Gypsum speleothems record the triple oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopic composition of cave dripwater: potential paleoenvironmental implications

Fernando Gazquez[1], Veronica Chiarini[2], Andrea Columbu[2], Jo De Waele[2], Philippe Audra[3], Didier Cailhol[4], Marco Vattano[5], Giuliana Madonia[5], Alena Giesche[6], José-María Calaforra[1], and David A. Hodell[6]

[1]University of Almeria, Department of Biology and Geology, Spain (f.gazquez@ual.es)

[2]Department of Biological, Geological and Environmental Sciences, University of Bologna, Italy.

[3]Polytech'Lab, University Cote d'Azur, Nice, France.

[4]Laboratoire EDYTEM, University Savoie – Mont-Blanc, CNRS, France.

[5]Earth and Marine Science Department, University of Palermo, Italy.

[6]Godwin Laboratory for Palaeoclimate Research. Department of Earth Sciences. University of Cambridge, United Kingdom.

Rationale

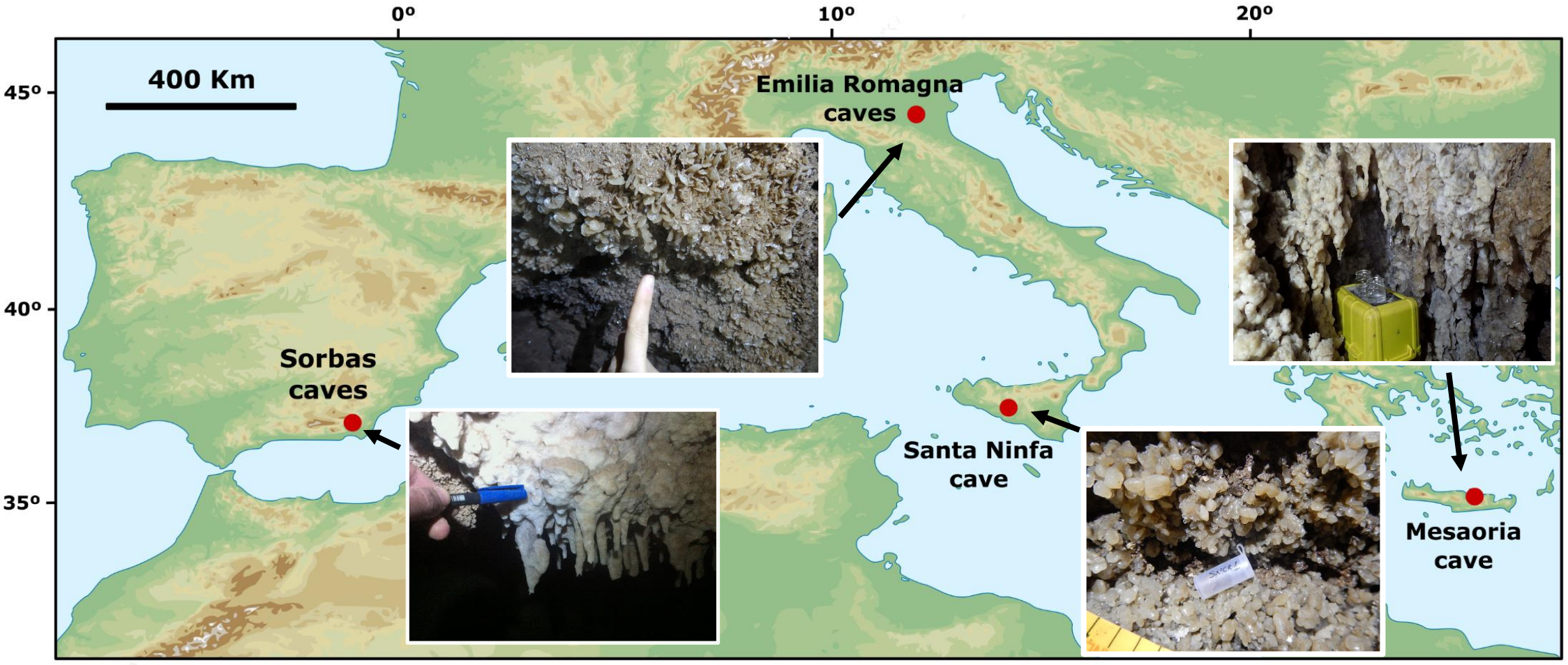
- Stable isotopes in gypsum ($CaSO4 \cdot 2H_2O$) hydration water can be used to **reconstruct the isotopic composition** ($\delta^{18}O$, $\delta^{17}O$ and δD) of the original solution, with **minor temperature** effects on water/gypsum fractionation factors.

- Gypsum ($CaSO_4 \cdot 2H_2O$) speleothems (i.e. stalactites, stalagmites, etc.) in caves form frequently through dissolution of the gypsum host-rock by seepage water and subsequent secondary mineral re-precipitation from gypsum-saturated solutions

- How gypsum speleothems form in different caves? (evaporation always?)

- Can gypsum speleothems be used for paleoclimate reconstructions?

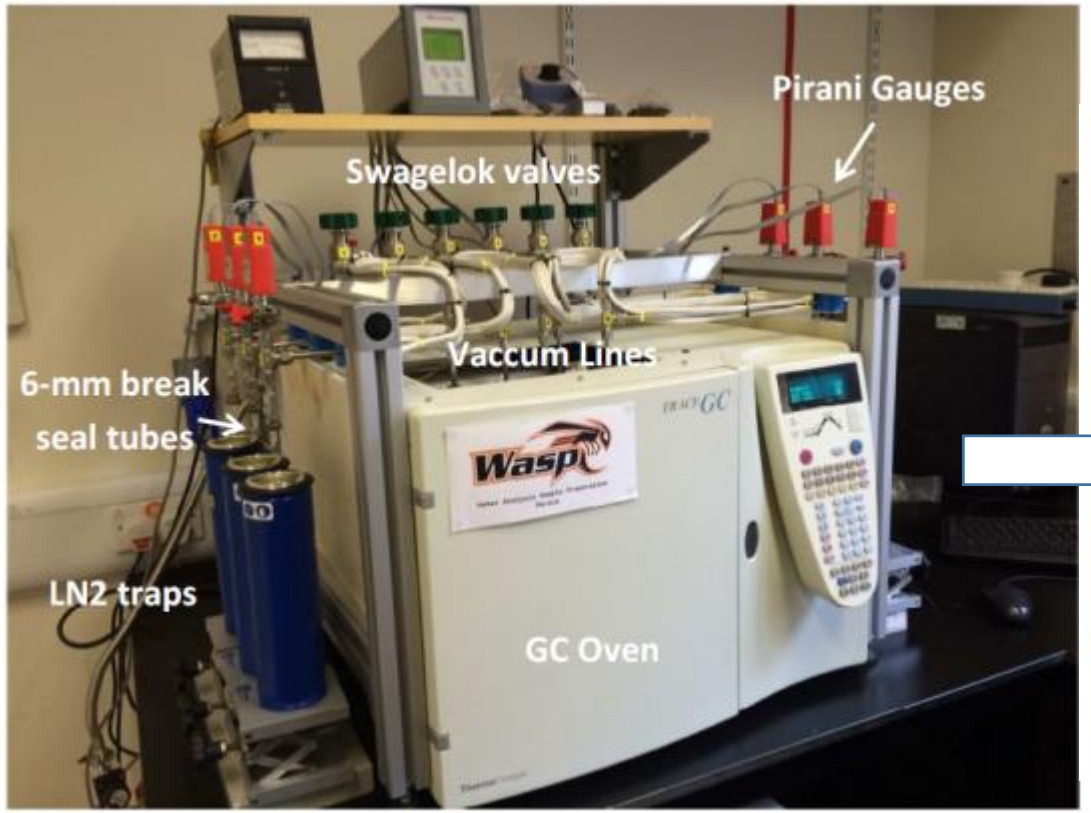
Gypsum speleothems in the Mediterranean region

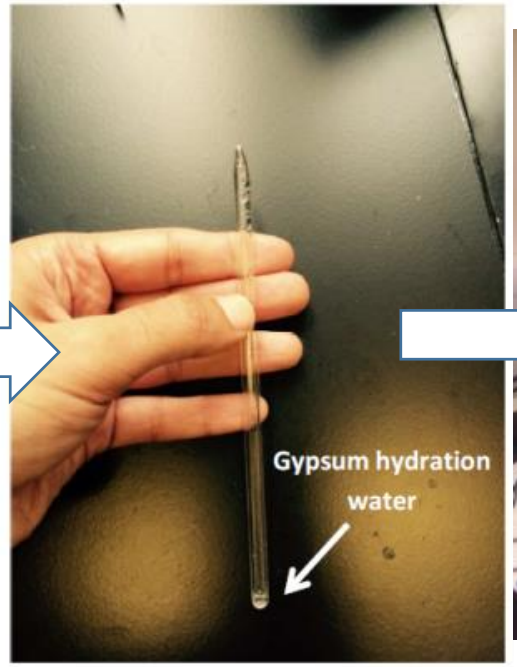


Method

Semi-automated procedure for extracting GHW by slowly heating the sample to 400°C *in vacuo* and cryogenically trapping the evolved water.

Analysis of triple oxygen and hydrogen isotopes in gypsum hydration water by CRDS





PICARRO L-2140-i
(TRIPLE OXYGEN ISOTOPE ANALYZER)

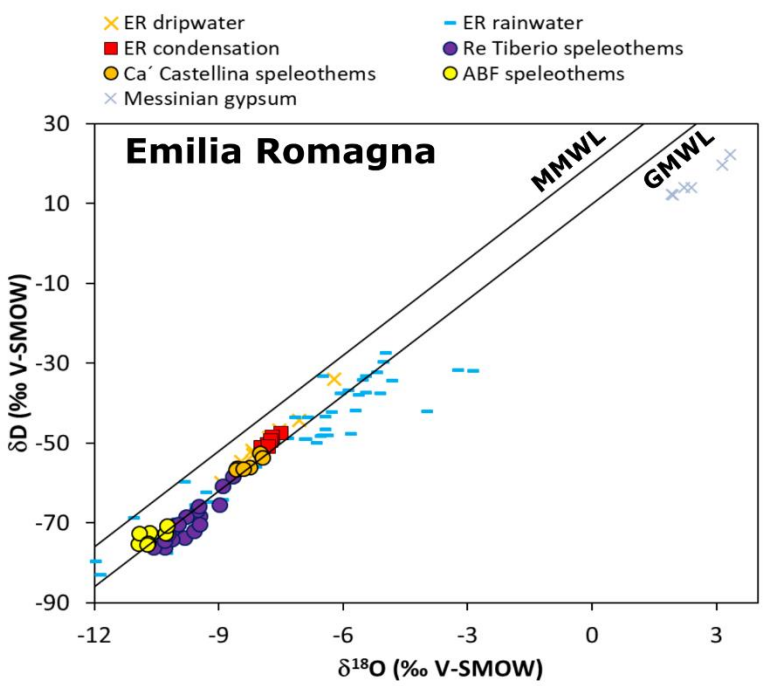
Gázquez F., Mather I., Rolfe J., Evans N. P., Herwartz D., Staubwasser M. and Hodell D. A., 2015b. Simultaneous analysis of $^{17}O/^{16}O$, $^{18}O/^{16}O$ and $^{2}H/^{1}H$ of gypsum hydration water by cavity ring-down laser spectroscopy. Rapid Commun. Mass Spectrom. 29, 1997–2006.

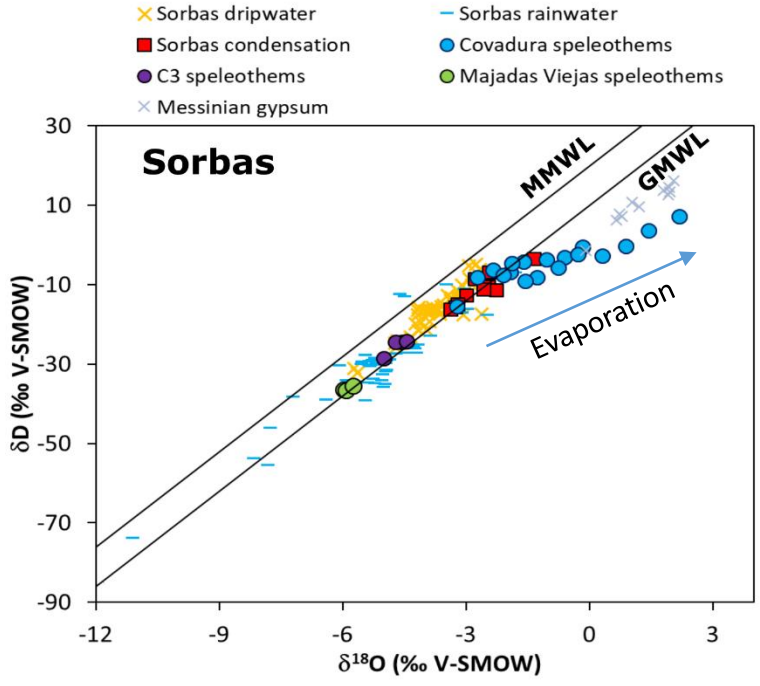
RESULTS

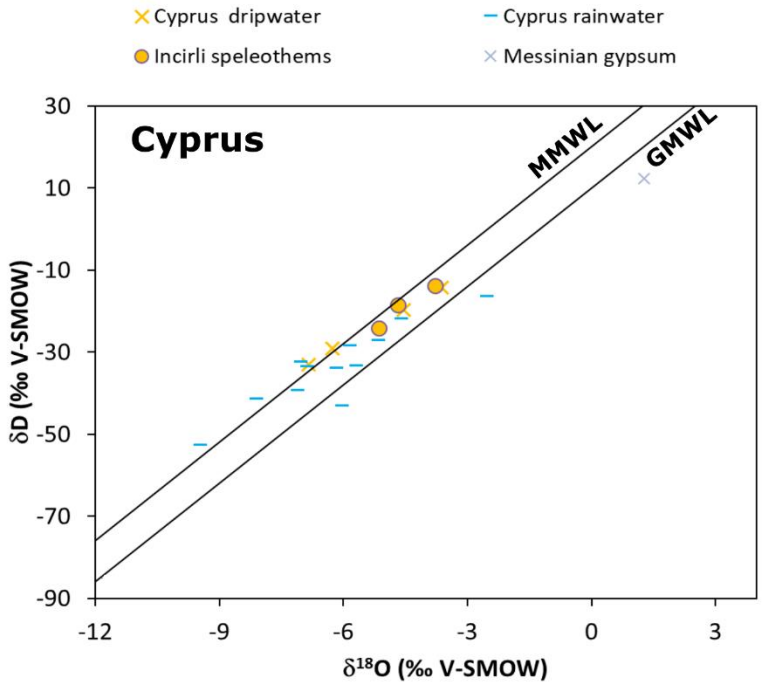
Emilia Romagna, Cyprus and Sicily speleothems fall on the LMWLs and have **similar values to the mean isotopic composition of rainfall in the setting of the caves**

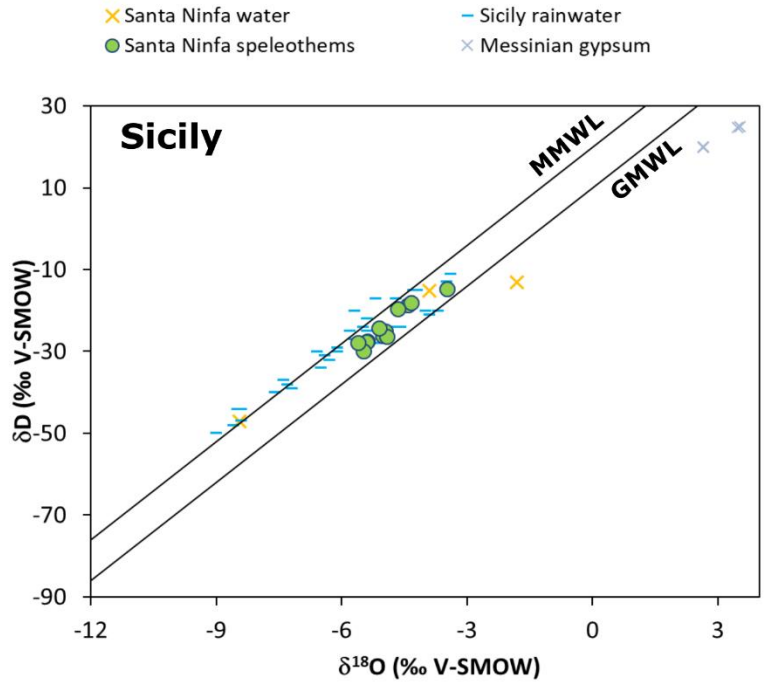
Most Sorbas (Spain) speleothems describe an **evaporation** trajectory

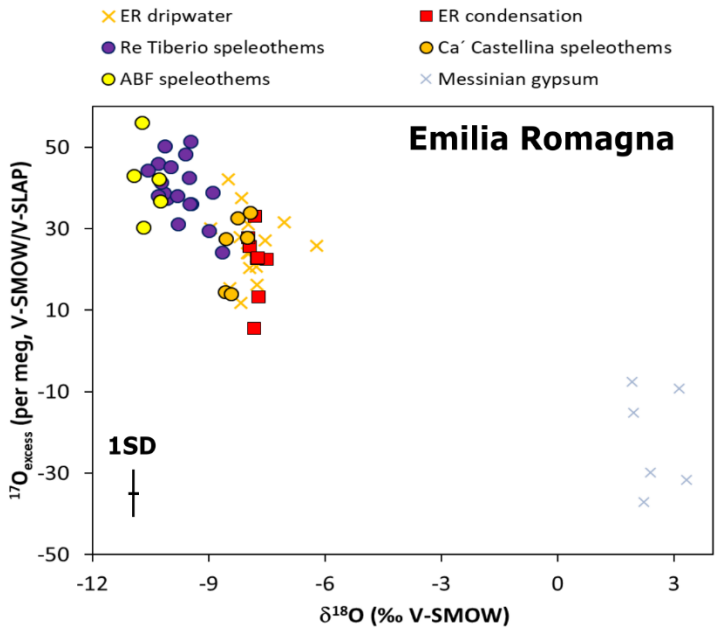
*Results of Messinian (marine) gypsum are displayed for comparison

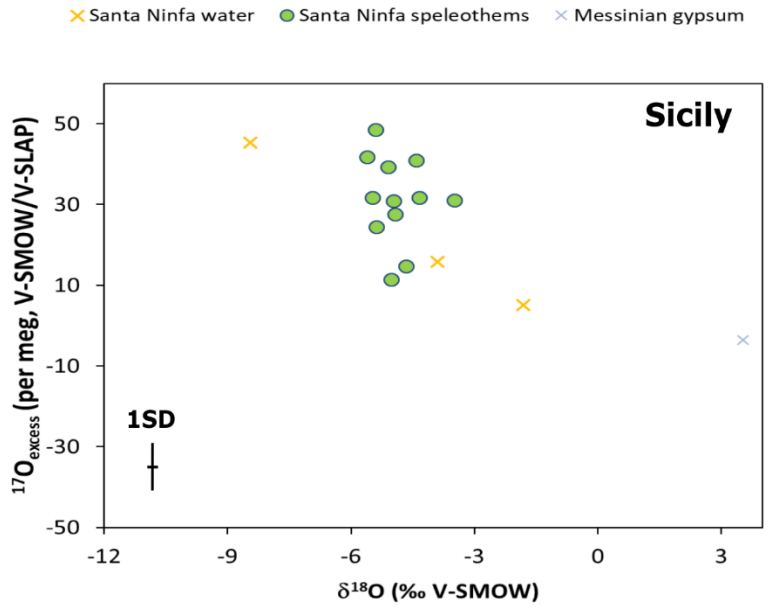


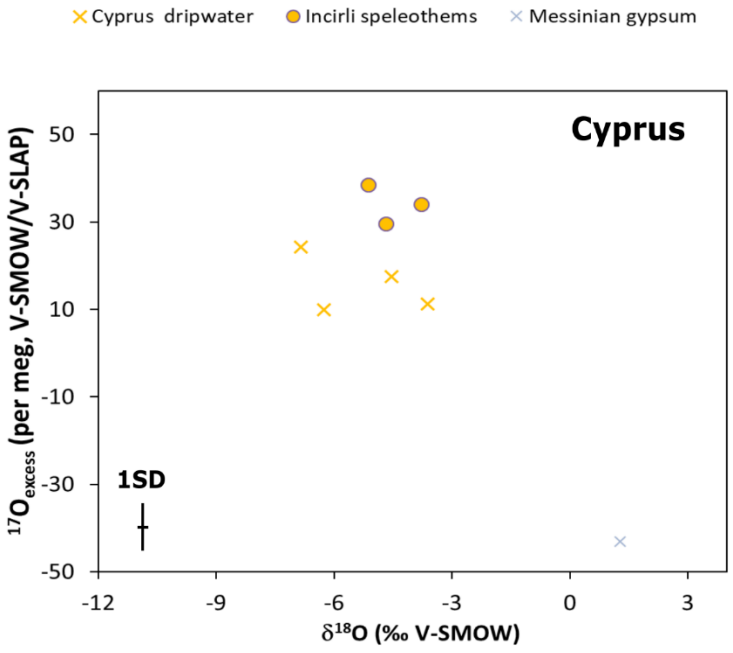


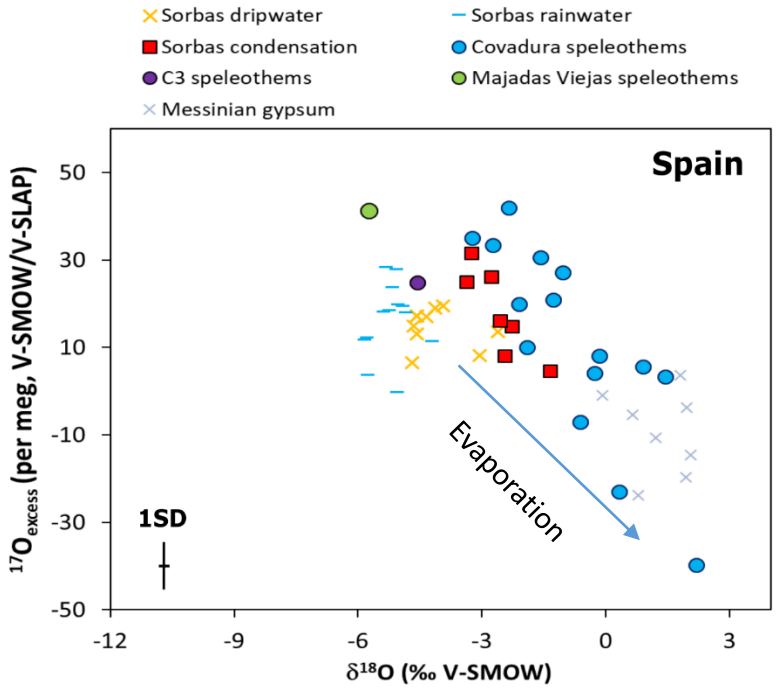












Emilia Romagna, Cyprus and Sicily speleothems formed from water with **isotope values similar to the mean of rainfall in those regions, with no signs of evaporation**

Most Sorbas (Spain) speleothems describe an **evaporation** trajectory

*Results of Messinian (marine) gypsum are displayed for comparison

Next steps

- U-Th dating of gypsum speleothems
- How subaerial gypsum speleothems can form with no evaporation? (Ostwald ripening???)
- Condensation water contributions?