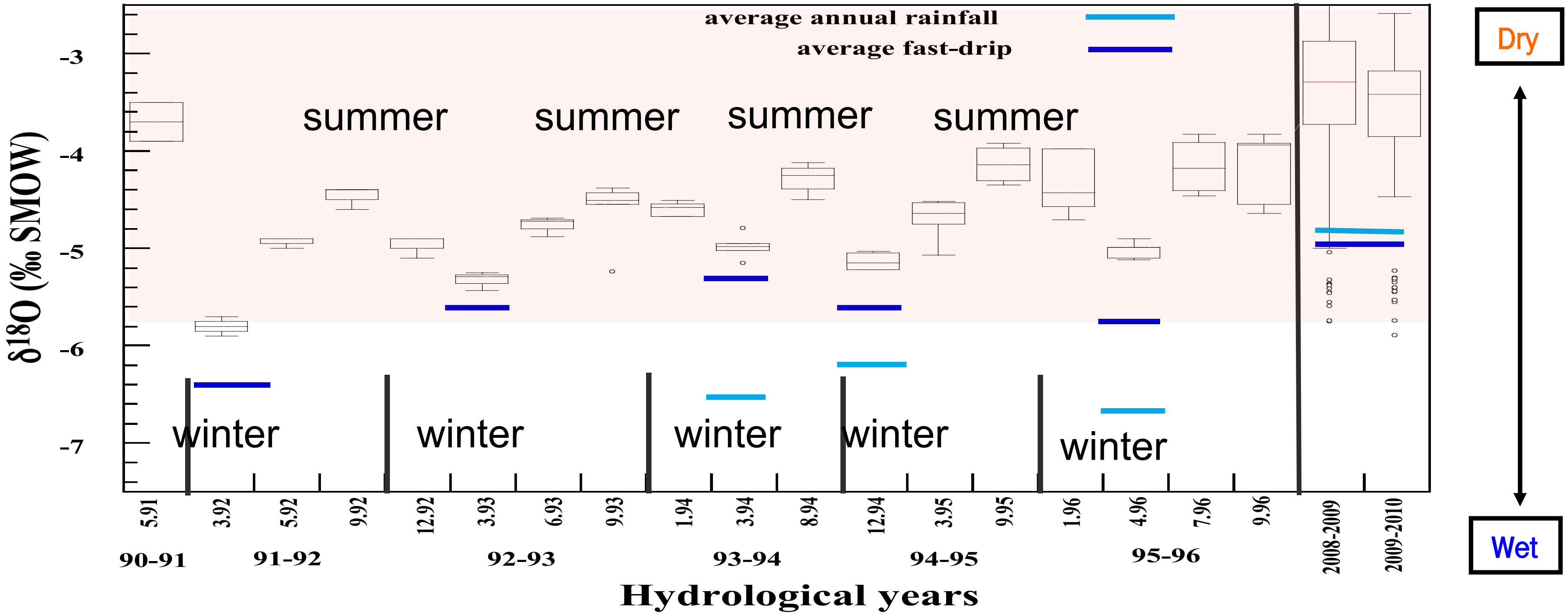
Annual rainfall since 1990
1‰ ~ 280 mm



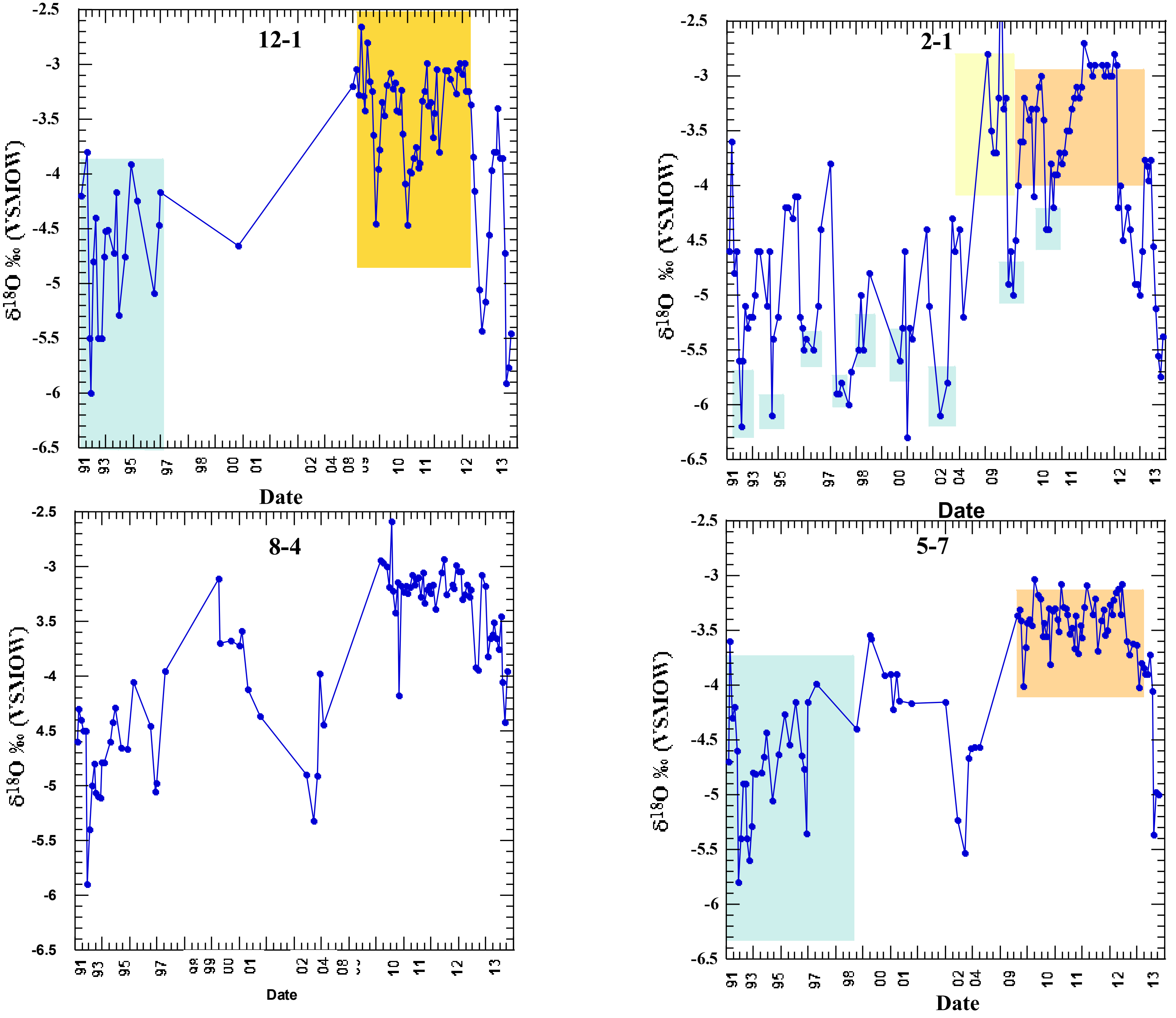

Annual rainfall since 1850



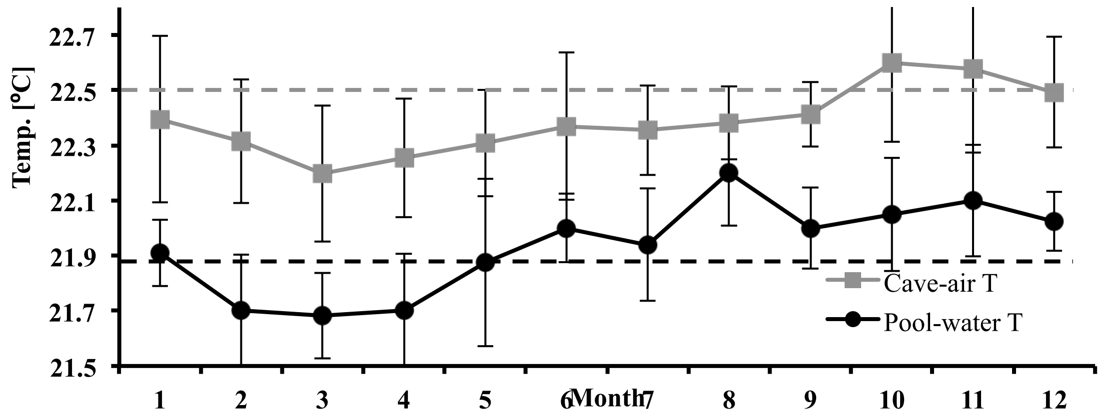
Cave Water Response



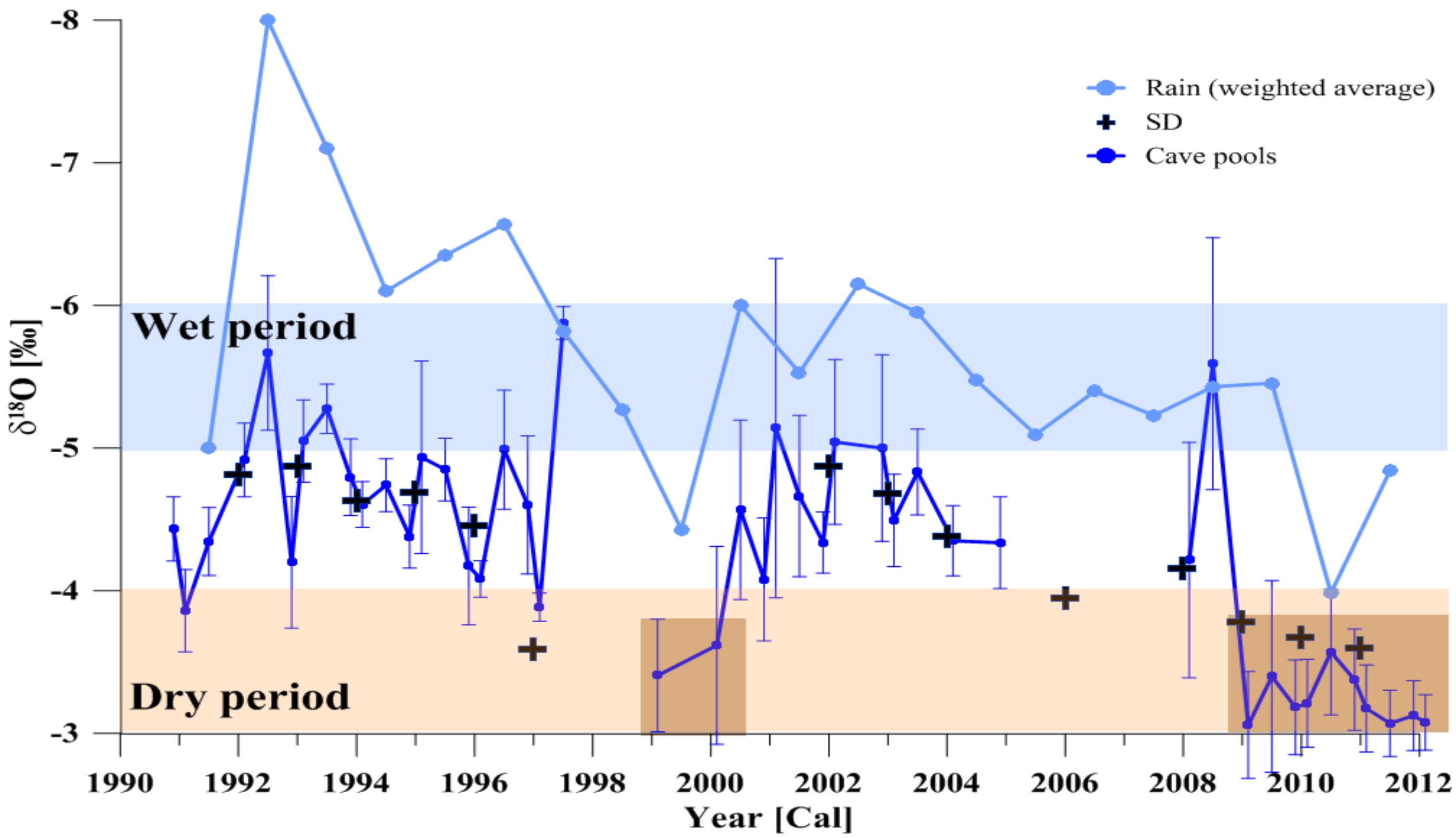
Cave Water Response - wet vs. dry periods



Constant T



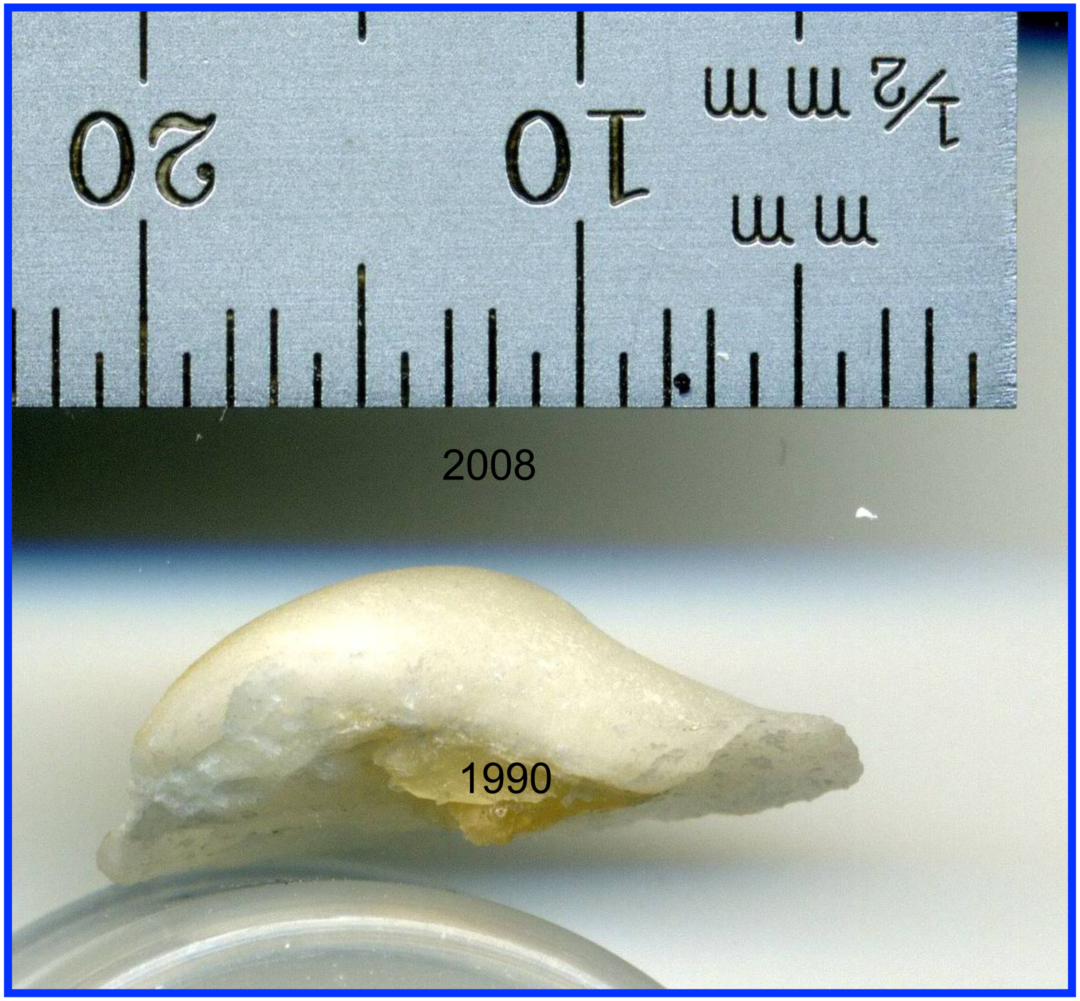
Temp. [ºC]
22.7
22.5
22.3
22.1
21.9
21.7
21.5
1
2
3
4
5
6
Month
7
8
9
10
11
12
Cave-air T
Pool-water T



δ18O [‰]
-8
-7
-6
-5
-4
-3
Wet period
Dry period
Rain (weighted average)
SD
Cave pools
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
2012
Year [Cal]

How changes in rainfall amount, rainfall $\delta^{18}O$-cave water $\delta^{18}O$ are recorded in speleothems?

Stalagmite 5-3-B grew on our water collector since 1990 until 2008, time period for which we have high resolution monitoring of rain and cave water.

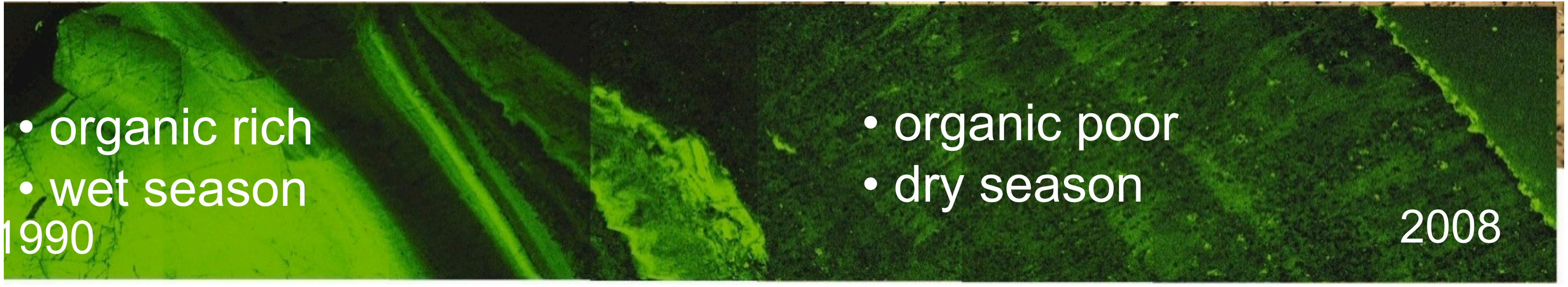


The response of recent speleothems to the cave hydrology

confocal fluorescent microscope and $\delta^{18}O$

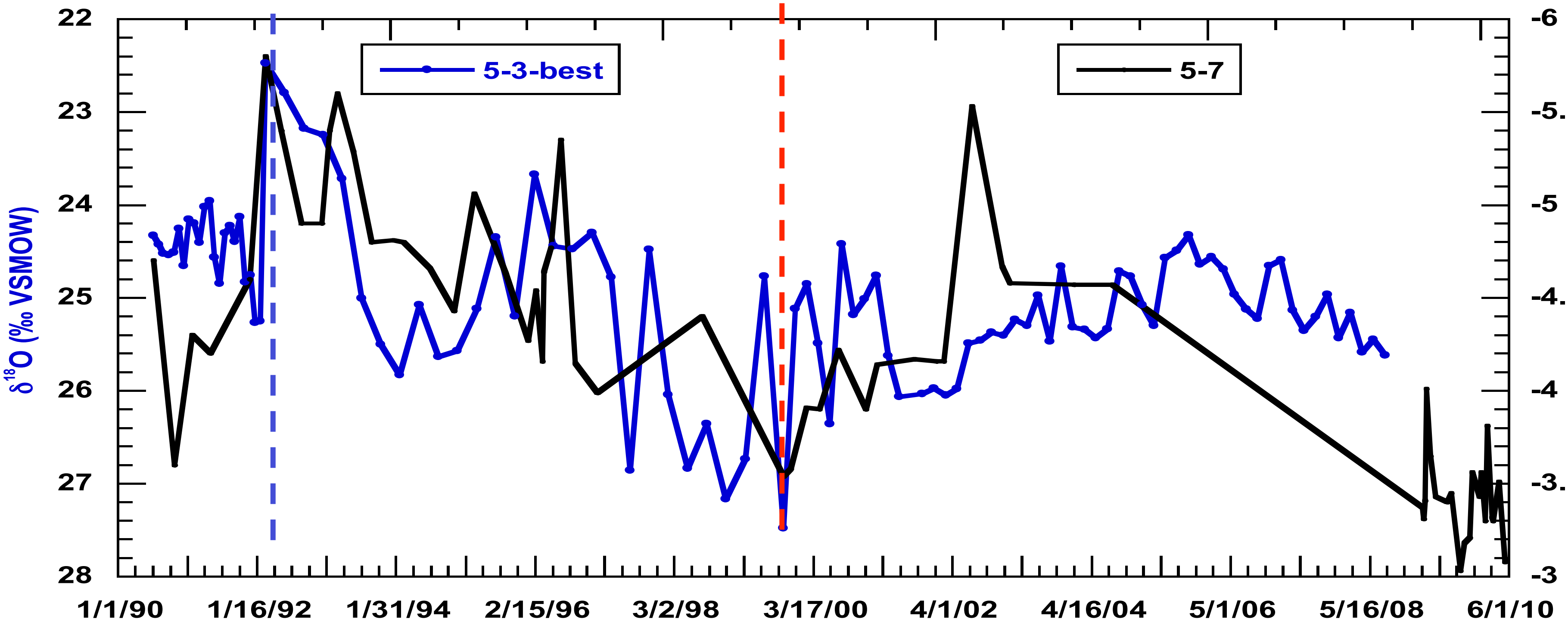
Reveals annual and seasonal changes to the input of organic acids from the soil.

$\delta^{18}O$ changes follow cave water

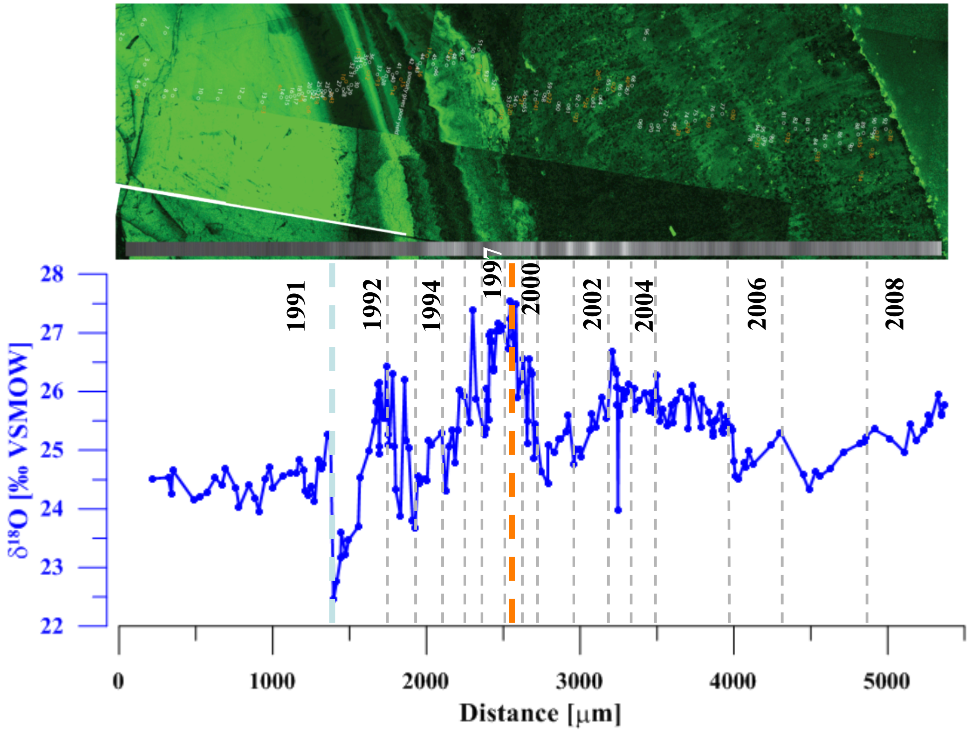


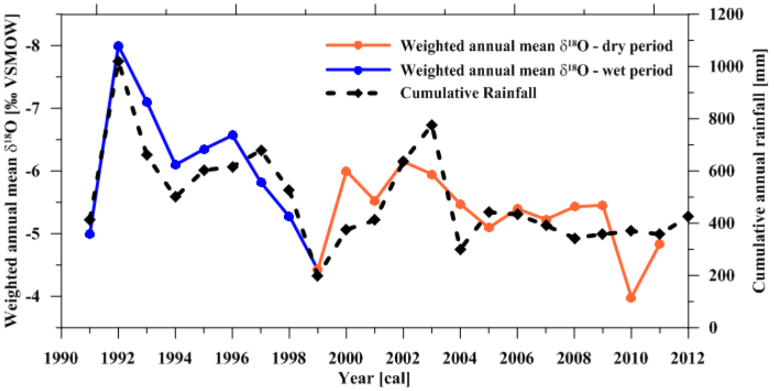
Following “wet” years large seasonality

Following “dry” years diffuse seasonality



The response of recent speleothems to the cave hydrology

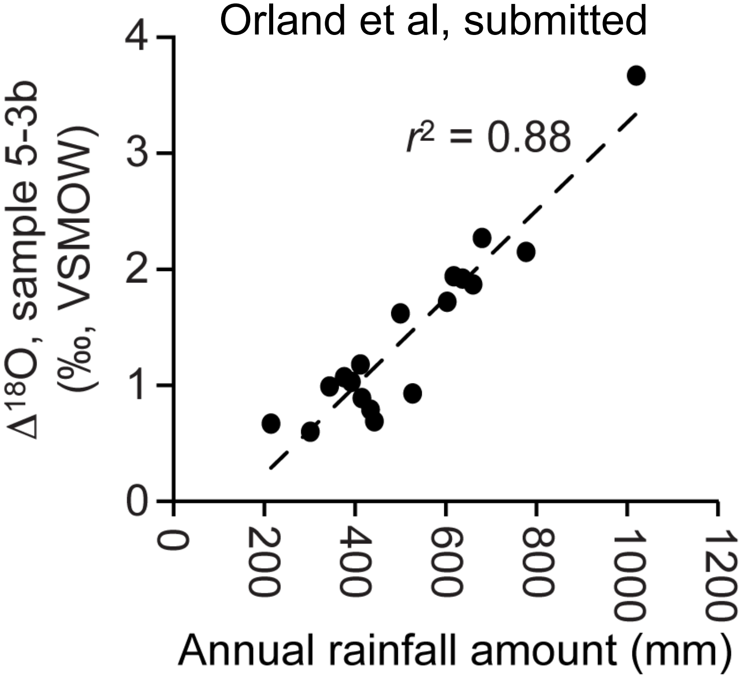




$\Delta^{18}O = \delta^{18}O$ dark - $\delta^{18}O$ light

$\Delta^{18}O = \delta^{18}O_{calcite}$ difference between bright and dark laminae as function of rainfall amount

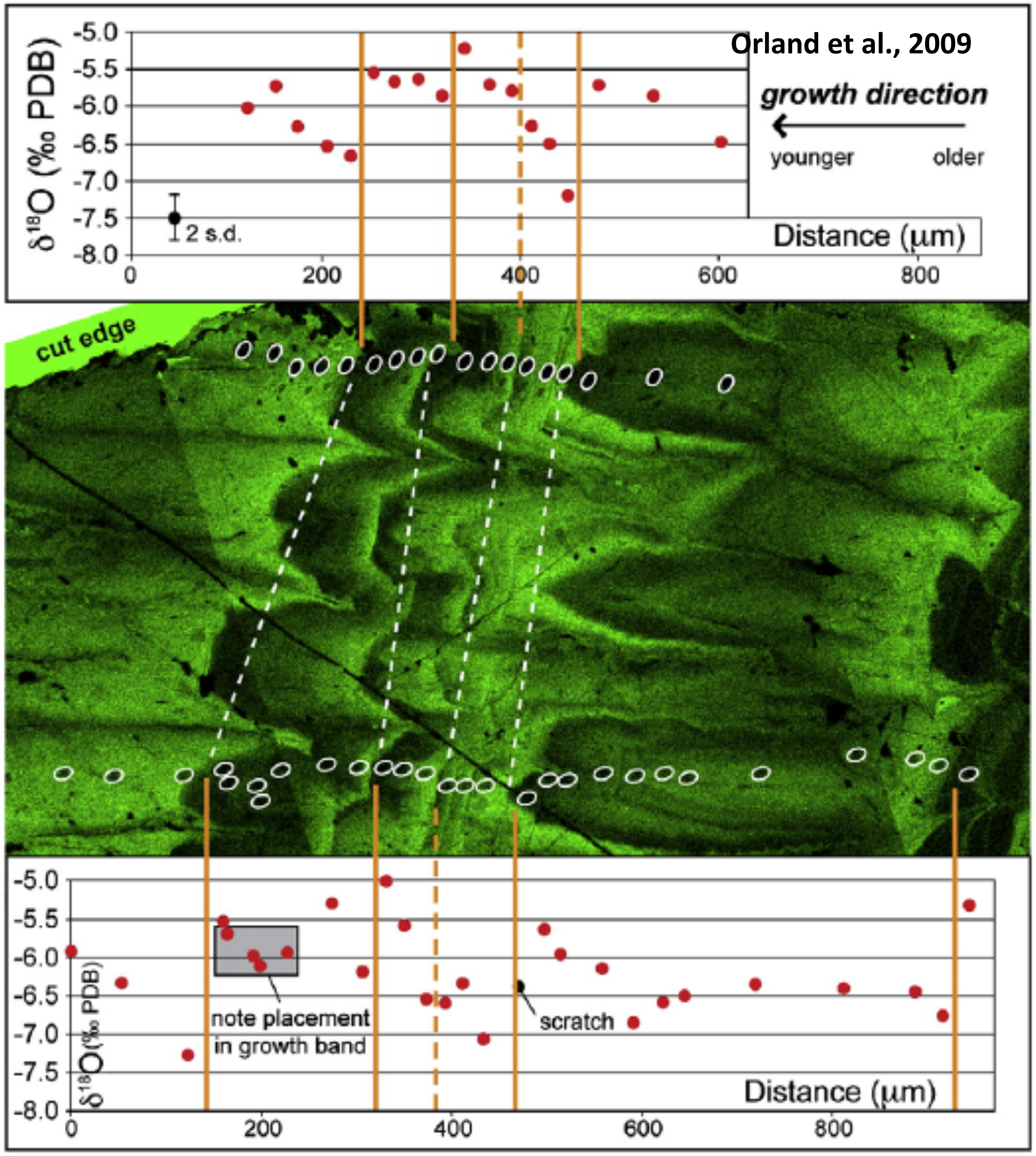
Orland et al, submitted



- organic poor
- dry season

- organic rich
- wet season

Late Holocene sample: Seasonal Sawtooth fluorescence banding during the Holocene, what does it mean?

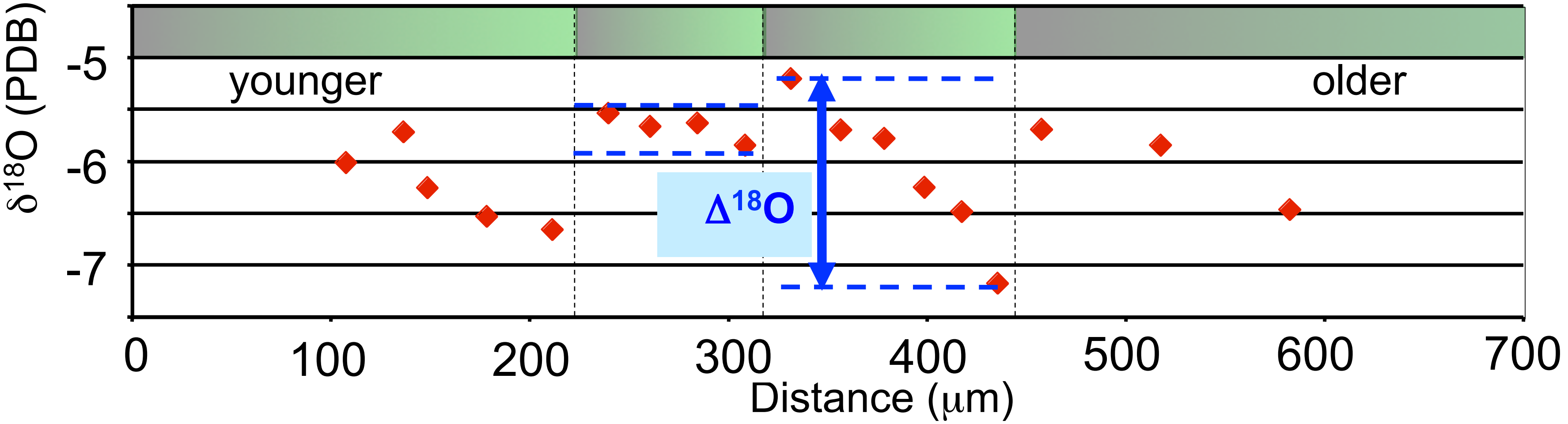


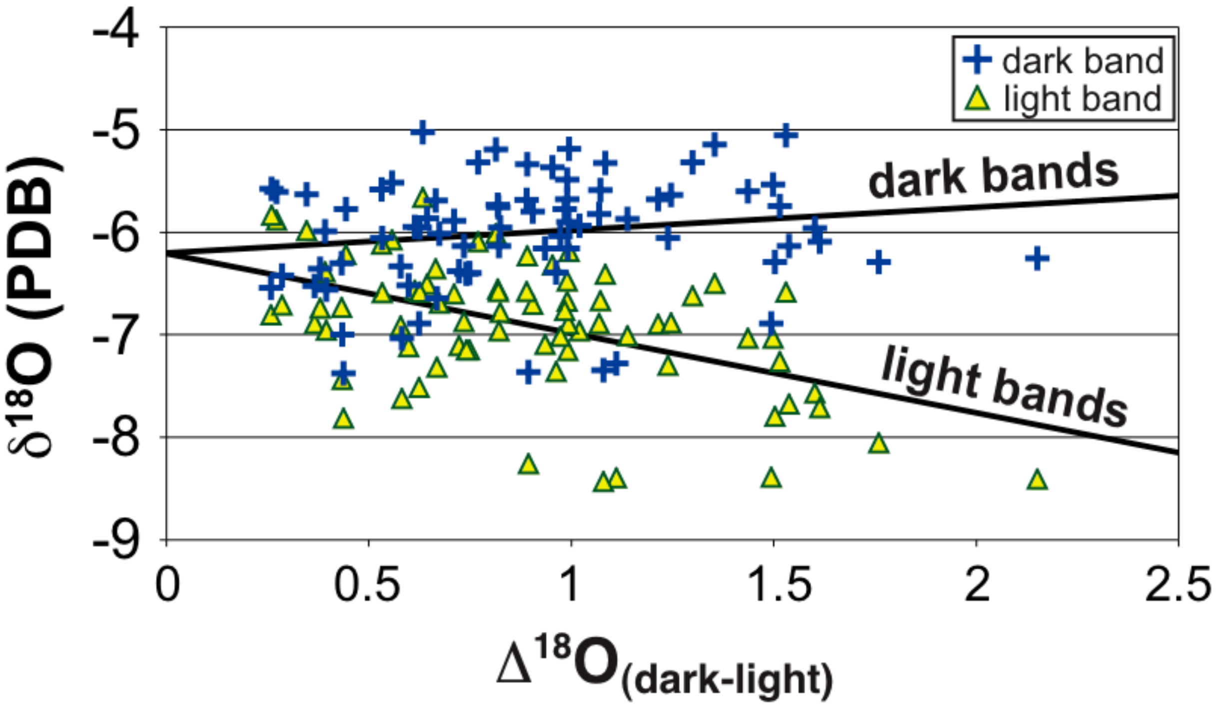
Each band has an abrupt onset of a bright low ^{18}O calcite followed by a gradient to dark higher ^{18}O calcite through time.

The pattern repeat itself and mimics the change in present-day isotopic composition of cave water between winter-summer.

Orland et al., 2009

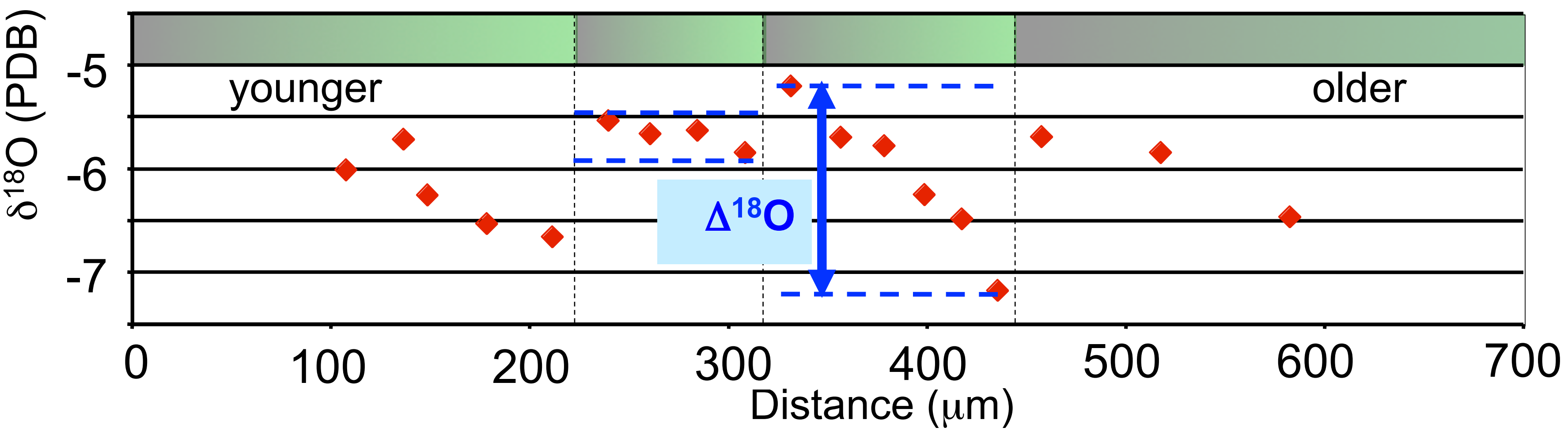
$\Delta^{18}O = \delta^{18}O\text{dark} - \delta^{18}O\text{light}$

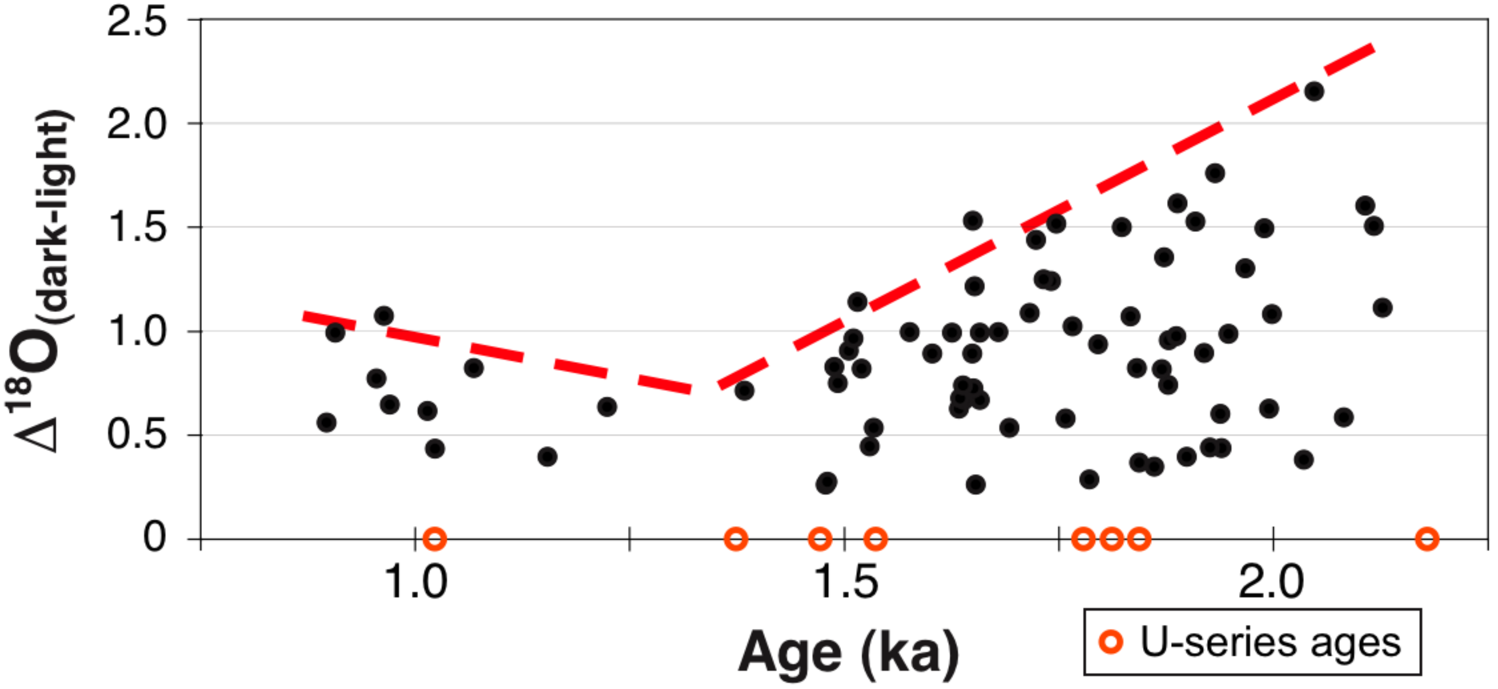




Orland et al., 2009

$\Delta^{18}\text{O} = \delta^{18}\text{Odark} - \delta^{18}\text{Olight}$

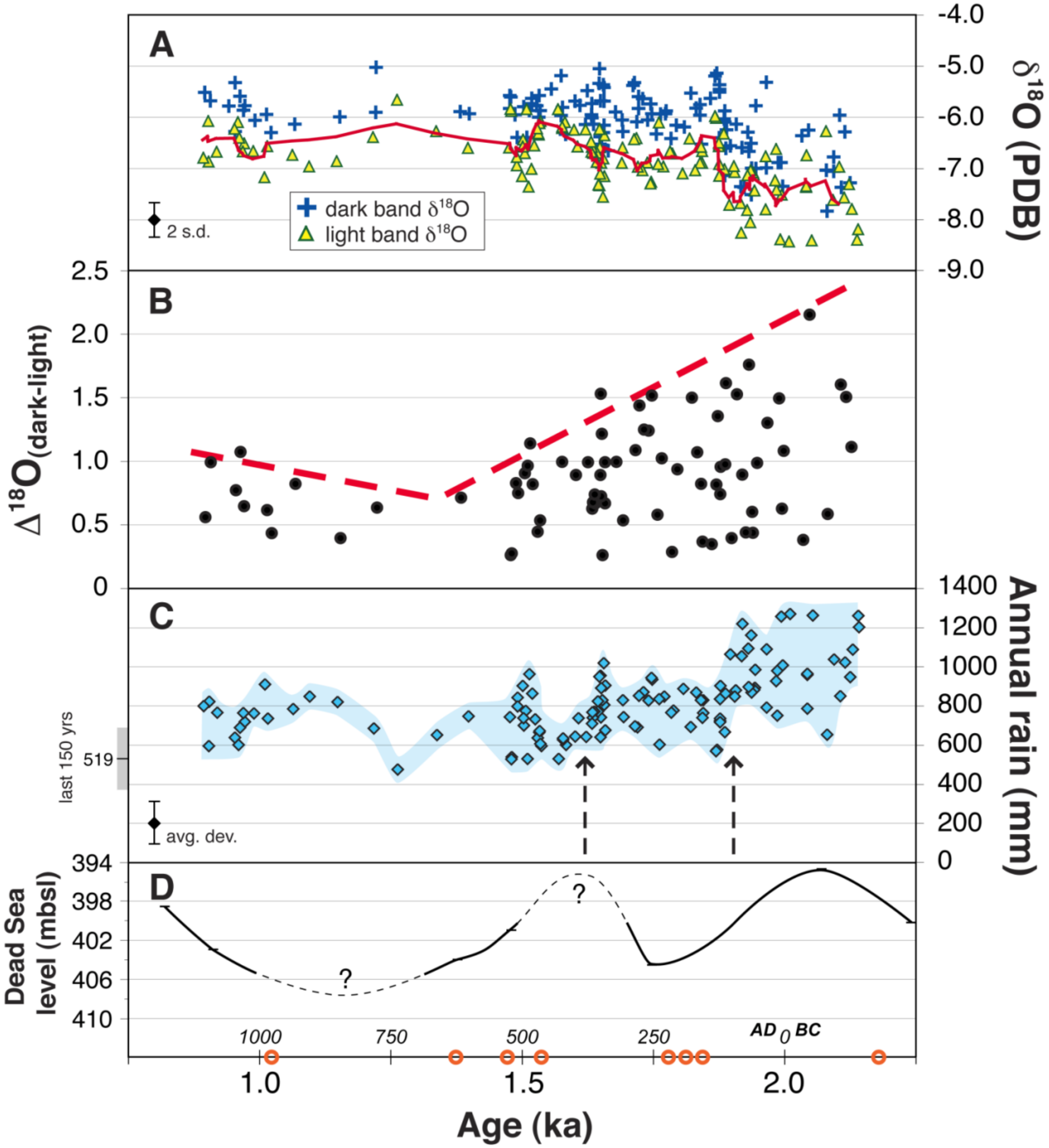




Orland et al., 2009

DRY

WET



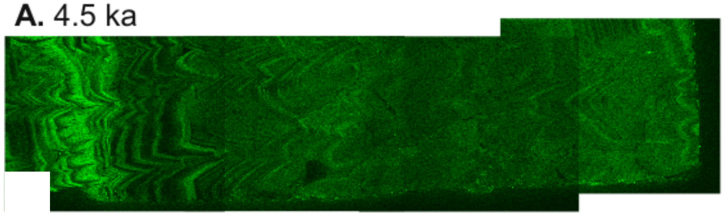
Connection to archeology

Orland et al., QR 2009

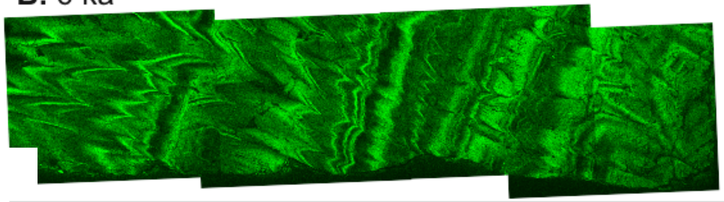
Gradual decrease in rainfall amount, contributed to the decline of the Roman and the Byzantine Empire in the Levant region.

Seasonality pattern: From last glacial into the Holocene

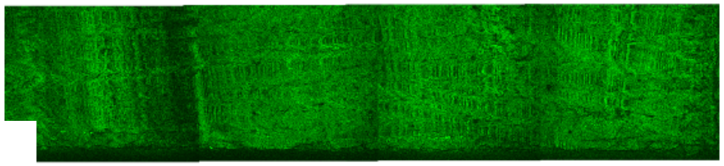
A. 4.5 ka



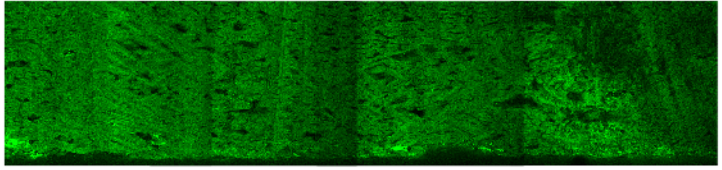
B. 6 ka

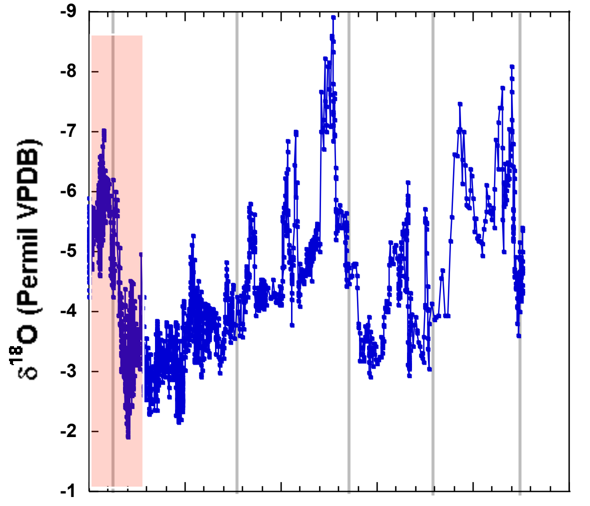


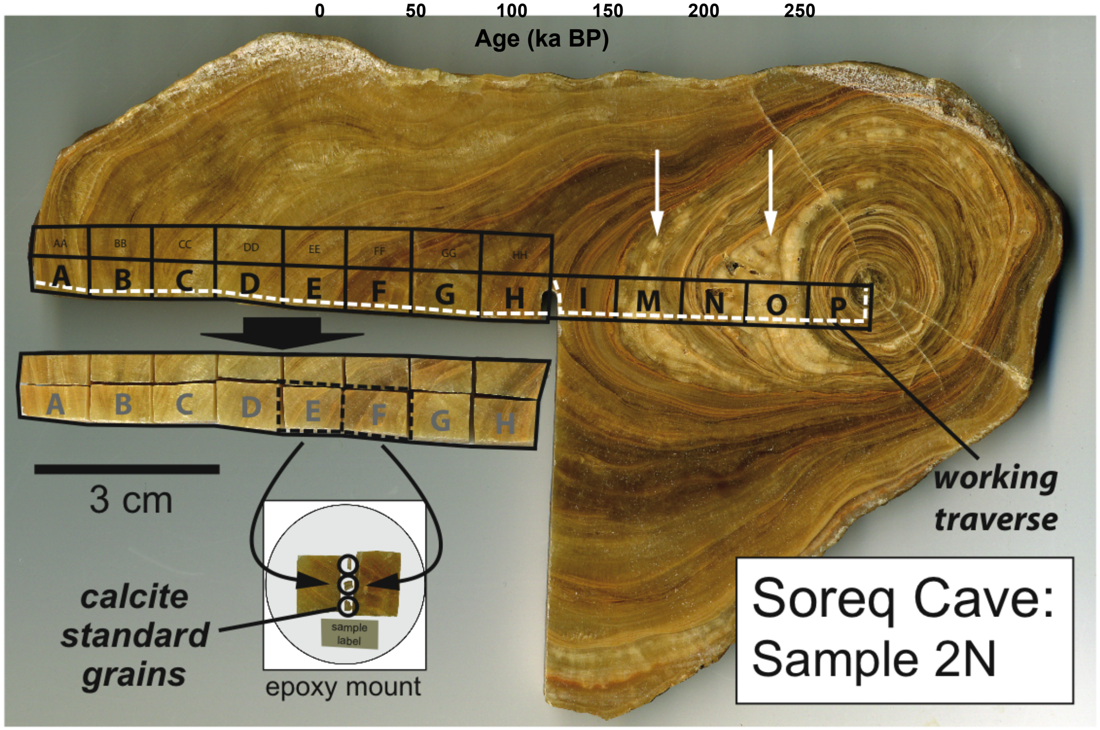
C. 12 ka



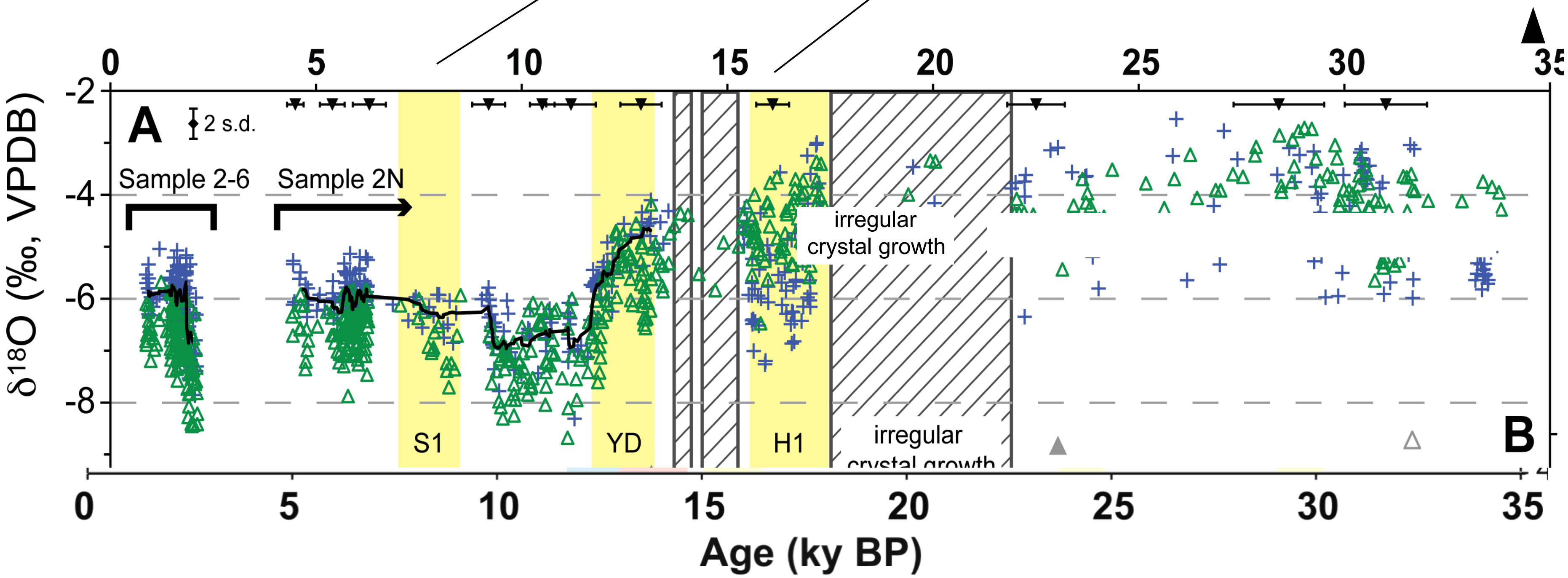
D. Irregular Banding, 15 ka







Types of fluorescence banding as function of climate the last 34 ka



Why during S1 Δd is smaller?

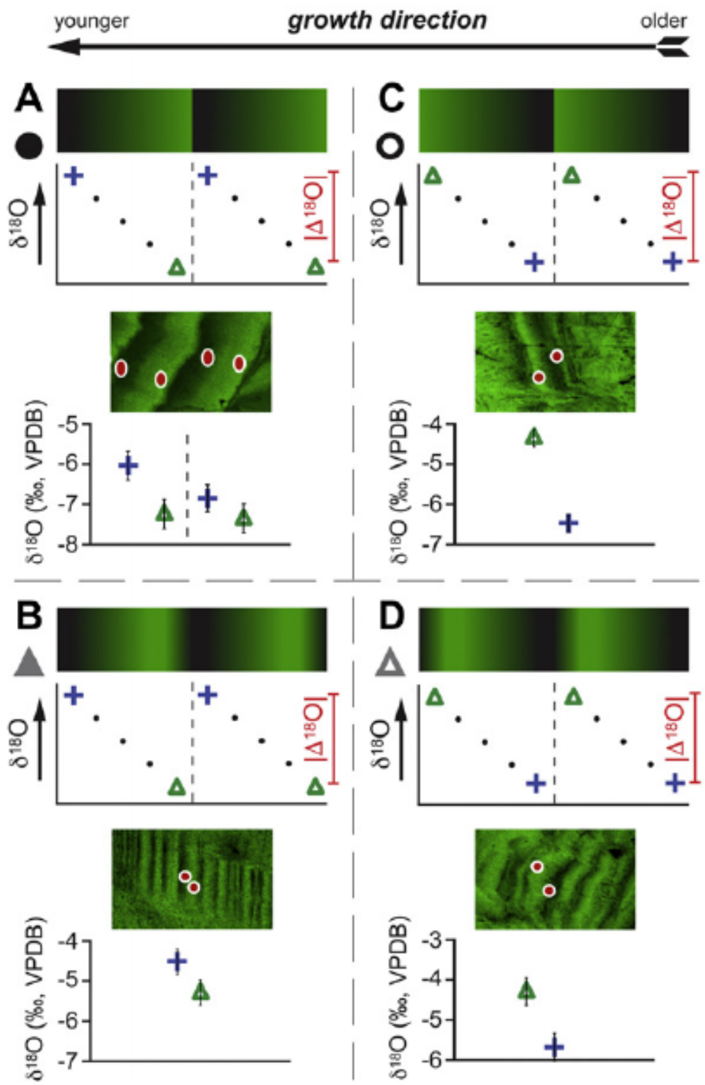
What cause Δd pattern during the YD? to differ from present-day and Holocene pattern?

Orland et al., GCA 2012

blue symbols: dark fluorescent calcite

green symbols: bright fluorescent calcite

Types of fluorescence banding as function of climate the last 34 ka



Green triangle bright laminae, blue cross dark laminae

Orland et al., 2012

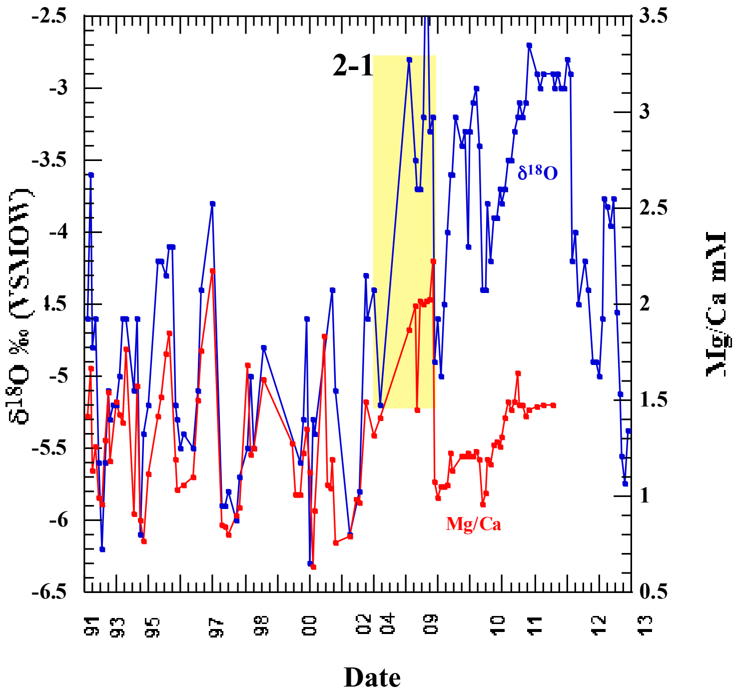
A. 10.5 to present; sawtooth fluorescence Distinct wet-dry seasons is the dominant climate regime in the EM since 10.5 ka.

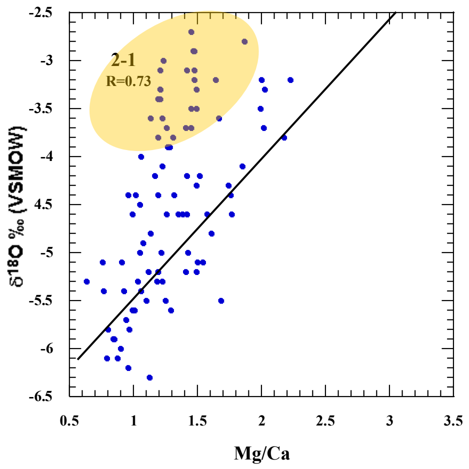
B. 13.5-11 ka – YD. Sinusoidal fluorescence, majority of bands have gradual gradient from bright to dark and from dark to bright. Water supply was more consistent probably due to reduced gradient in seasonal rainfall, and or change in the organic acid production.

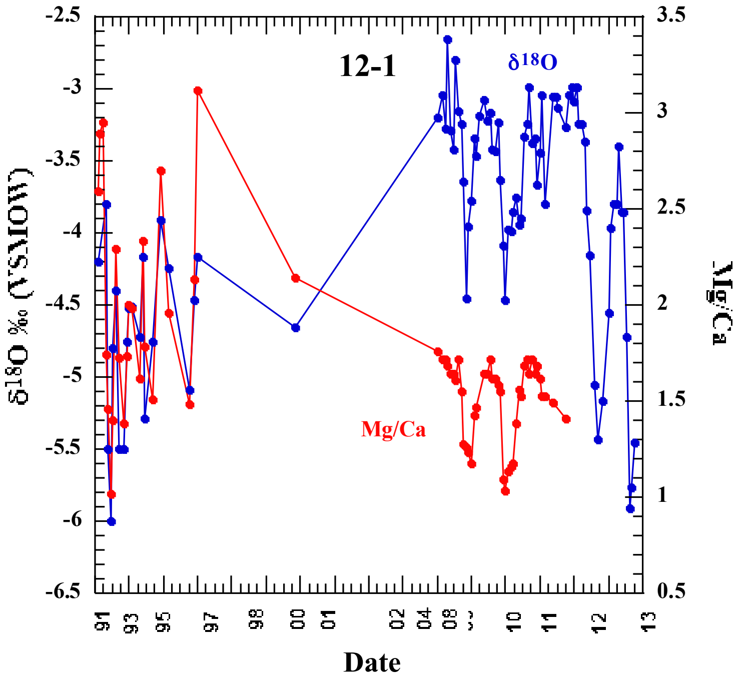
C. Before 15 ka. Reversed sawtooth fluorescence. Onset of dark, gradual transition to bright. Suggesting change in the timing or rate of organic acid production in the soil, reduced seasonal differences, snowfall or frozen ground during winter H1 and YD

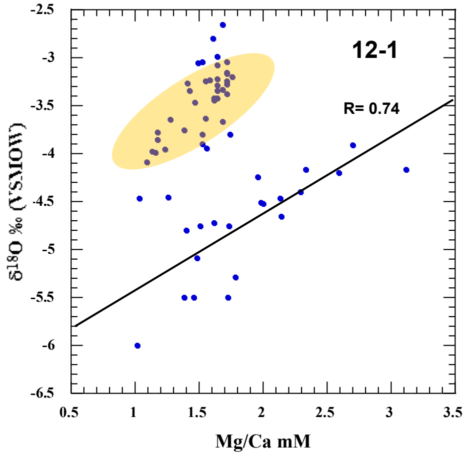
G. H1 and the LGM, reversed sinusoidal fluorescence

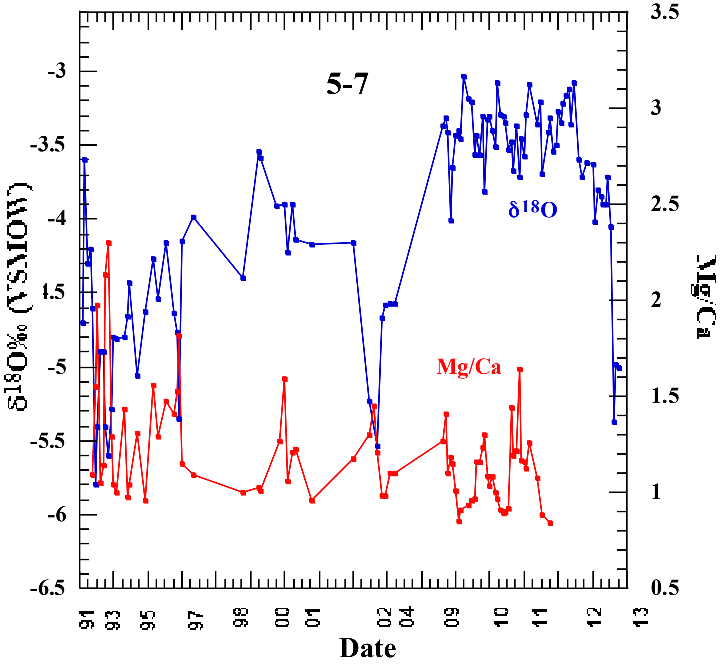
Thank you

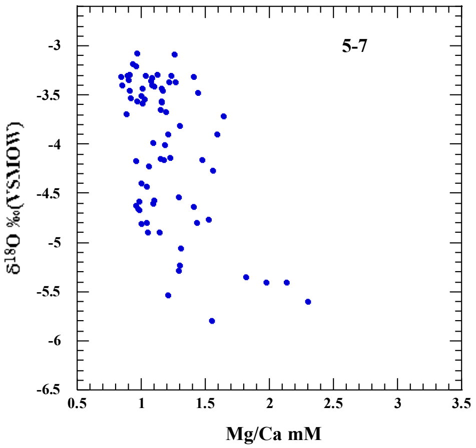

2-1
δ18O
Mg/Ca
δ18O ‰ (VSMOW)
Mg/Ca mM
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
02
04
09
10
11
12
13
Date

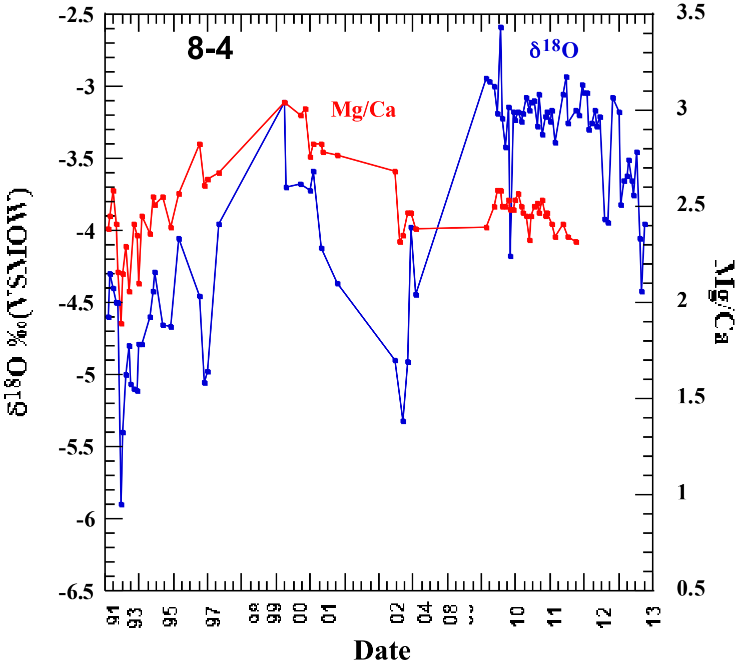

2-1
R=0.73
δ18O ‰ (VSMOW)
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
0.5
1
1.5
2
2.5
3
3.5
Mg/Ca

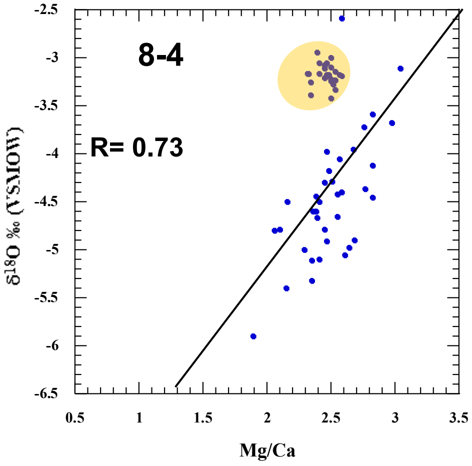

12-1
δ18O
Mg/Ca
δ18O ‰ (VSMOW)
Mg/Ca
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
01
02
04
08
10
11
12
13
Date

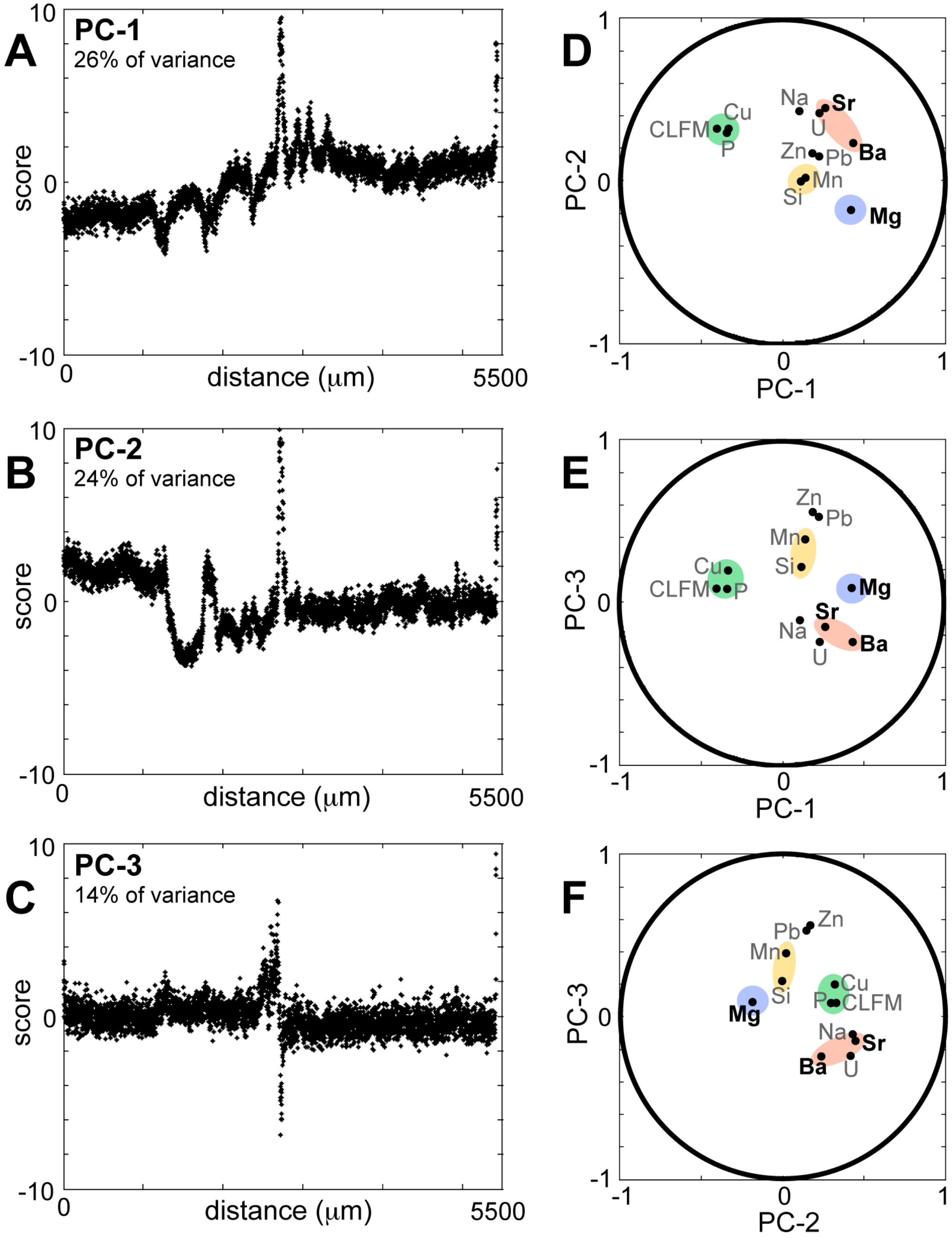

12-1
R= 0.74
δ18O ‰ (VSMOW)
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
0.5
1
1.5
2
2.5
3
3.5
Mg/Ca mM


5-7
δ18O
Mg/Ca
δ18O‰ (VSMOW)
Mg/Ca
Date
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
01
02
04
09
10
11
12
13

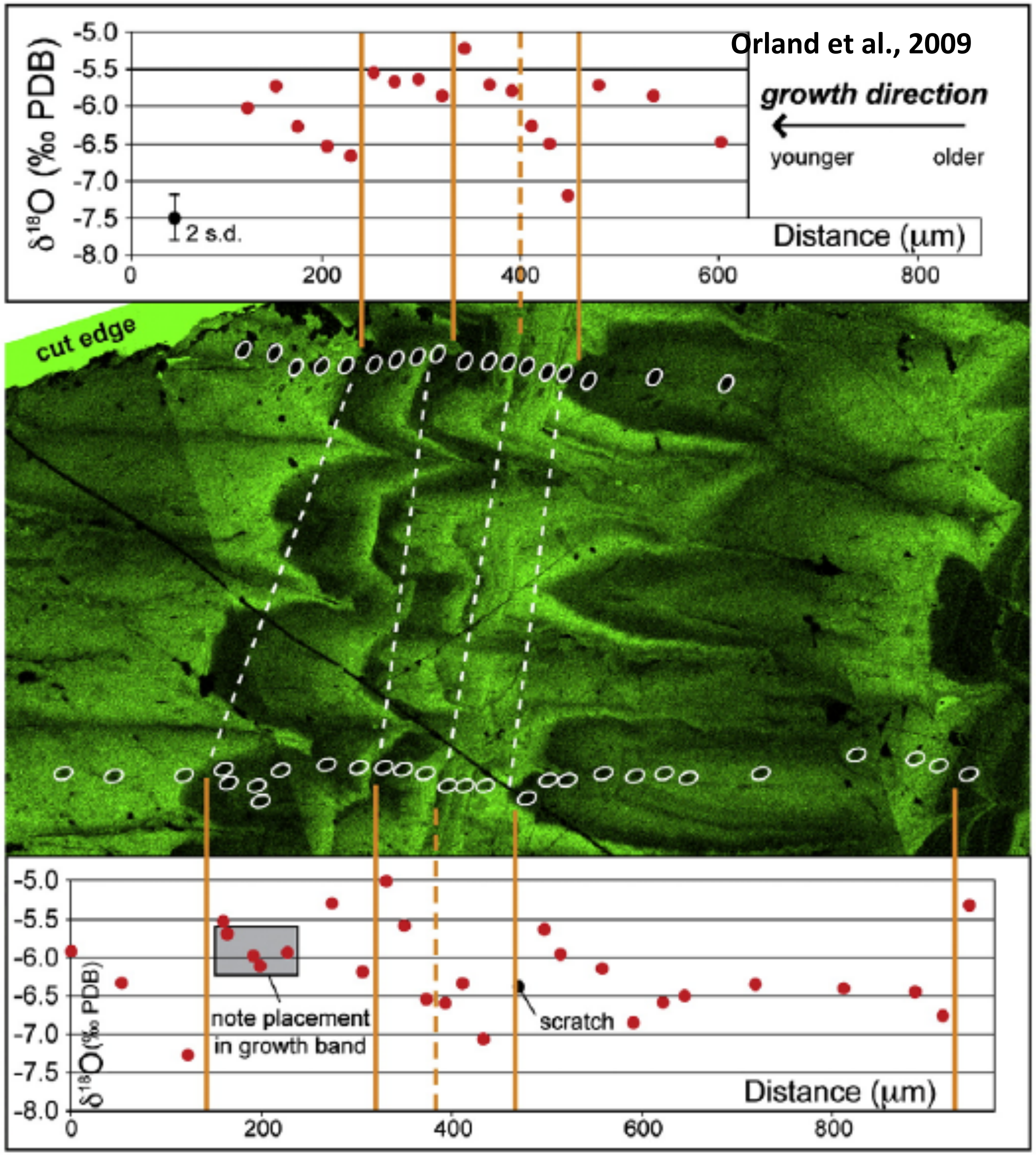

5-7
δ18O ‰ (VSMOW)
Mg/Ca mM
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
0.5
1
1.5
2
2.5
3
3.5


8-4
δ18O
Mg/Ca
δ18O ‰ (VSMOW)
Mg/Ca
Date
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
99
00
01
02
04
08
10
11
12
13


8-4
R= 0.73
δ18O ‰ (VSMOW)
Mg/Ca
-2.5
-3
-3.5
-4
-4.5
-5
-5.5
-6
-6.5
0.5
1
1.5
2
2.5
3
3.5


A
PC-1
26% of variance
score
10
0
-10
0
distance (μm)
5500
B
PC-2
24% of variance
C
PC-3
14% of variance
D
E
F
PC-1
PC-2
PC-3
1
0
-1
CLFM
Cu
P
Na
Sr
U
Ba
Zn
Pb
Mn
Si
Mg

Seasonal Sawtooth fluorescence banding during the Holocene, what does it mean?

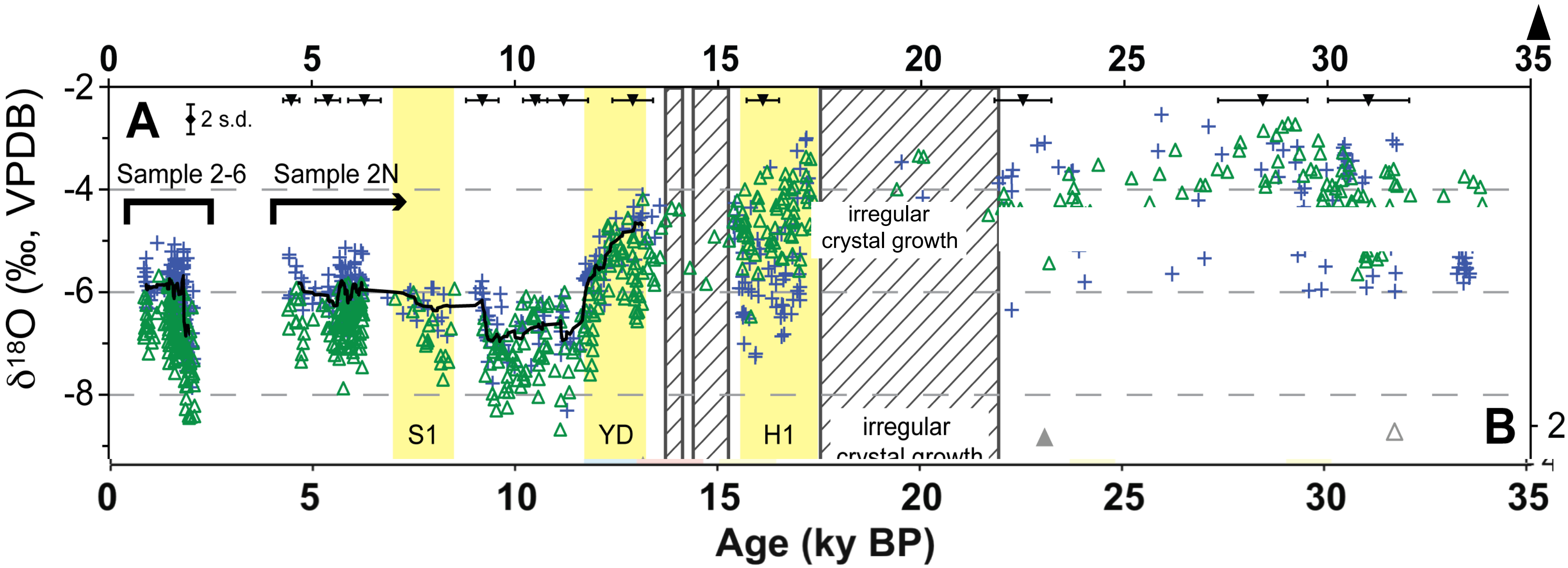


Each band has an abrupt onset of a bright low ^{18}O calcite followed by a gradient to dark higher ^{18}O calcite through time.

The pattern repeat itself and mimics the change in present-day isotopic composition of cave water between winter-summer.

Orland et al., 2009

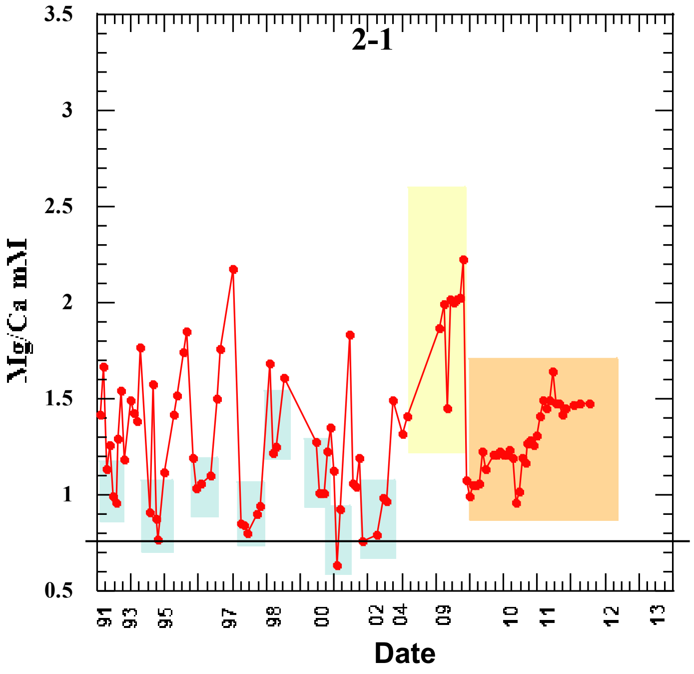
Types of fluorescence banding as function of climate the last 34 ka

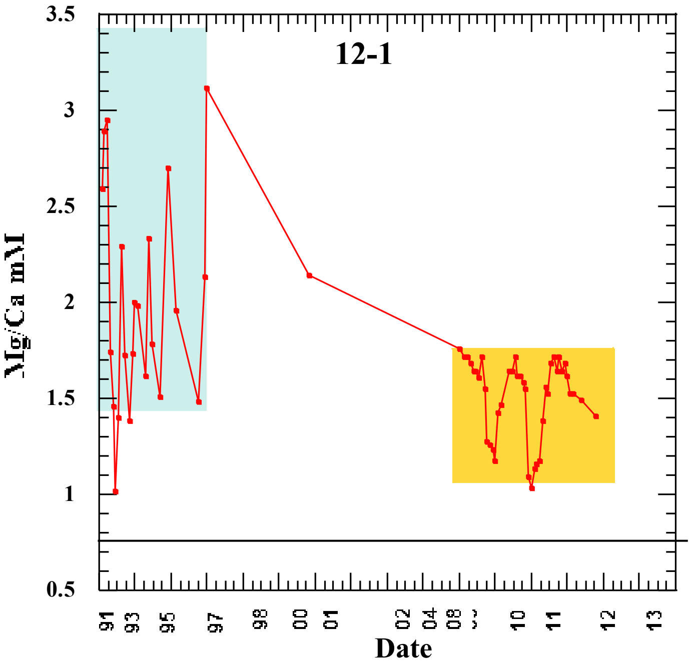


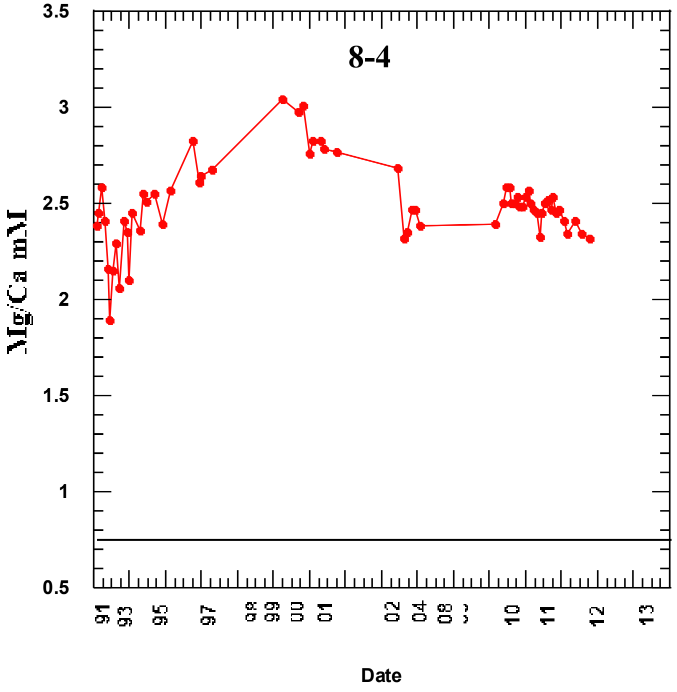
Orland et al., GCA 2012

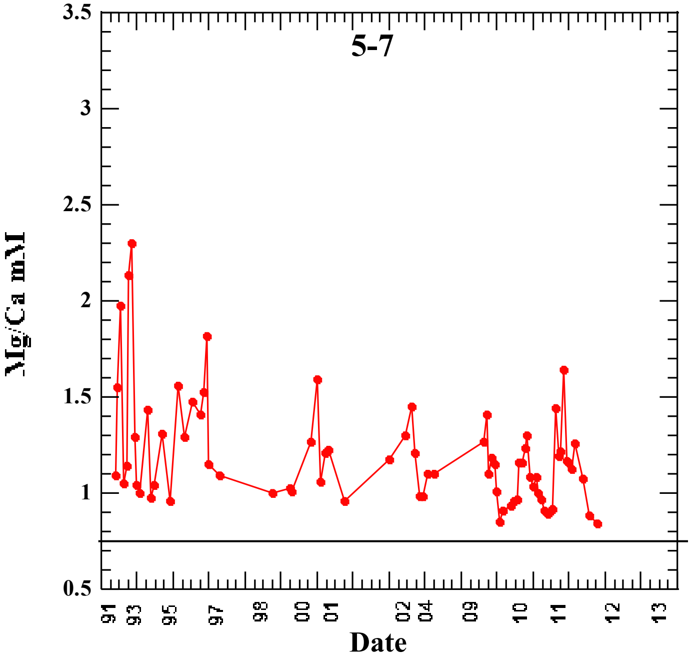
blue symbols: dark fluorescent calcite

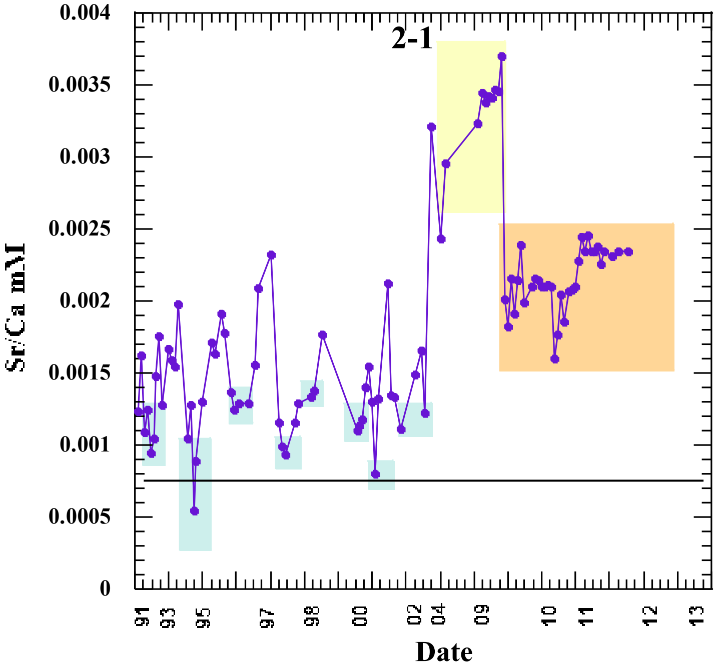
green symbols: bright fluorescent calcite

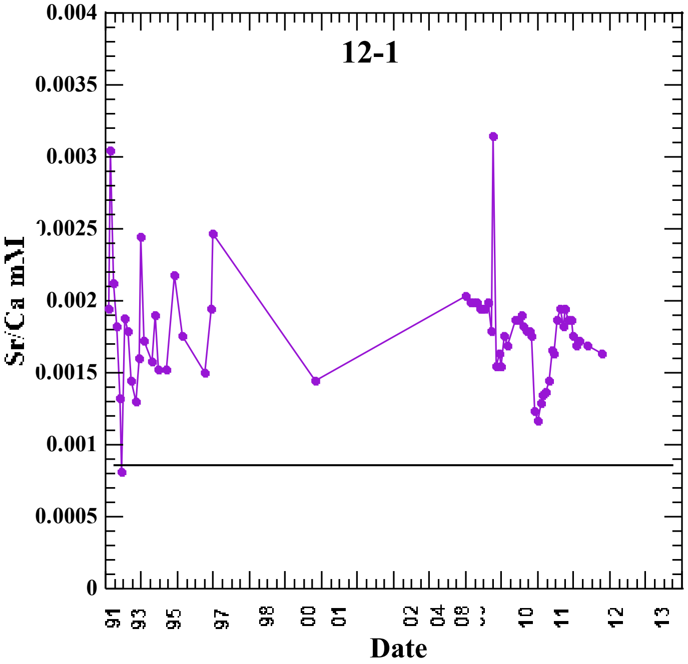

2-1
Mg/Ca mM
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
02
04
09
10
11
12
13
Date

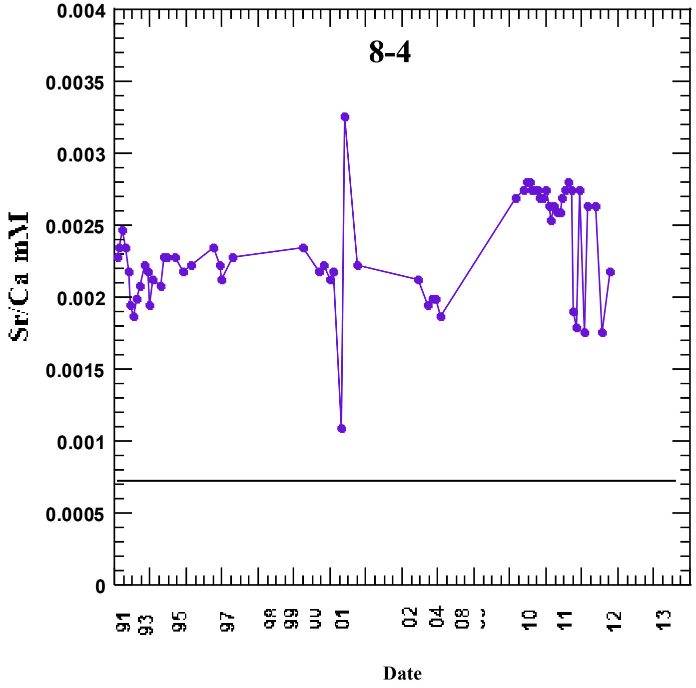

12-1
Mg/Ca mM
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
01
02
04
08
10
11
12
13
Date


8-4
Mg/Ca mM
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
99
00
01
02
04
08
10
11
12
13
Date


5-7
Mg/Ca mM
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
01
02
04
09
10
11
12
13
Date


2-1
Sr/Ca mM
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
91
93
95
97
98
00
02
04
09
10
11
12
13
Date


12-1
Sr/Ca mM
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
91
93
95
97
98
00
01
02
04
08
10
11
12
13
Date


8-4
Sr/Ca mM
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
91
93
95
97
98
99
00
01
02
04
08
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11
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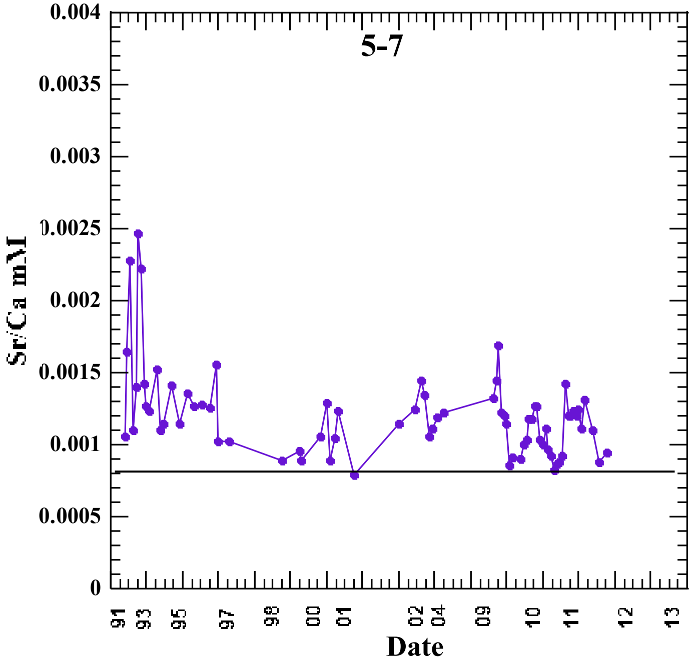
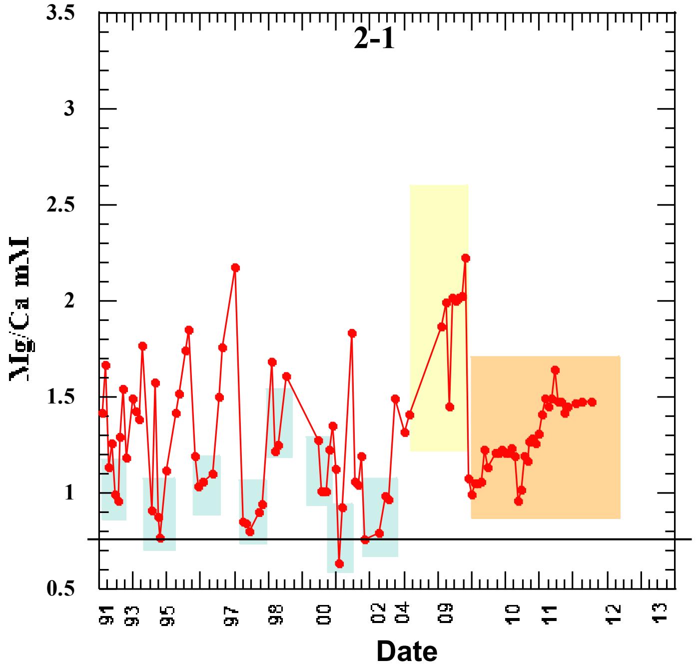
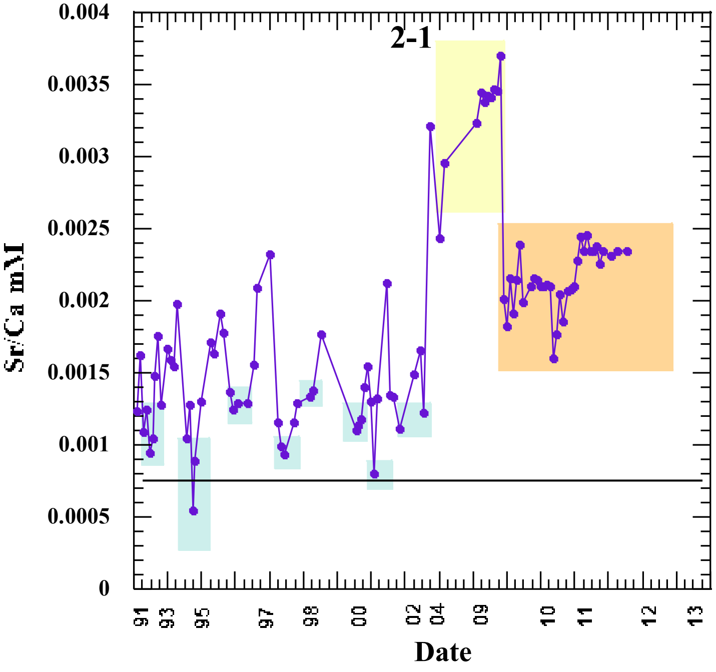
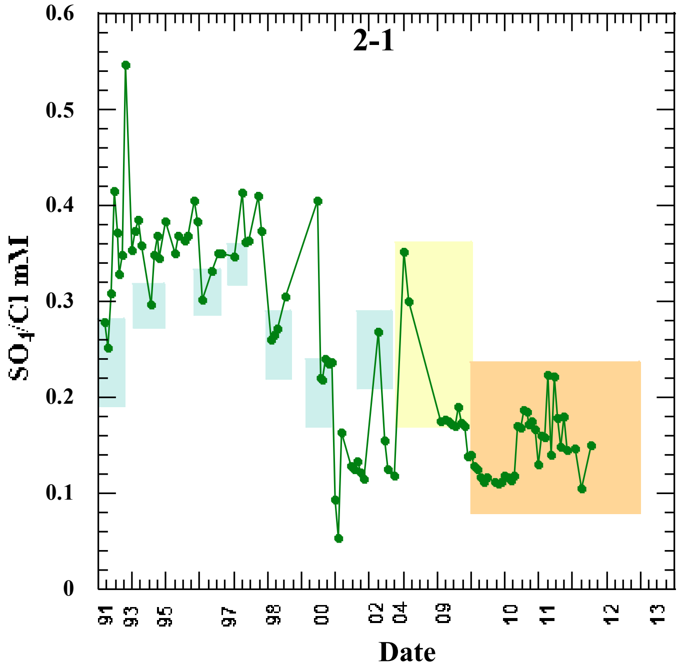
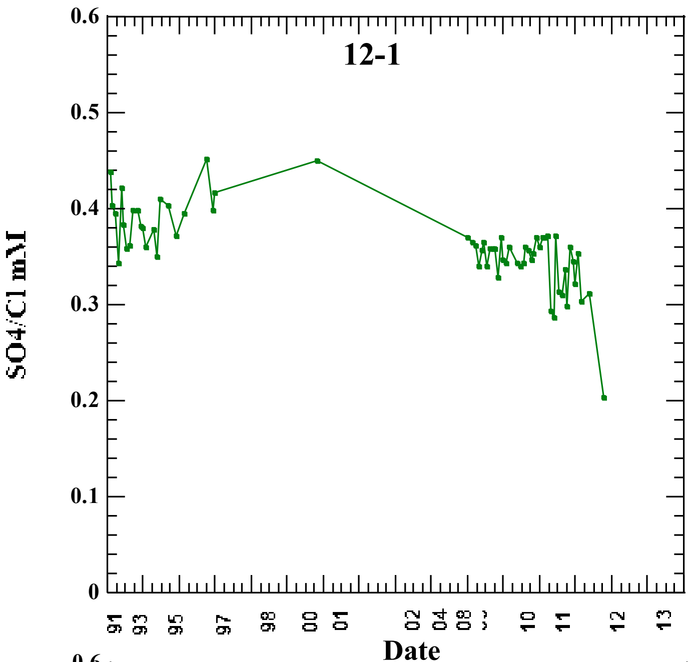
13
Date

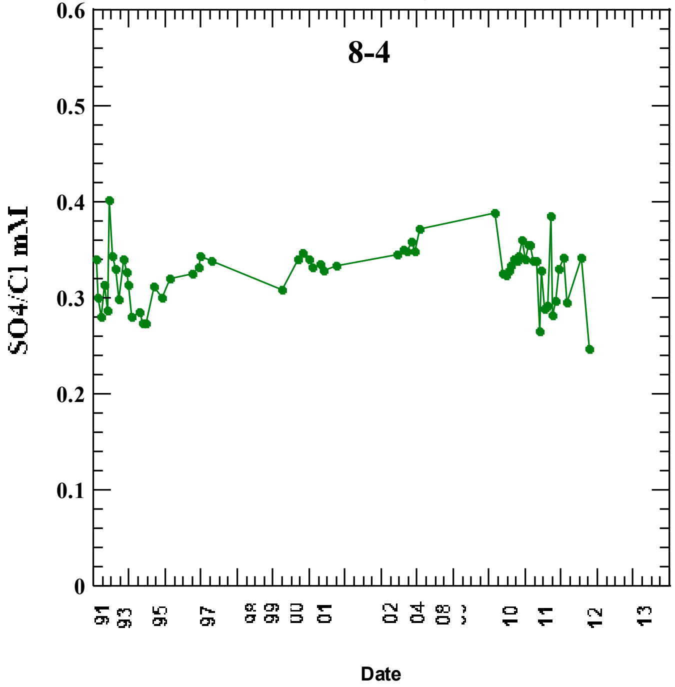

5-7
Sr/Ca mM
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
91
93
95
97
98
00
01
02
04
09
10
11
12
13
Date

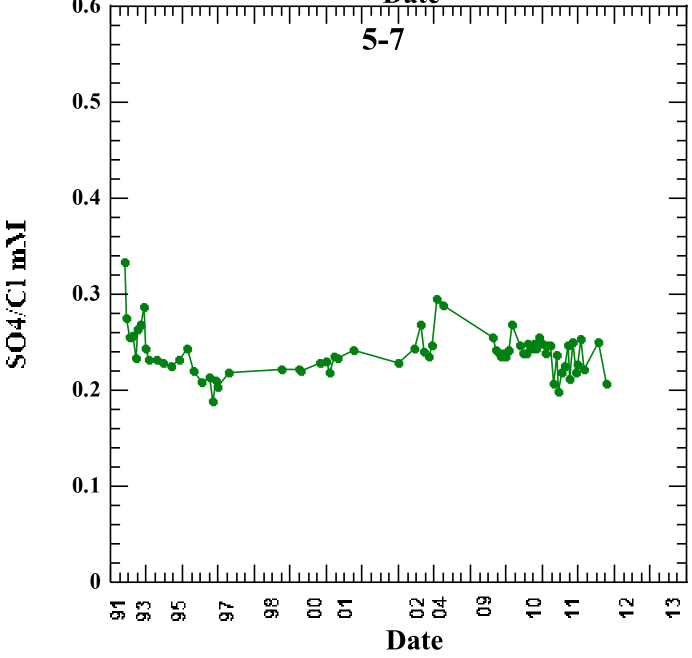

2-1
Mg/Ca mM
3.5
3
2.5
2
1.5
1
0.5
91
93
95
97
98
00
02
04
09
10
11
12
13
Date


2-1
Sr/Ca mM
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
91
93
95
97
98
00
02
04
09
10
11
12
13
Date


2-1
SO$_4$/Cl mM
0.6
0.5
0.4
0.3
0.2
0.1
0
91
93
95
97
98
00
02
04
09
10
11
12
13
Date


12-1
SO4/Cl mM
0.6
0.5
0.4
0.3
0.2
0.1
0
91
93
95
97
98
00
01
02
04
08
10
11
12
13
Date

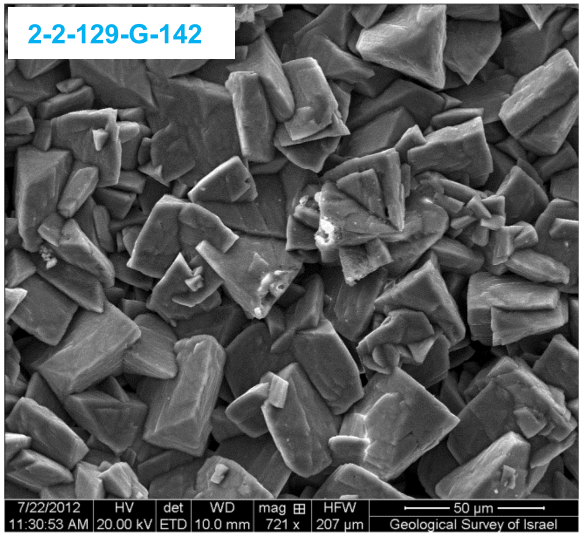

8-4
SO4/Cl mM
0.6
0.5
0.4
0.3
0.2
0.1
0
91
93
95
97
98
99
00
01
02
04
08
10
11
12
13
Date

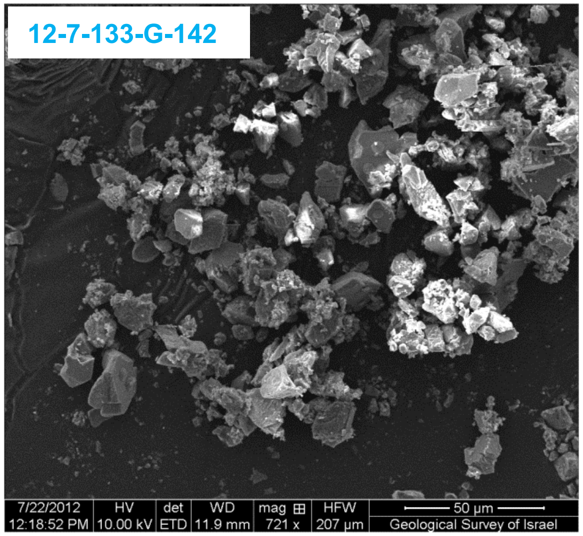

5-7
SO4/Cl mM
0.6
0.5
0.4
0.3
0.2
0.1
0
91
93
95
97
98
00
01
02
04
09
10
11
12
13
Date

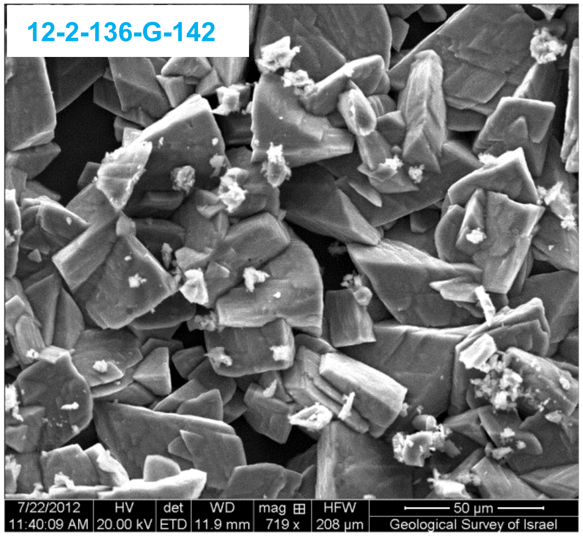
Isotopic equilibrium – Modern calcite

Same habit and fabric

Smallest crystals


2-2-129-G-142

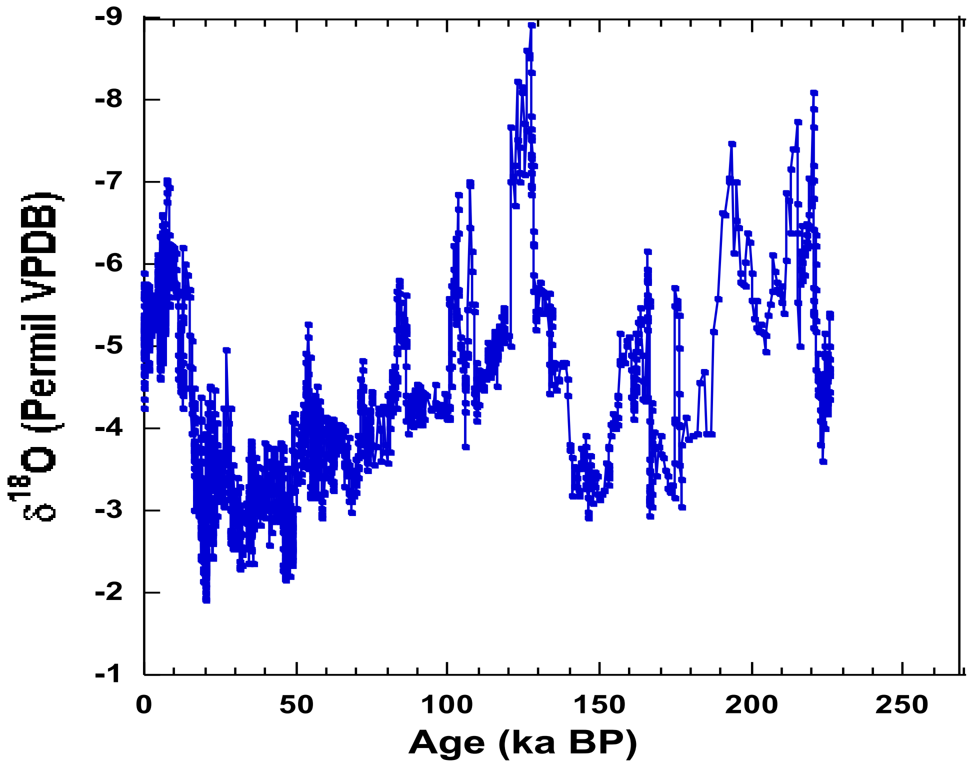

12-7-133-G-142

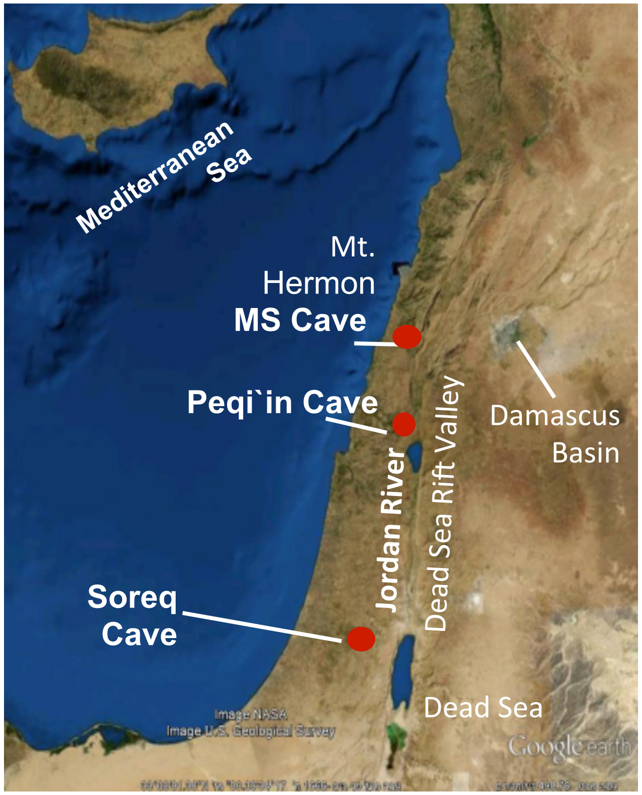

12-2-136-G-142

Fastest drip rate

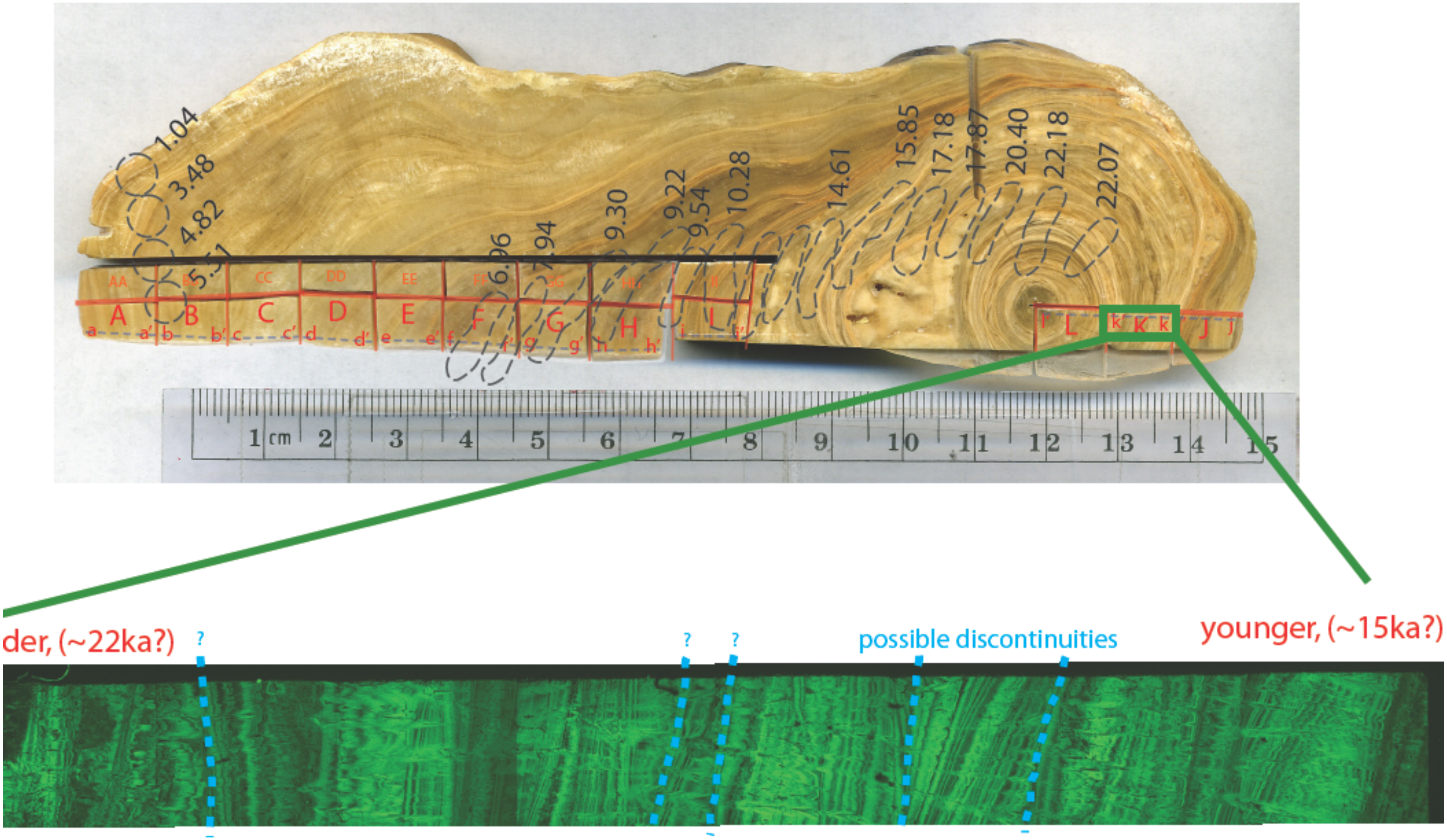
Slowest drip rate

α

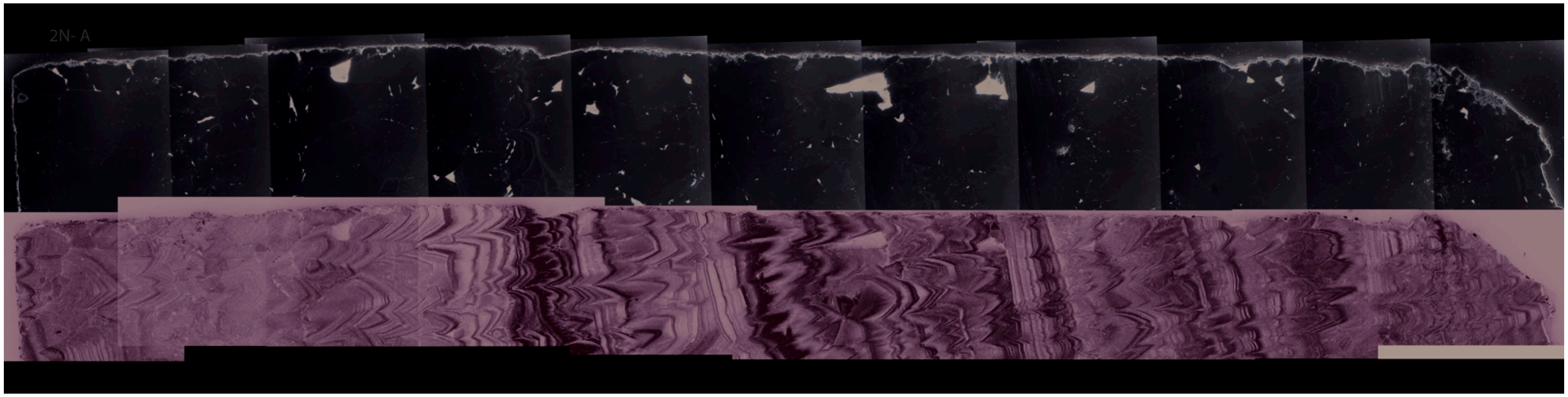




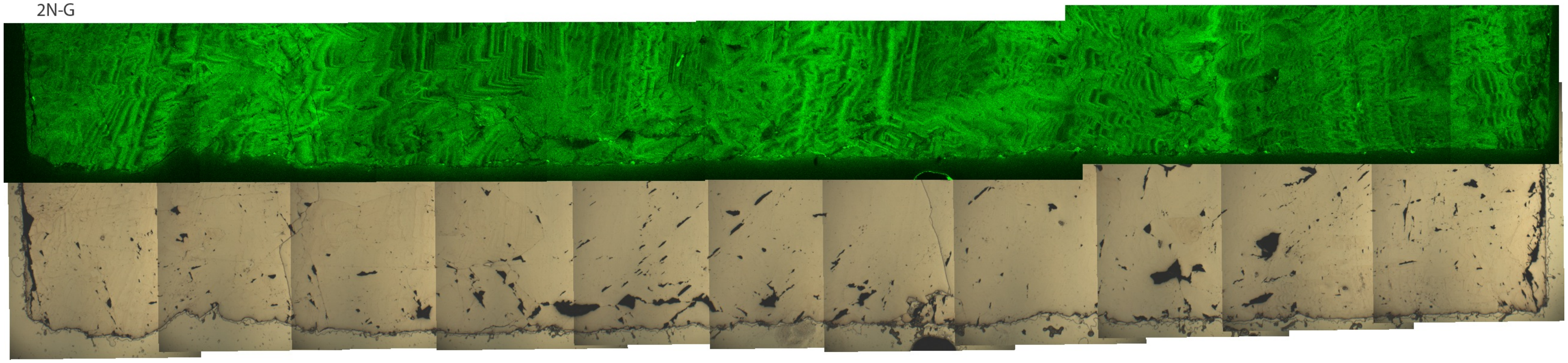
Source
Ice volume
Sea level
Temperature 1‰ = 4°C


1.04
3.48
4.82
5.51
6.96
7.94
9.30
9.22
9.54
10.28
14.61
15.85
17.18
17.87
20.40
22.18
22.07
AA
BB
CC
DD
EE
FF
GG
HH
II
A
B
C
D
E
F
G
H
I
L
K
J
a a' b b' c c' d d' e e' f f' g g' h h' i i'
l' k' k k' j j'
1 cm 2 3 4 5 6 7 8 9 10 11 12 13 14 15
der, (~22ka?)
?
?
?
possible discontinuities
younger, (~15ka?)

2N- A

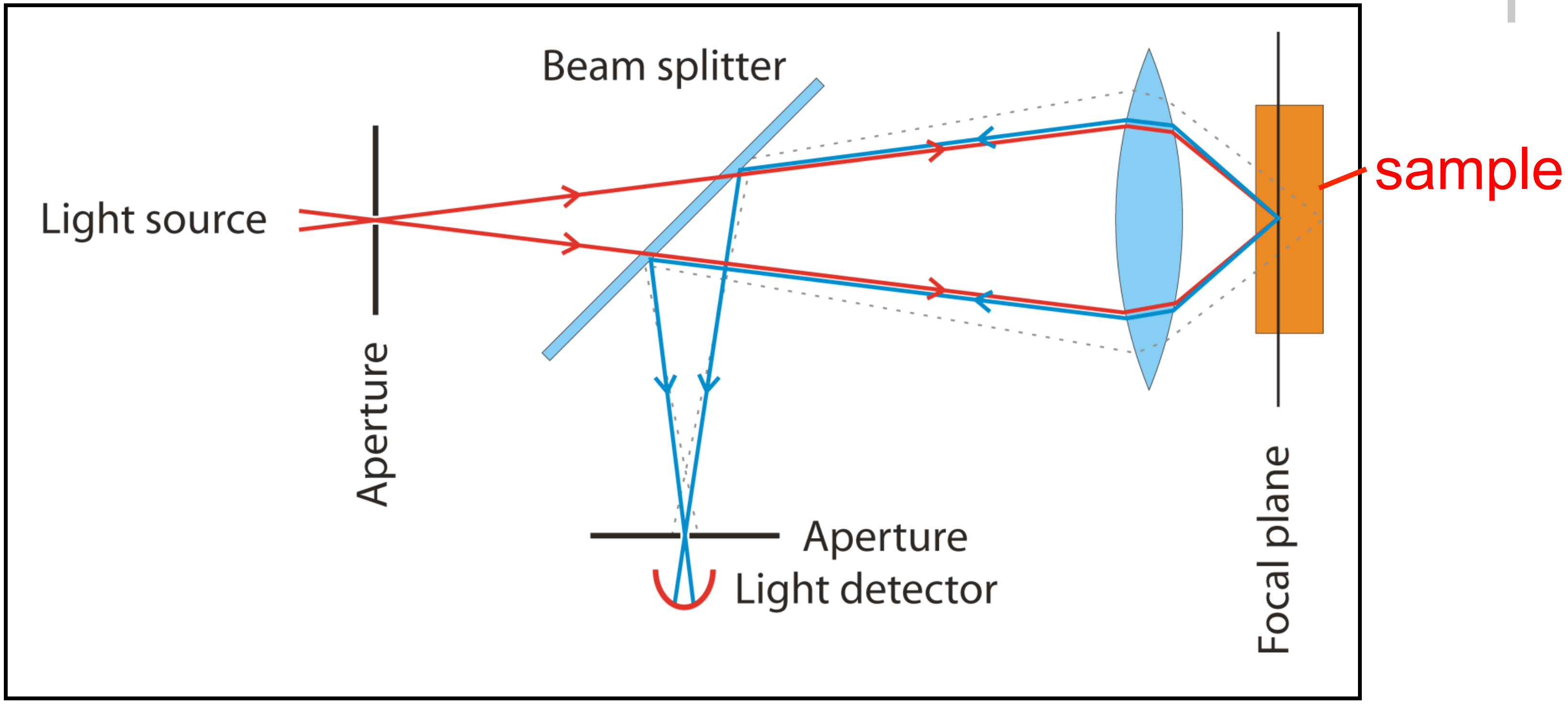


2N-G




20 21 22 23 24 25 26 27
2-1-77

Confocal microsc

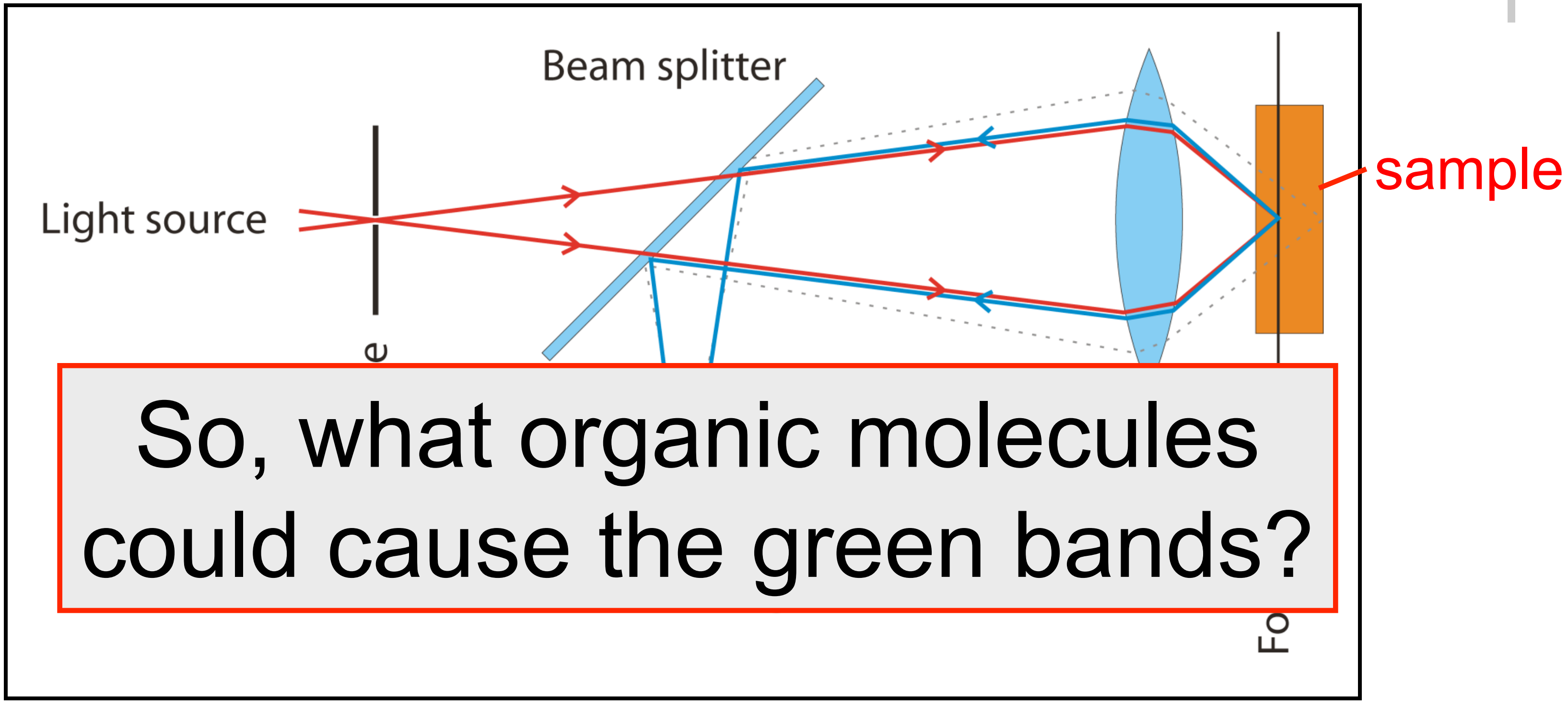


- Light emitted at a specific wavelength (488 nm).
- Incident light re-emitted with a **characteristic** wavelength.

(Organic molecules vibrate with specific frequencies.)

- Pinhole aperture isolates a narrow focal plane.

Confocal microsc



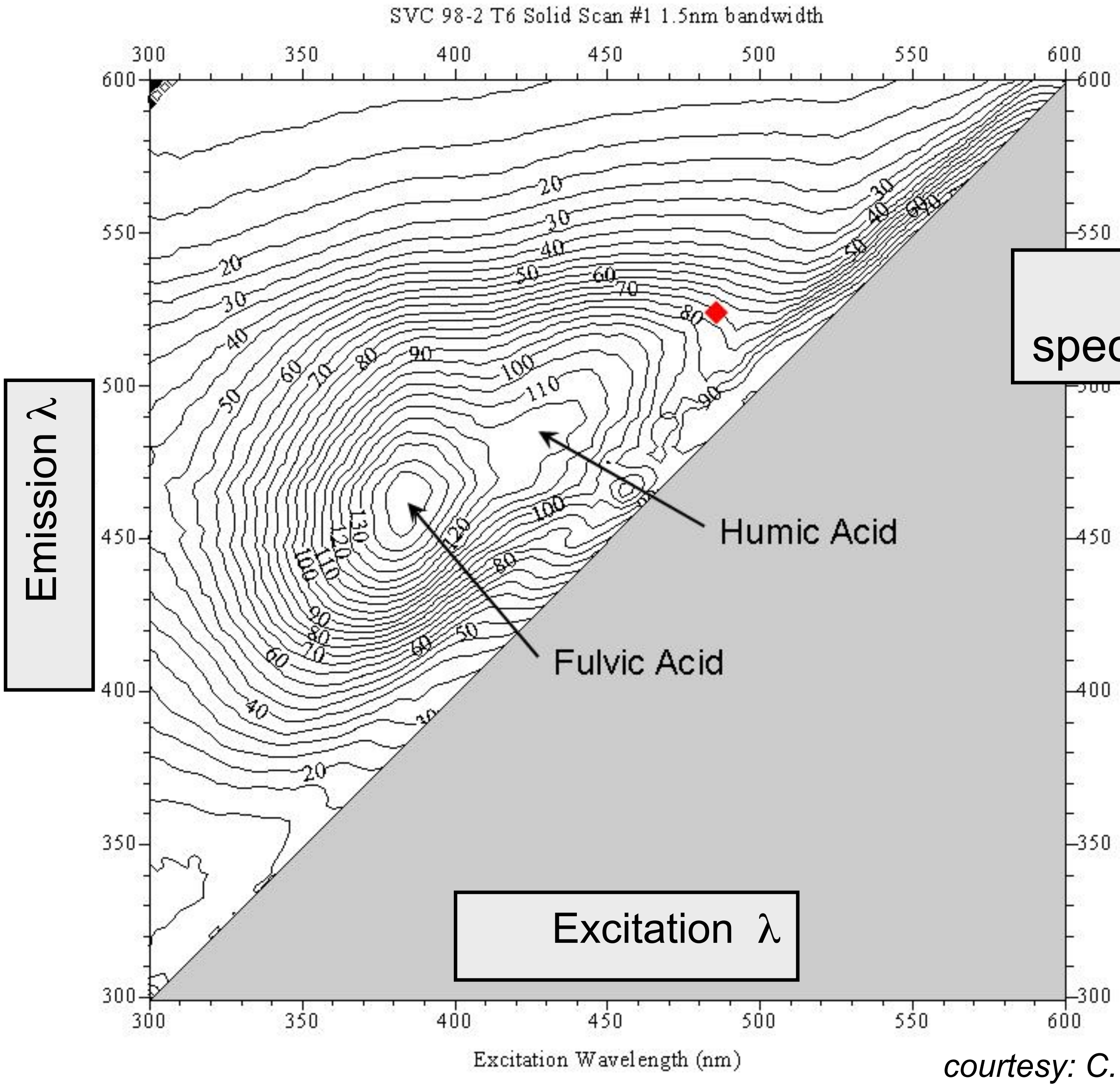
So, what organic molecules could cause the green bands?

- Light emitted at a specific wavelength (488 nm).
- Incident light re-emitted with a **characteristic** wavelength.

(Organic molecules vibrate with specific frequencies.)

- Pinhole aperture isolates a narrow focal plane.

Confocal microsc



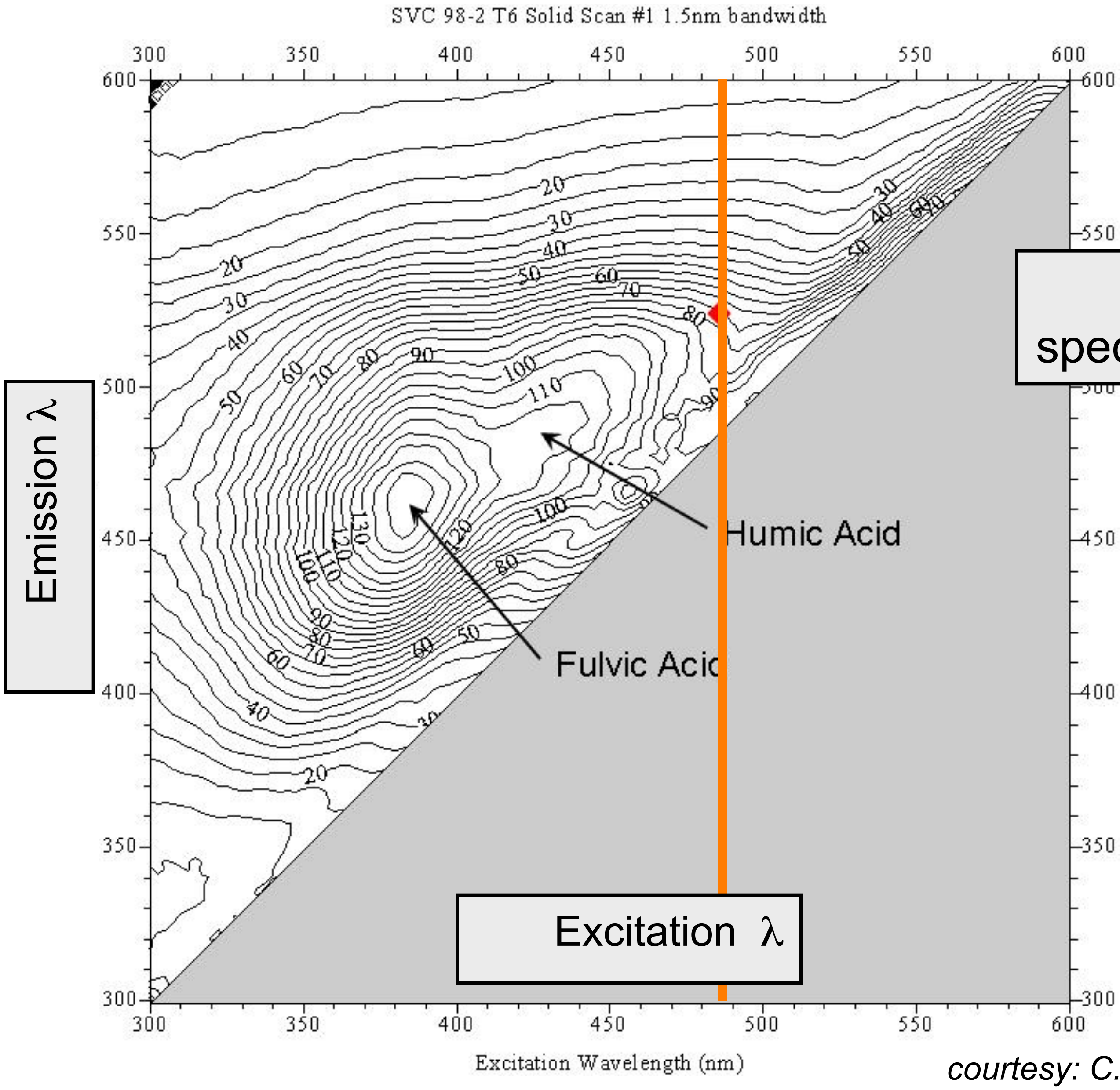
scanning spectrofluorophotometer

Scan of solid Speleothem

1.5 nm bandwidth

courtesy: C. Alexander, Univ. of Minnesota

Confocal microsc



scanning spectrofluorophotometer

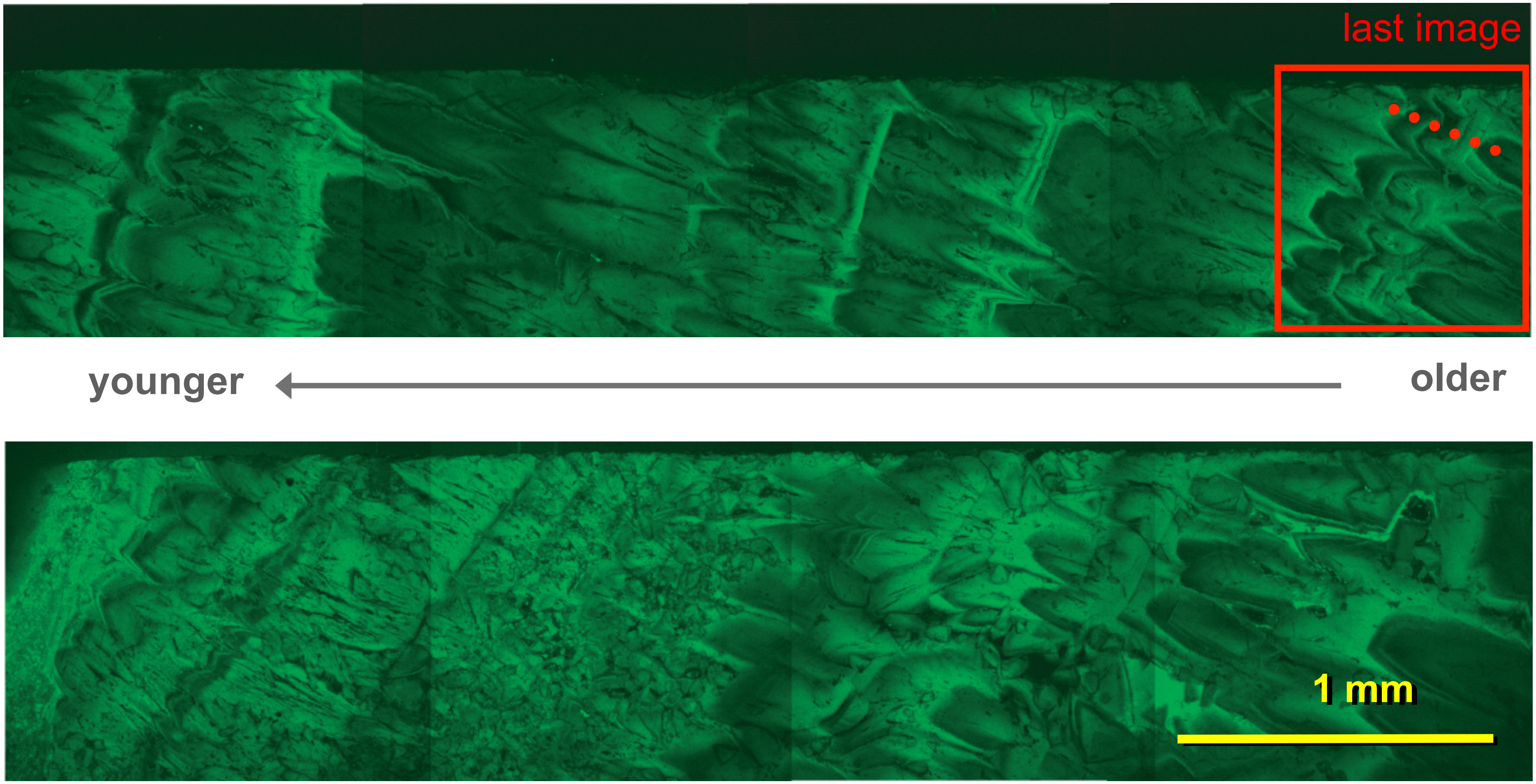
Scan of solid Speleothem

1.5 nm bandwidth

courtesy: C. Alexander, Univ. of Minnesota

Fluorescent band g

- 182 major bands (>10μm), ~176 minor bands

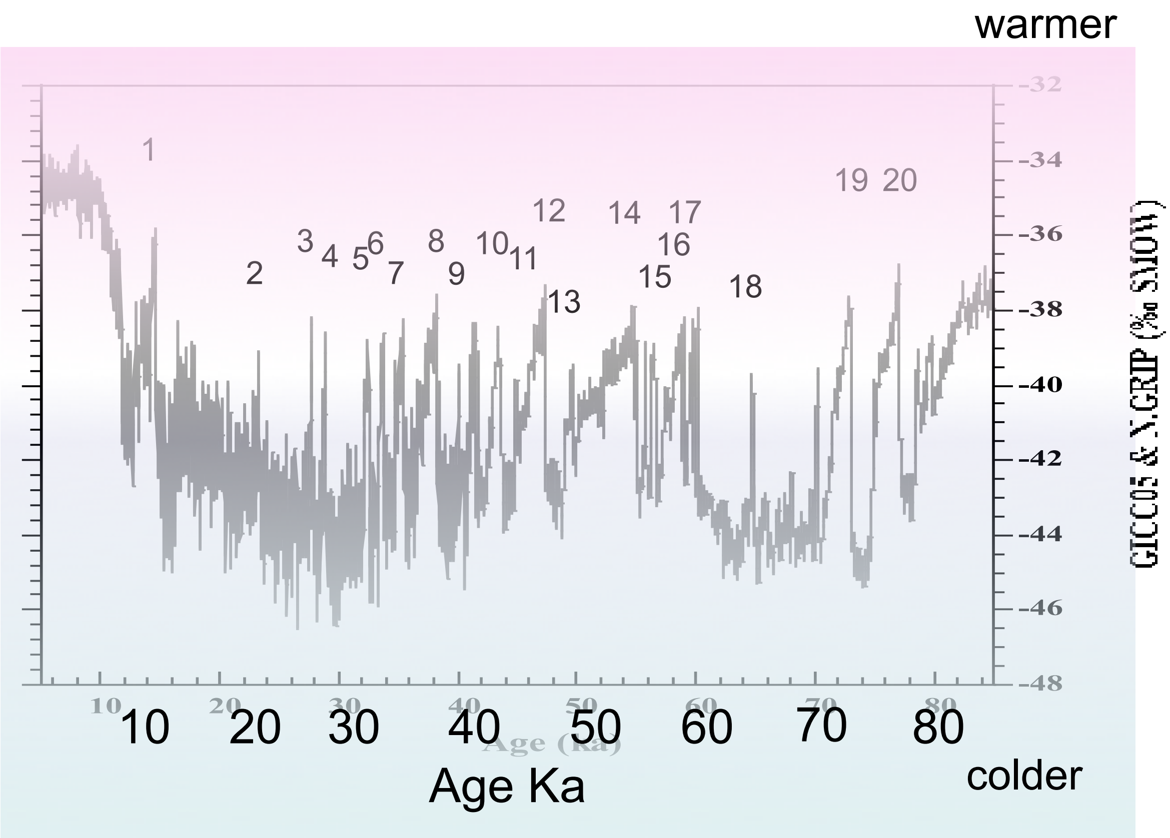


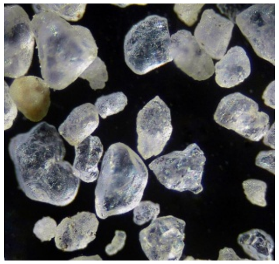
Dansgaard-Oeschger (D-O) events

Drilling into high latitude and altitude ice sheets revolutionized our understanding of paleoclimate, mainly with regards to millennia and shorter time scales changes.

D-O events first reported in Greenland ice cores and occur in irregular 1,470 year cycles. Each cycle represent abrupt warming (matter of decades) to near-interglacial conditions and slower cooling.

D-O events are considered to be a part of a seesaw effect between the hemispheres due to the thermohaline circulation and the capacity to transport heat energy through the ocean.

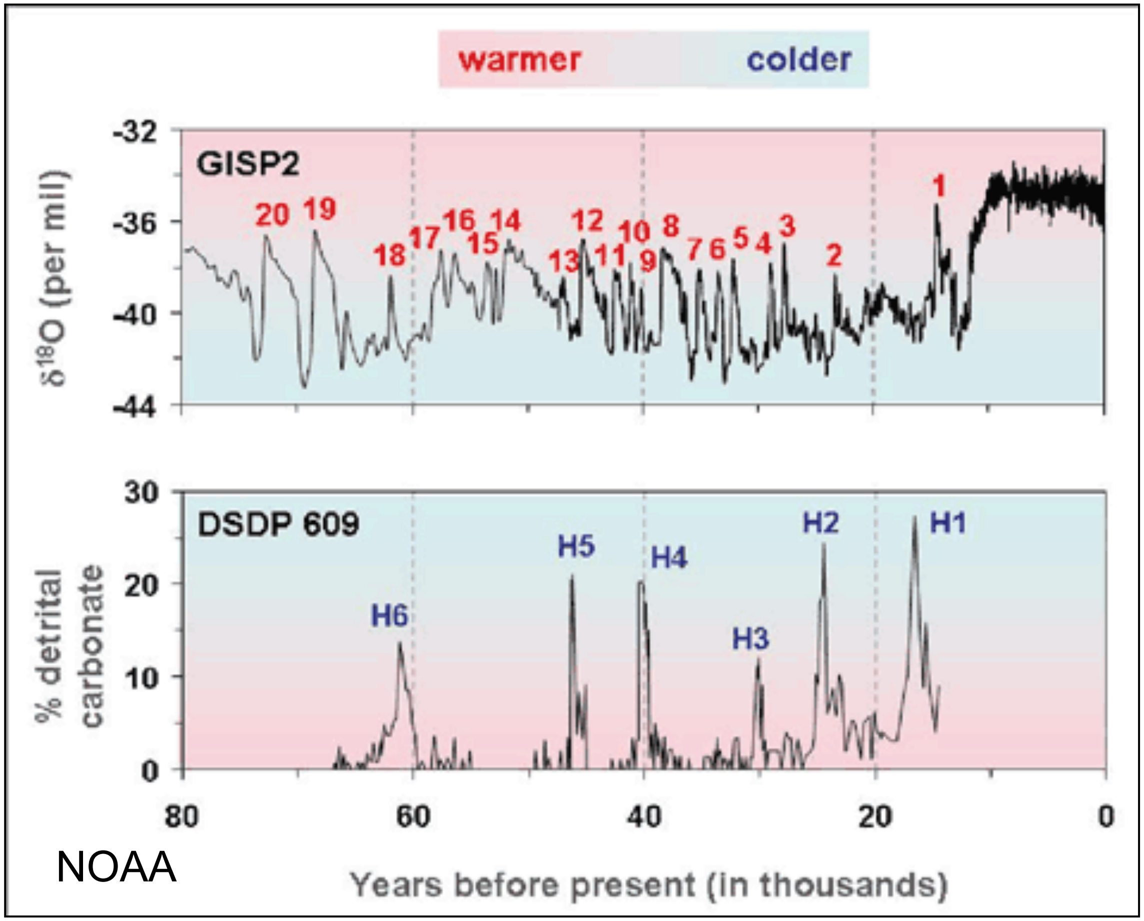




Heinrich (H) Events

H events (named after H. Heinrich), identified as ice rafted debris. They were found across large areas of the North Atlantic, and are associated with some of the coldest intervals between D-O events.

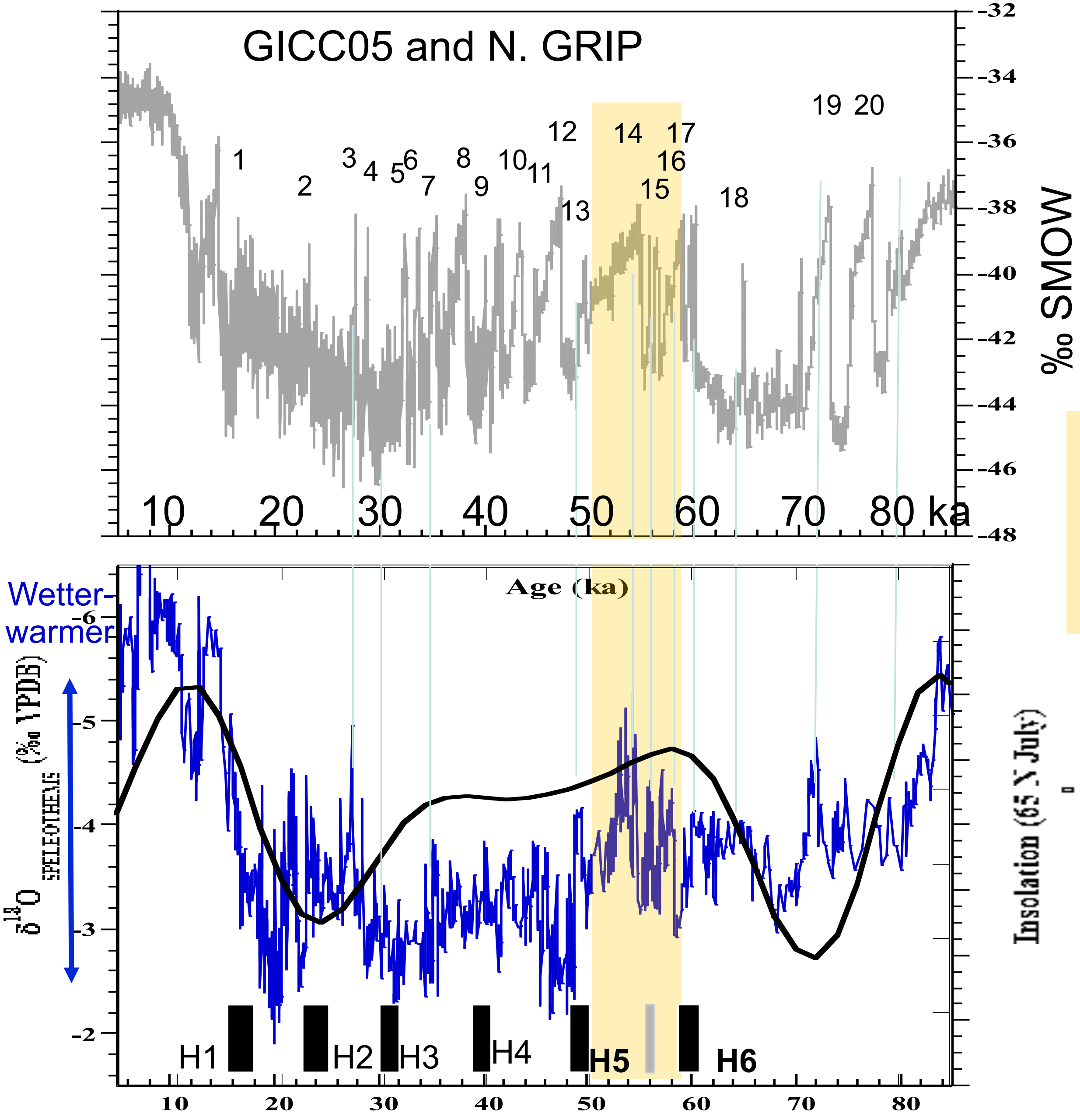
Injection of freshwater into the ocean followed by dilution of the ocean, slow the thermohaline circulation.



NOAA

During cold phases in the North Atlantic, large regions of N. America and Eurasia became colder and drier. The tropical rain belt moves southward moistening many parts of the Southern Hemisphere.

D-O and H events and their potential connection to the last Great Expansion Out of Africa ~60-50 ka?

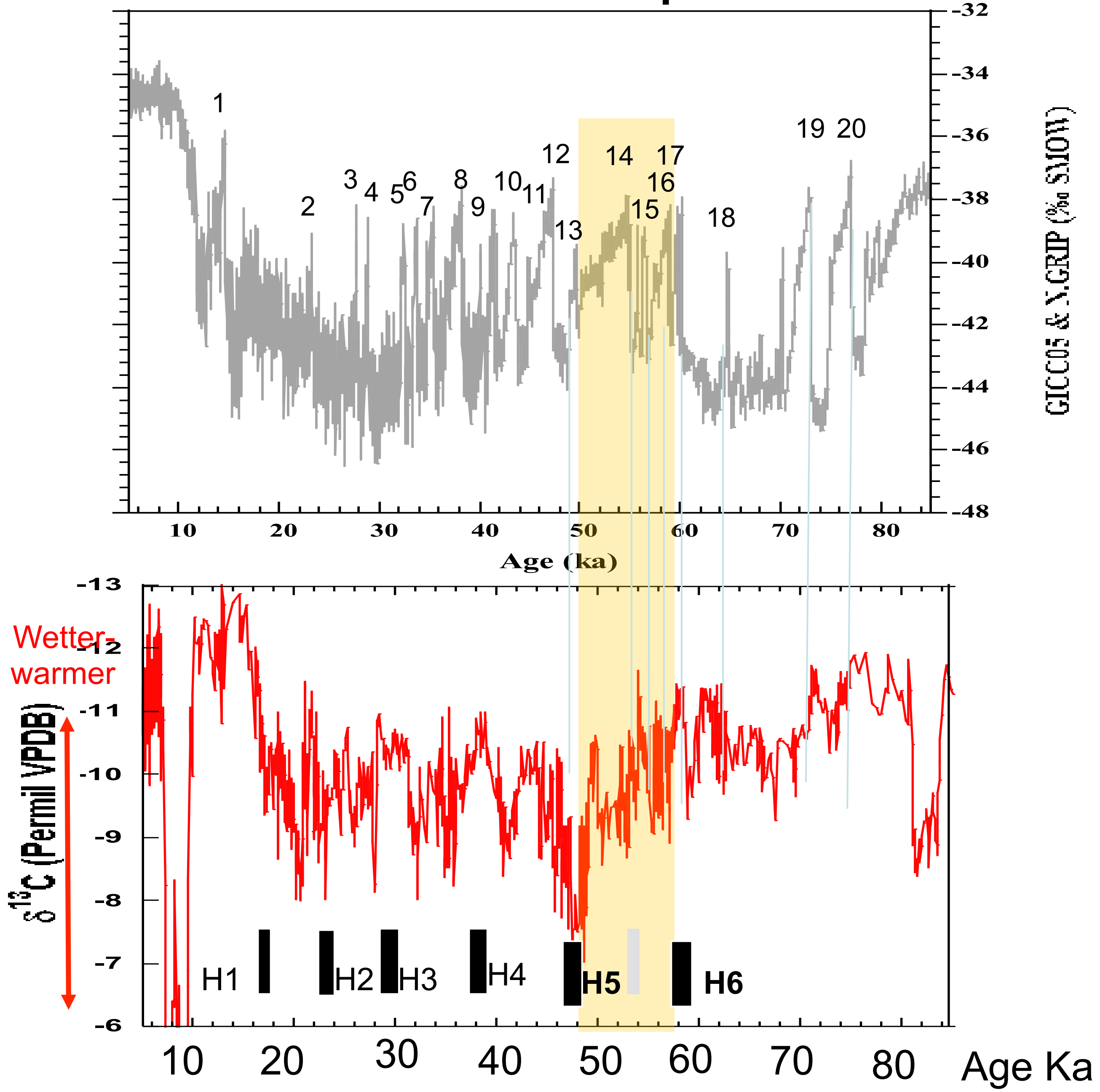


D-O and H events are recorded in EM speleothems.

The most pronounced $\delta^{18}O$ oscillations occur between H6 and H5, ~60 - 50 ka, during D-O 16 to D-0 13.

the sharpest transition to almost interglacial wet conditions is at D-O 14, at ~54 ka, followed by gradual change to full dry glacial conditions at ~50-48 ka.

D-O and H events in EM speleothems

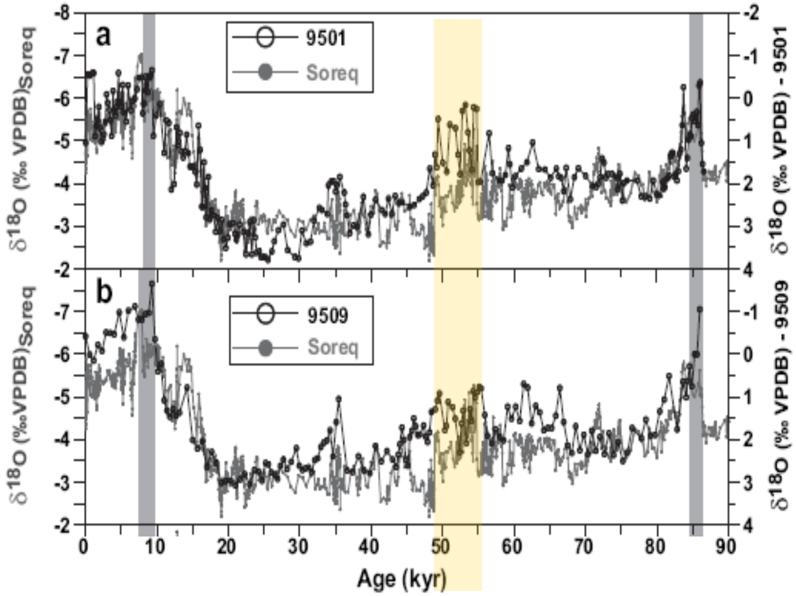


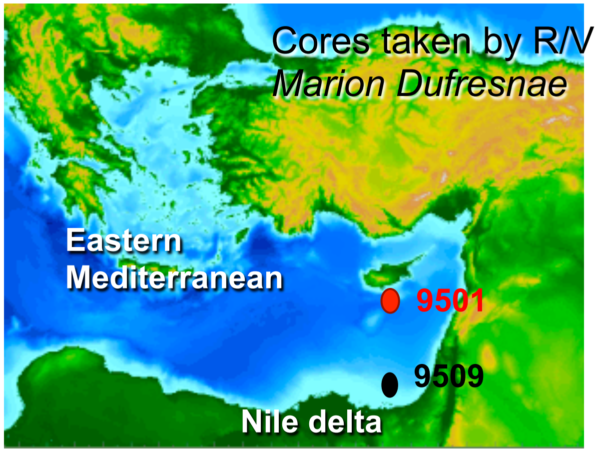
Vegetation response

The carbon isotopic composition increase from ~60-50 ka, suggesting transition from C3 Mediterranean type vegetation to more dominant C4 type vegetation.

D-O and H events in EM marine record

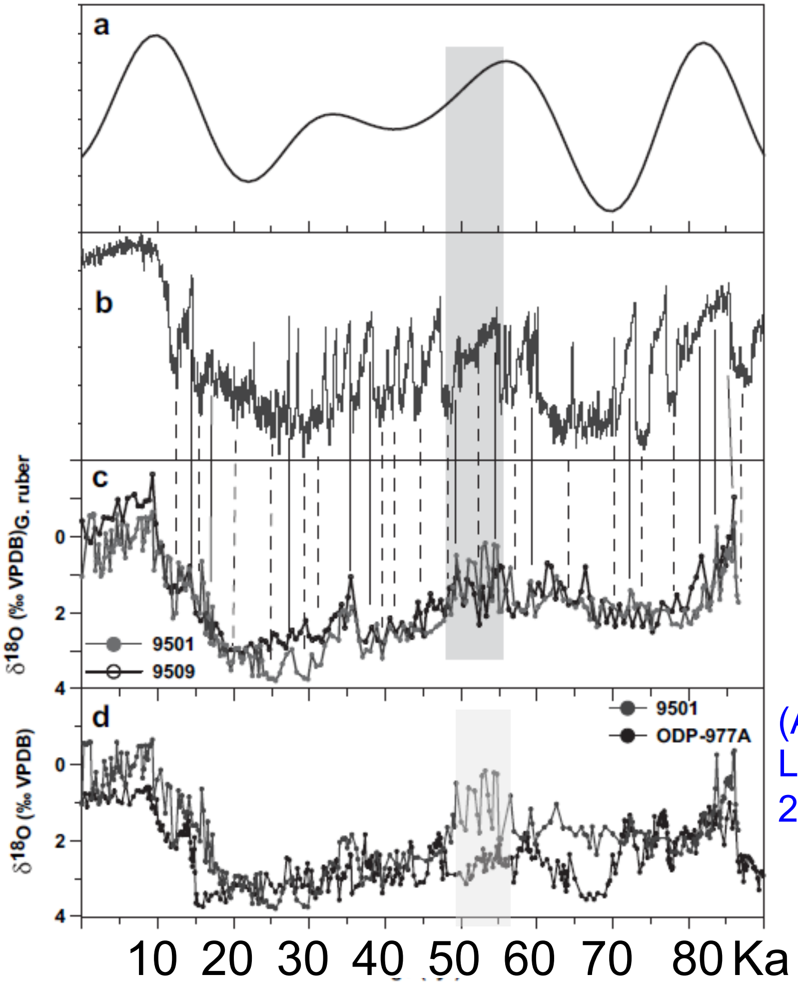
Accurate dating of the marine record based on the speleothems record





The $\delta^{18}O$ record of the planktonic foraminifera *G. ruber* from the EM reveals correlation with D-O cycles.

The most pronounced is from ~58-50 ka

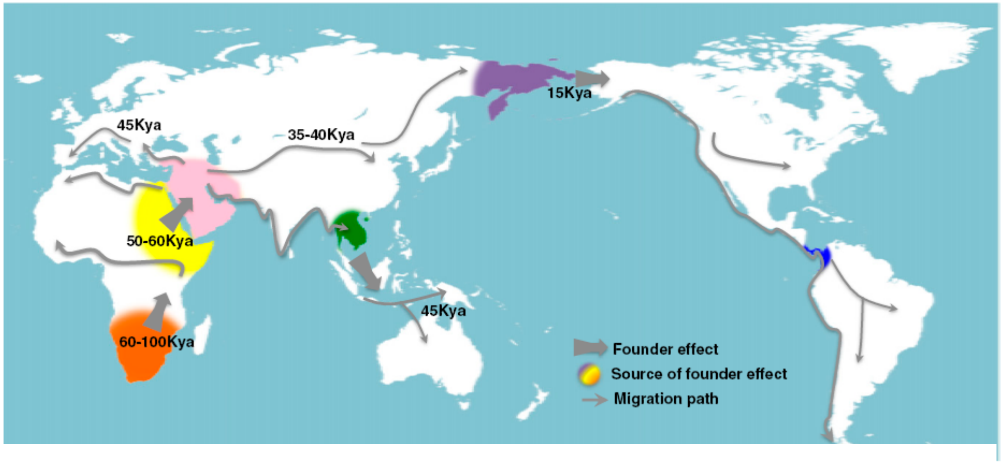


(Almogi-Labin et al., 2009)

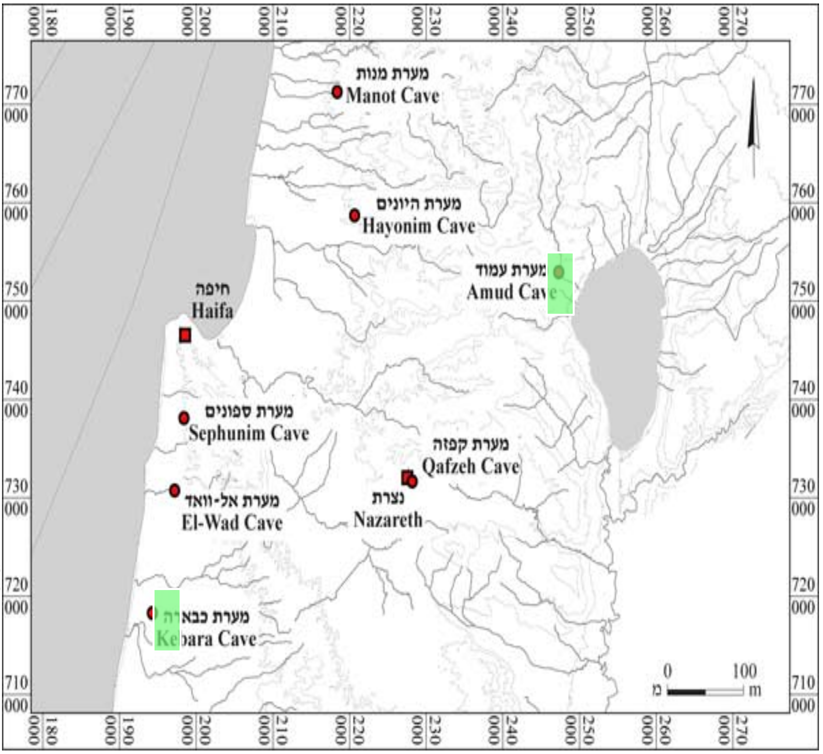
The Human Connection

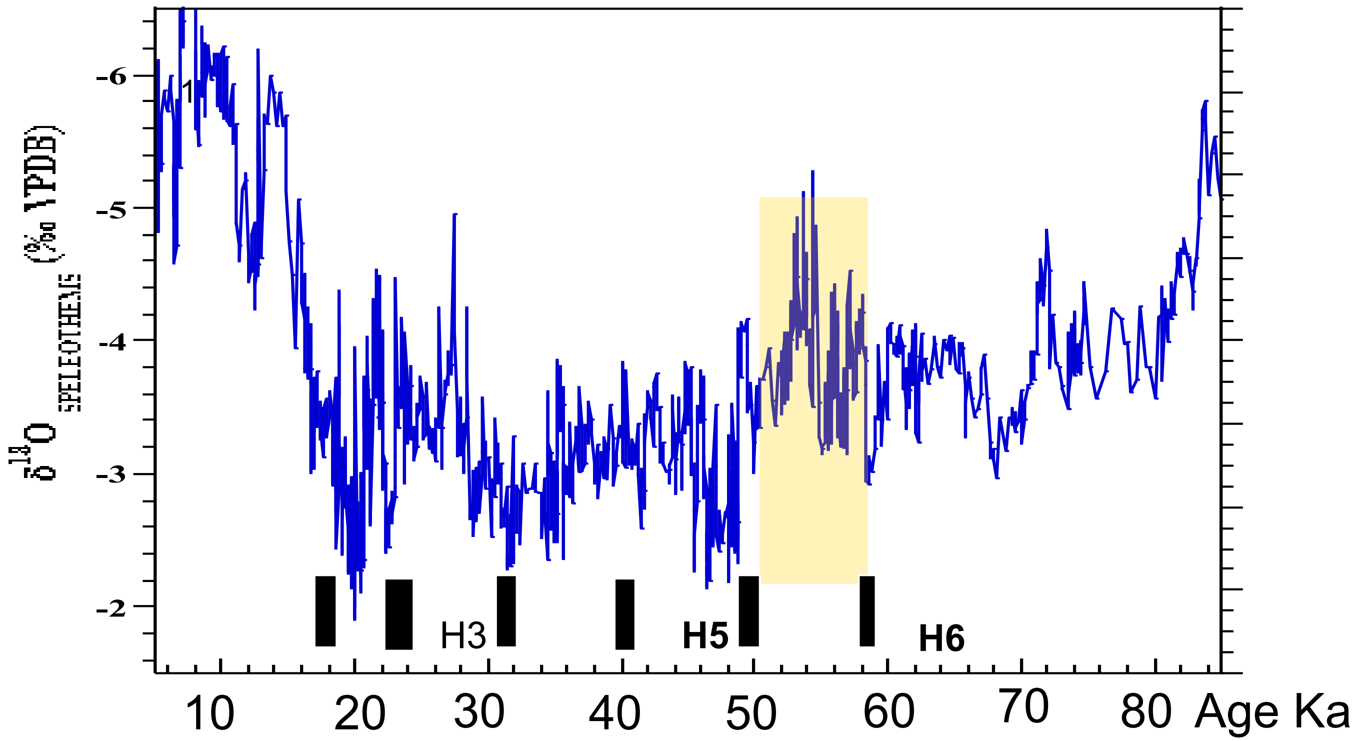
A problem. **Why is there evidence for the existence of Anatomically Modern Human fossils in the Levant during MIS 5, but there is no evidence for their existence during MIS4?** **Is there evidence missing?**

On the contrary, there are several sites of Neanderthal fossils in the regions (among the best- known from Dederiyeh Cave northern Syria, Amud, Kebara and Tabun caves – Israel).

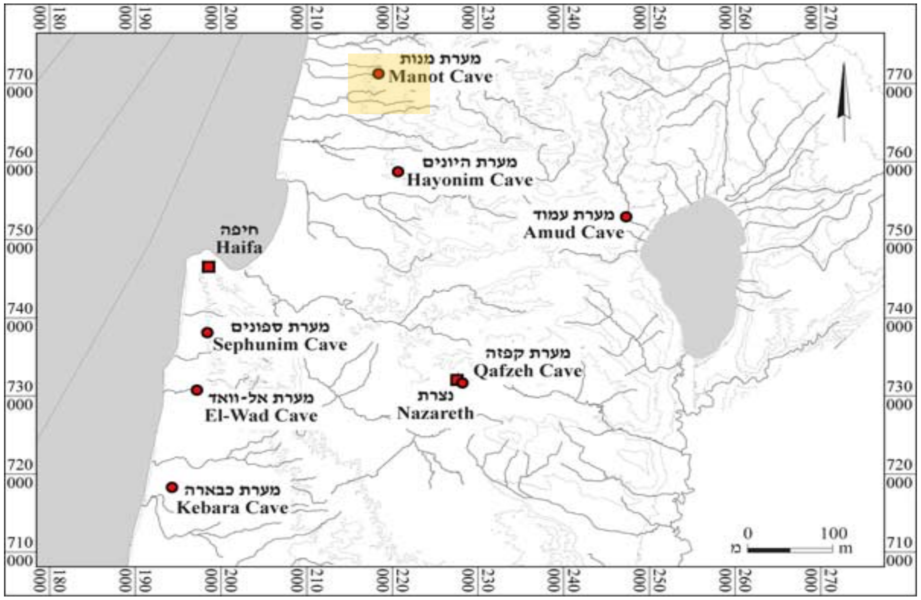


Henn et al., PNAS 2012





Latest preliminary results :



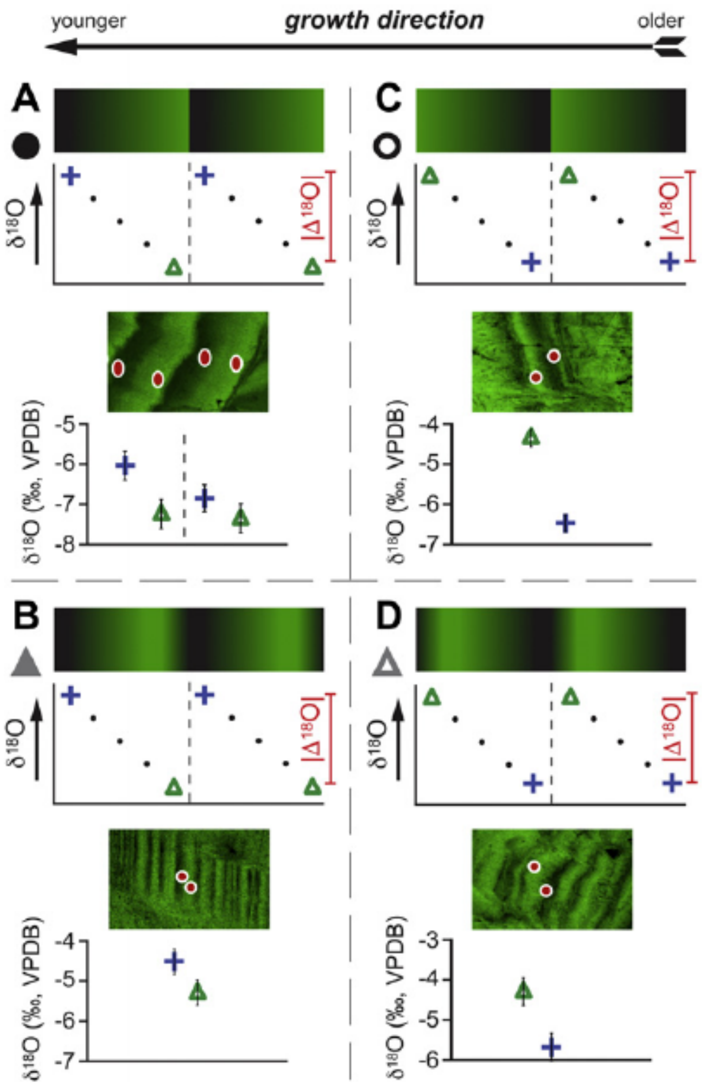
Three dimensional analyses of the skull show close relations with Modern humans of upper paleolithic found in Europe and Africa (Ofer Marder, Israel Hershkovitz, Omri Barzilai)

Manot Cave, western Galilee

Preliminary U-Th ages of carbonate crust on skull, suggest minimum age of ~58-52 ka (Gal Yasur)

Why we have such high oscillations when we increase resolution?

Types of fluorescence banding as function of climate the last 34 ka



A. In the Holocene, the ubiquitous sawtooth pattern of both d18O and fluorescence variability (Fig. 2A) indicates that the modern seasonal regime of wet winters and dry summers has been consistent since 10.5 ka. Smaller |Δ18O| values indicate dryer years.

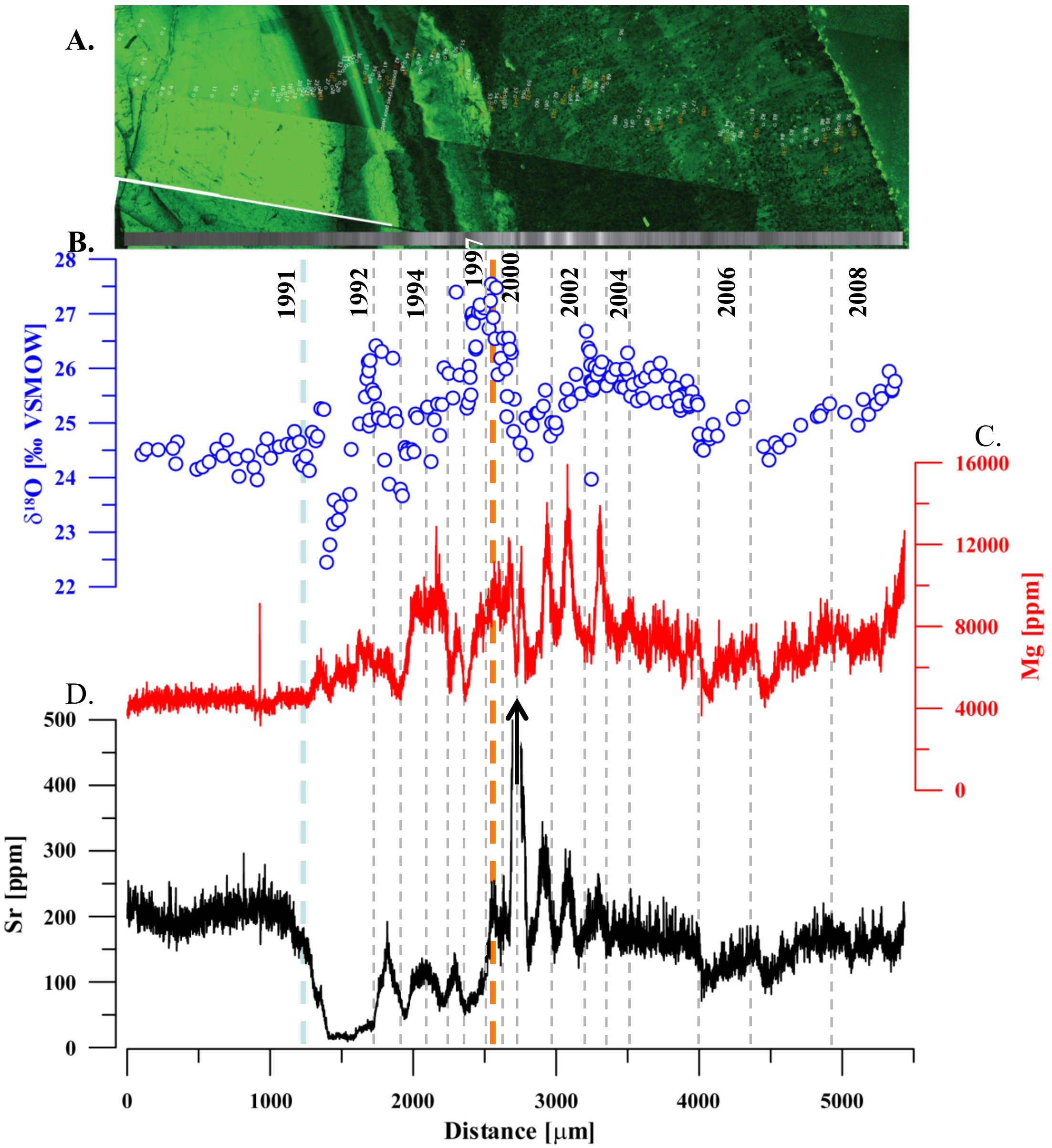
B. 13.5-11 ka – YD. Sinusoidal intensity of fluorescent banding, suggests that dripwater supply from the overlying soil column was more consistent throughout the year than in the Holocene.

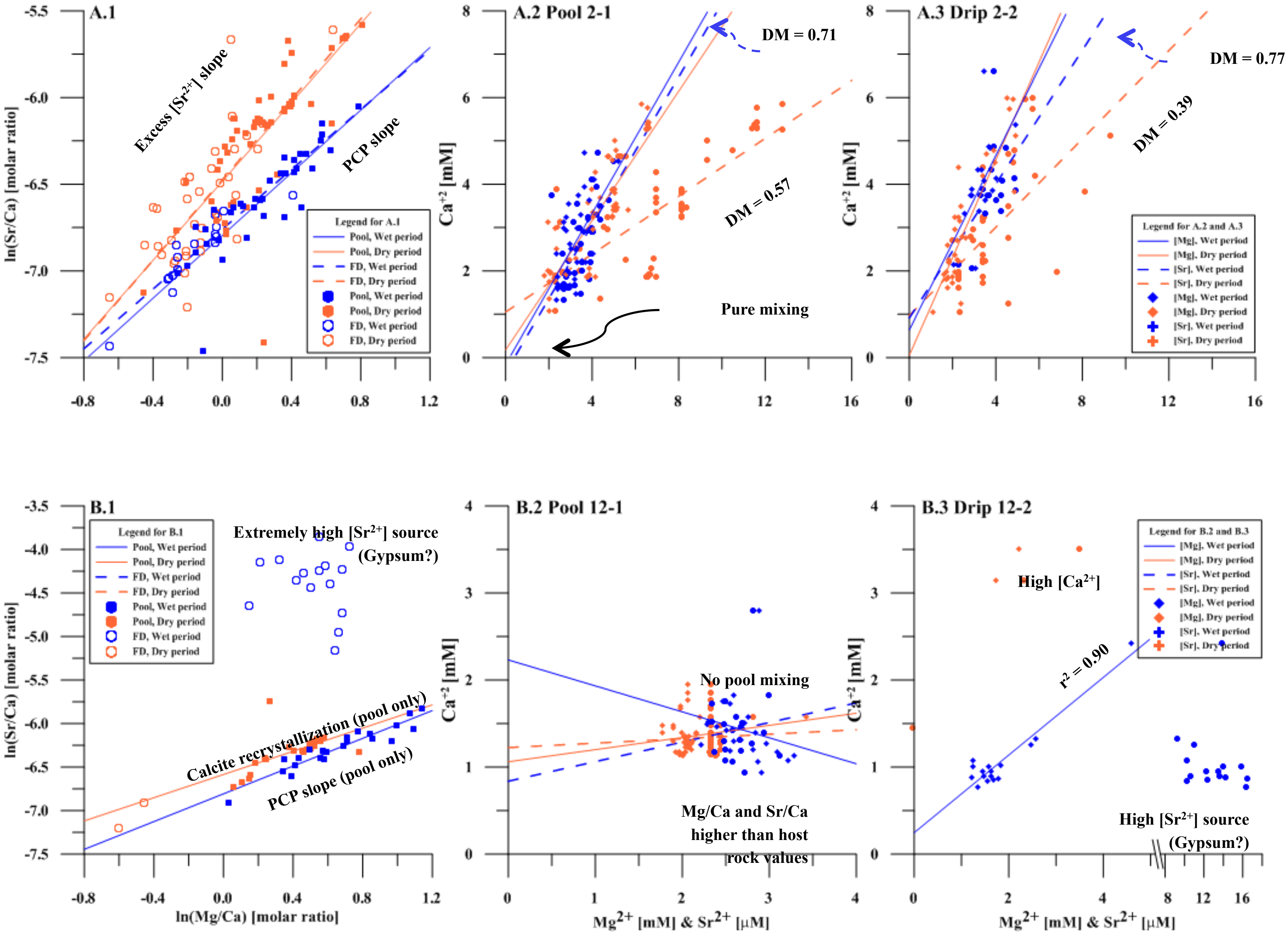
C. The isotope record of the YD termination occurs in multiple stages, and last ~12 years.

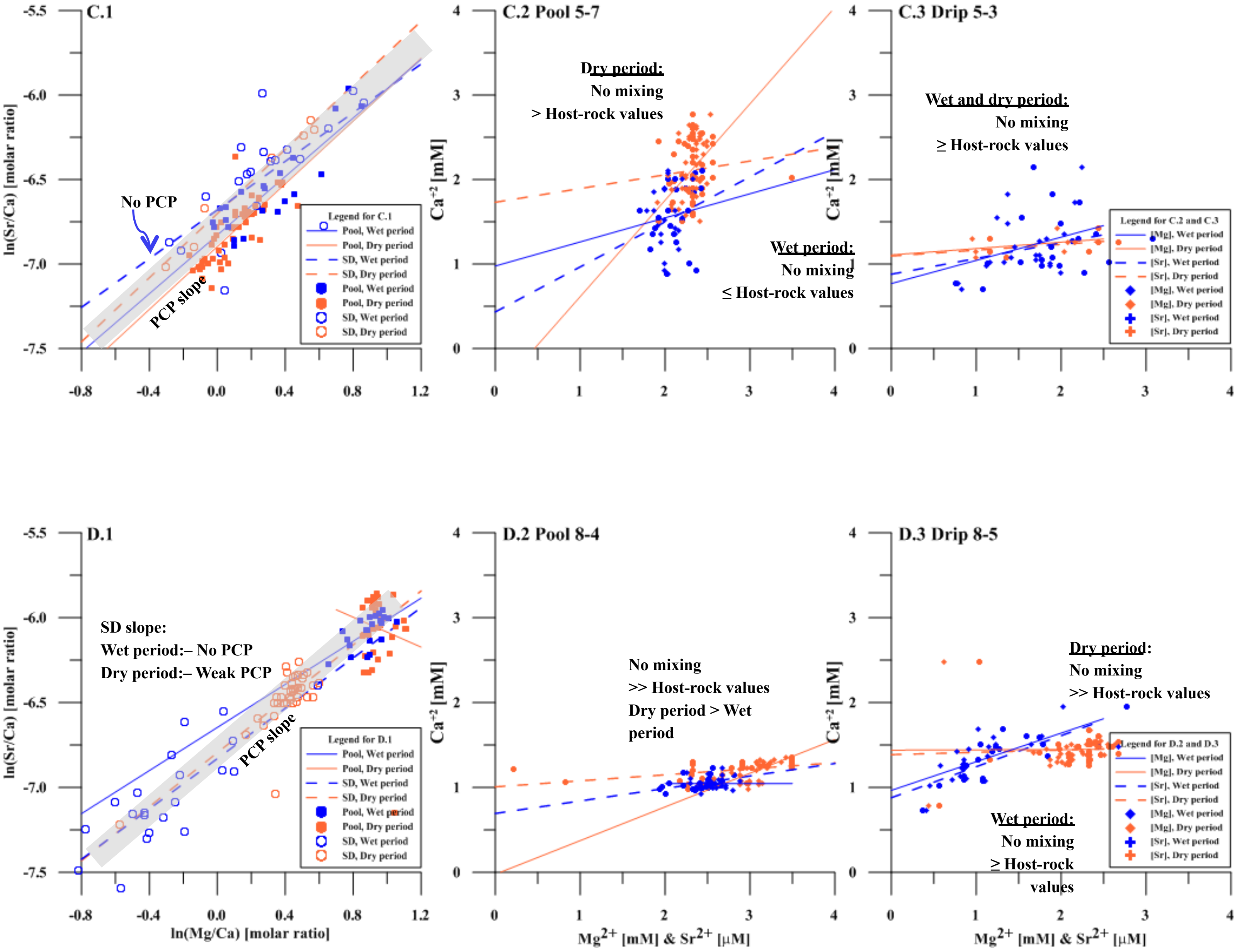
D. The Heinrich 1 event is characterized reversal in the fluorescent banding pattern (i.e. dark-before-bright banding) relative to that in the Holocene. Furthermore, the mean |Δ18O| value is higher than during the YD and Holocene. Decreased seasonal rainfall gradients, regular snow cover, and different overlying vegetation are proposed as possible causes for these observations. Water supply was more consistent probably due to reduced gradient in seasonal rainfall, and or change in the organic acid production.

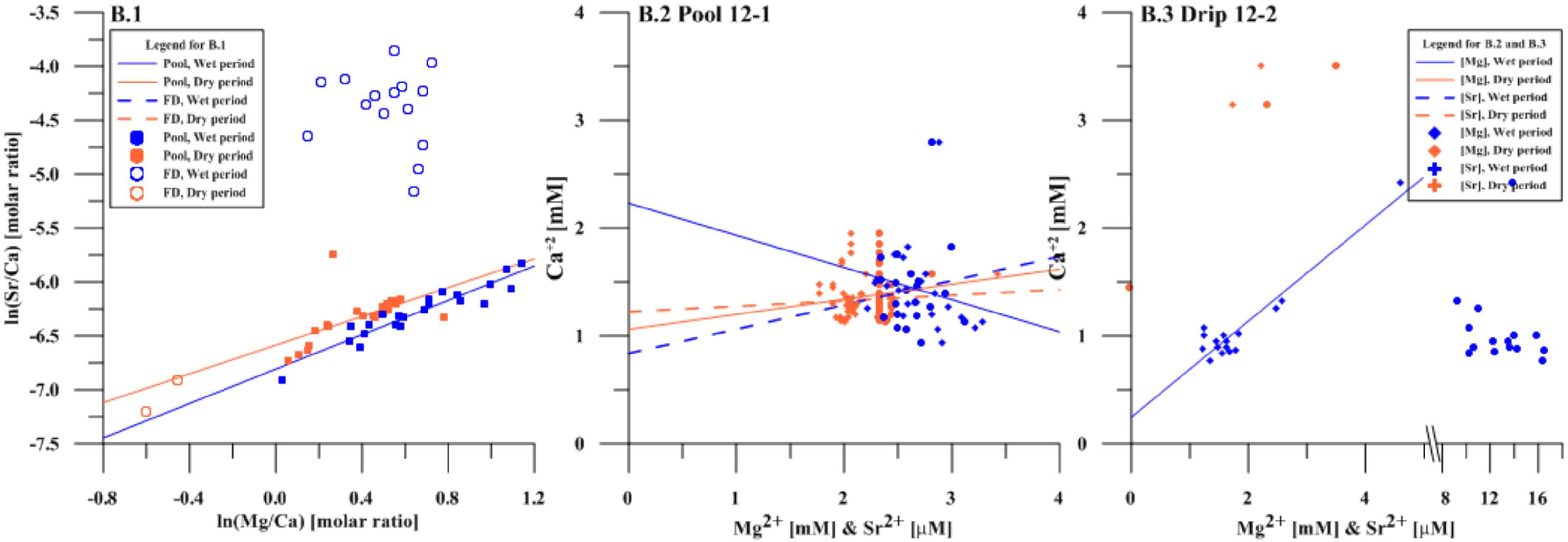
Green triangle bright laminae, blue cross dark laminae

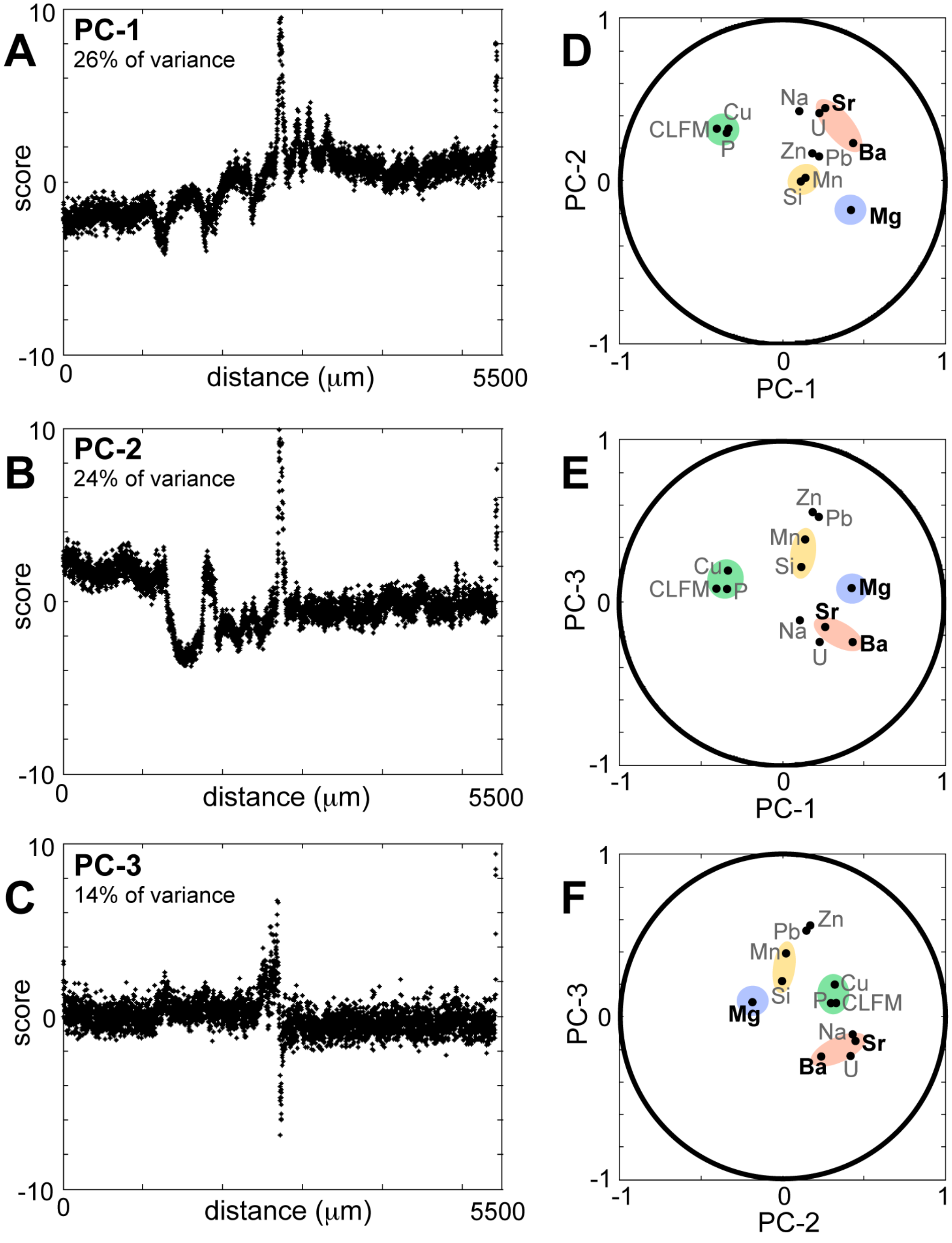
Orland et al., 2012


A.
B.
C.
D.
1991
1992
1994
1997
2000
2002
2004
2006
2008
δ¹⁸O [‰ VSMOW]
28
27
26
25
24
23
22
Mg [ppm]
16000
12000
8000
4000
0
Sr [ppm]
500
400
300
200
100
0
Distance [µm]
0
1000
2000
3000
4000
5000

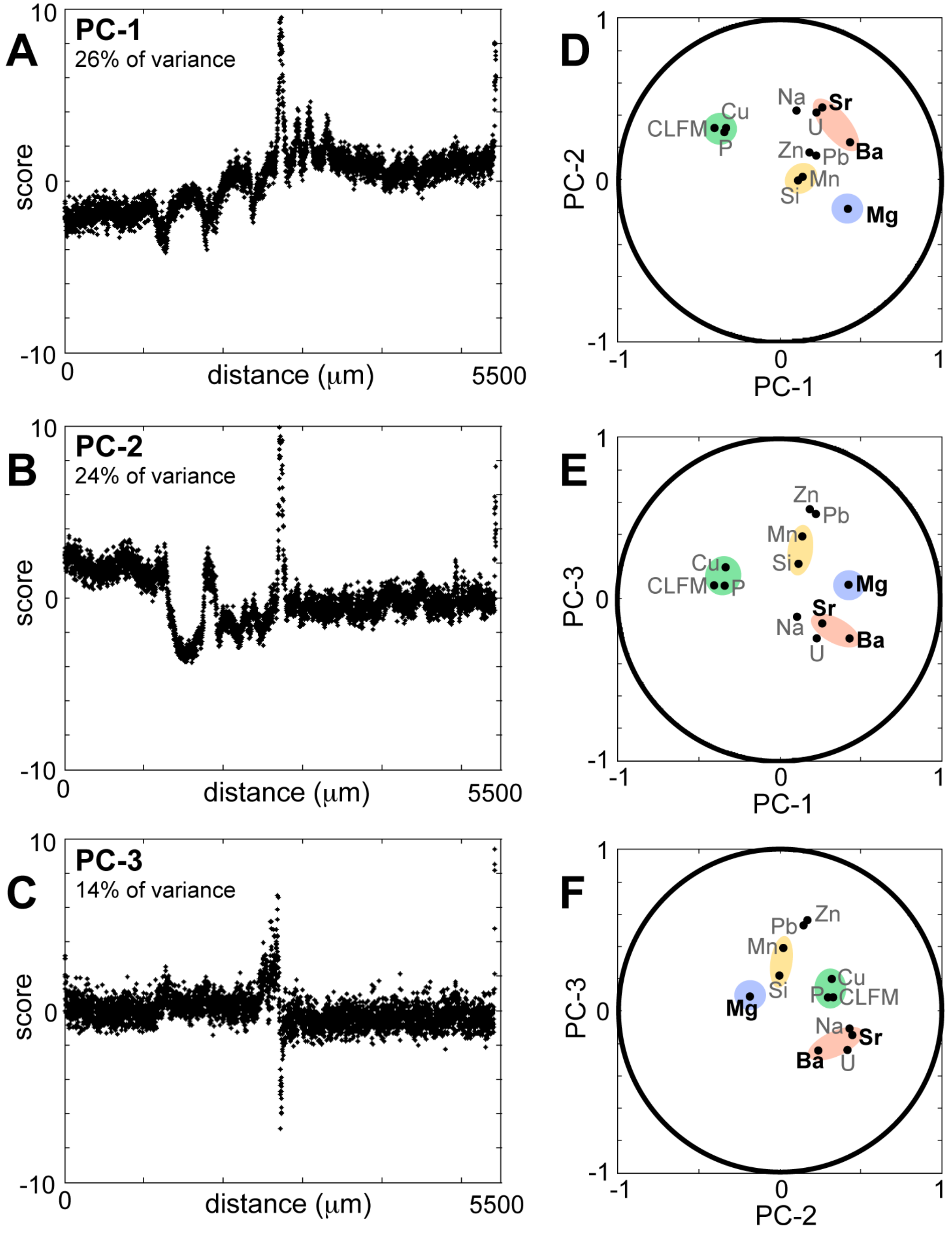

A.1
Excess [Sr2+] slope
PCP slope
Legend for A.1
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
ln(Sr/Ca) [molar ratio]
-5.5
-6.0
-6.5
-7.0
-7.5
-0.8
-0.4
0.0
0.4
0.8
1.2
A.2 Pool 2-1
DM = 0.71
DM = 0.57
Pure mixing
Ca+2 [mM]
8
6
4
2
0
0
4
8
12
16
A.3 Drip 2-2
DM = 0.77
DM = 0.39
Ca+2 [mM]
Legend for A.2 and A.3
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
B.1
Legend for B.1
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
Extremely high [Sr2+] source
(Gypsum?)
Calcite recrystallization (pool only)
PCP slope (pool only)
ln(Sr/Ca) [molar ratio]
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-0.8
-0.4
0.0
0.4
0.8
1.2
ln(Mg/Ca) [molar ratio]
B.2 Pool 12-1
No pool mixing
Mg/Ca and Sr/Ca
higher than host
rock values
Ca+2 [mM]
4
3
2
1
0
0
1
2
3
4
Mg2+ [mM] & Sr2+ [μM]
B.3 Drip 12-2
Legend for B.2 and B.3
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
High [Ca2+]
r2 = 0.90
High [Sr2+] source
(Gypsum?)
Ca+2 [mM]
0
2
4
8
12
16
Mg2+ [mM] & Sr2+ [μM]


C.1
C.2 Pool 5-7
C.3 Drip 5-3
ln(Sr/Ca) [molar ratio]
Ca+2 [mM]
No PCP
PCP slope
Legend for C.1
Pool, Wet period
Pool, Dry period
SD, Wet period
SD, Dry period
Dry period:
No mixing
> Host-rock values
Wet period:
No mixing
≤ Host-rock values
Wet and dry period:
No mixing
≥ Host-rock values
Legend for C.2 and C.3
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
D.1
D.2 Pool 8-4
D.3 Drip 8-5
SD slope:
Wet period:– No PCP
Dry period:– Weak PCP
Legend for D.1
No mixing
>> Host-rock values
Dry period > Wet period
Dry period:
No mixing
>> Host-rock values
Wet period:
No mixing
≥ Host-rock values
Legend for D.2 and D.3
ln(Mg/Ca) [molar ratio]
Mg2+ [mM] & Sr2+ [µM]
-5.5
-6.0
-6.5
-7.0
-7.5
-0.8
-0.4
0.0
0.4
0.8
1.2
0
1
2
3
4


B.1
Legend for B.1
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
Pool, Wet period
Pool, Dry period
FD, Wet period
FD, Dry period
ln(Sr/Ca) [molar ratio]
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-0.8
-0.4
0.0
0.4
0.8
1.2
ln(Mg/Ca) [molar ratio]
B.2 Pool 12-1
Ca+2 [mM]
4
3
2
1
0
0
1
2
3
4
Mg2+ [mM] & Sr2+ [μM]
B.3 Drip 12-2
Legend for B.2 and B.3
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
[Mg], Wet period
[Mg], Dry period
[Sr], Wet period
[Sr], Dry period
Ca+2 [mM]
4
3
2
1
0
0
2
4
8
12
16
Mg2+ [mM] & Sr2+ [μM]



- **Figure 5 (next page):** PCA results for 12 datasets that traverse sample 5-3b, including 11 records of trace element concentration from LA-ICP-MS analysis and one record of fluorescence intensity acquired by CLFM. Section 3.4 explains the PCA terminology. **A-C** show the scores of PCs 1-3, respectively, plotted versus distance from the base of 5-3b. The percentage of total variance (%) represented by each PC is indicated in the upper-left corner of panels A-C. **D-F** show the loadings of the 12 observed datasets for PC2 vs. PC1, PC3 vs. PC1, and PC3 vs. PC2, respectively. Since the sum of the squared loading values of a trace element on all of the principal components equals 1, the unit circles in panels D-F outline the maximum range of possible loadings. For example, if one trace element has a loading of 1 on any principal component, it must have a loading of zero on all others. Notable classes of elements are highlighted in color to facilitate comparison of their relative loadings; divalent cations are colored blue (Mg) and red (Sr, Ba), while elements transported by organic colloids or silicates are green (P, Cu) and yellow (Si, Mn). The similar variability of fluorescence intensity (CLFM) to that of P and Cu likely indicates that fluorescence in sample 5-3b is caused by P- and Cu-laden organic colloids.


A
PC-1
26% of variance
score
10
0
-10
0
distance (μm)
5500
B
PC-2
24% of variance
C
PC-3
14% of variance
D
PC-1
PC-2
1
0
-1
CLFM
Cu
P
Na
Sr
U
Ba
Zn
Pb
Mn
Si
Mg
E
PC-3
F