

Applying "clumped-isotopes" thermometry to pedogenic carbonates and speleothems

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SOILS

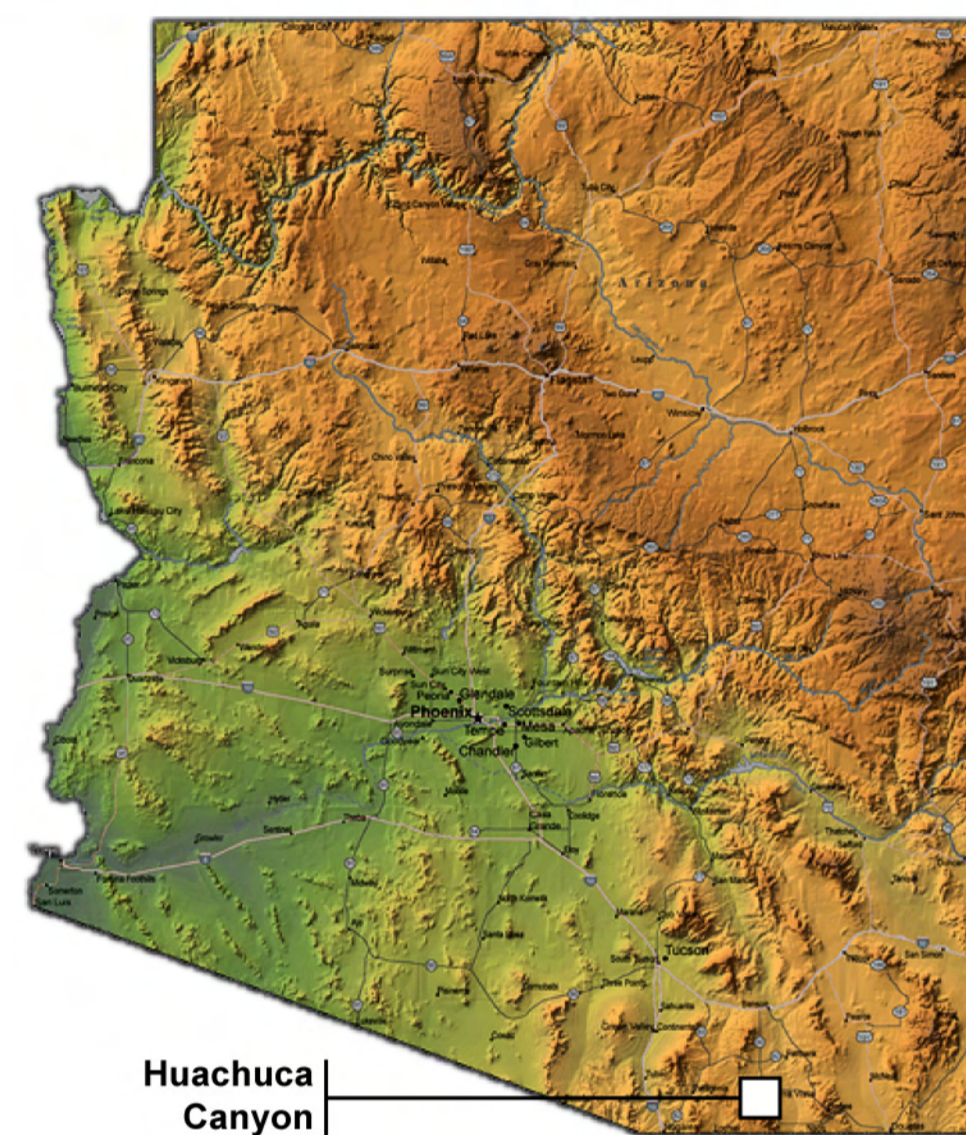


Figure 1: Huachuca Canyon is located in southern Arizona, ~1900 m a.s.l. There, we sampled a "modern" (Late Holocene) soil on an abandoned fluvial terrace.

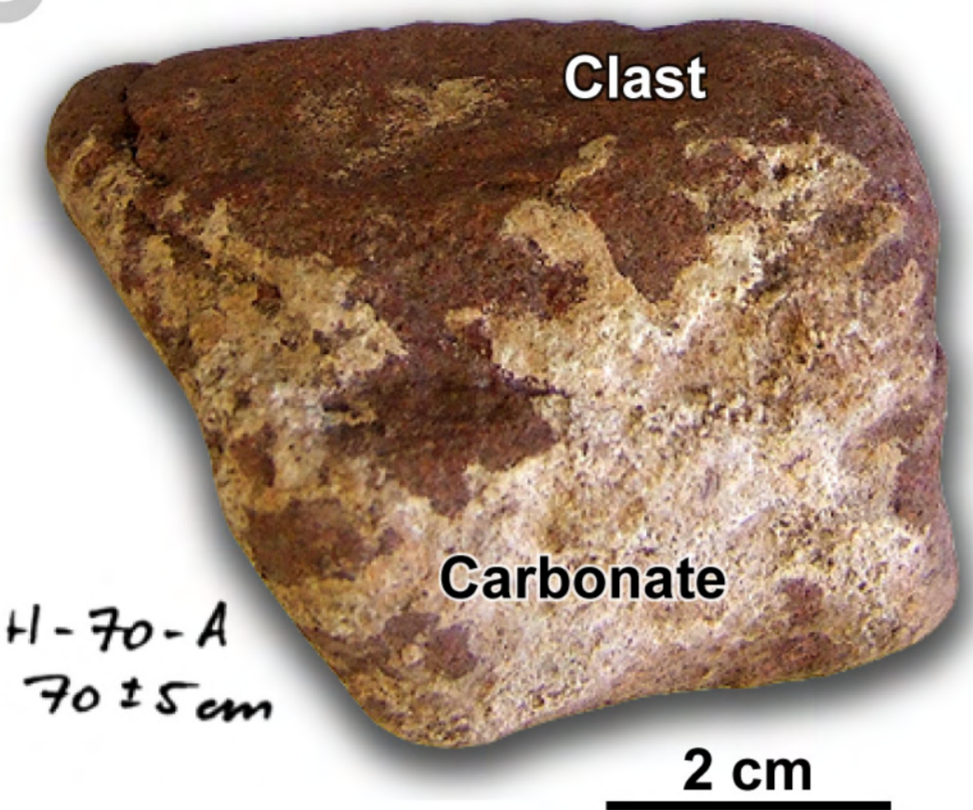


Figure 2: We collected clasts of various sizes (3-15 cm in diameter), which are partially covered with "stage I" (i.e. earliest precipitation stage) carbonate coatings. Such coatings are found at depths between 70 and 150 cm. Composition of the clasts themselves is virtually carbonate-free, and scraping the coatings yields authigenic, quasi-pure (>90% mass) calcite, which is then measured for $\Delta 47$.

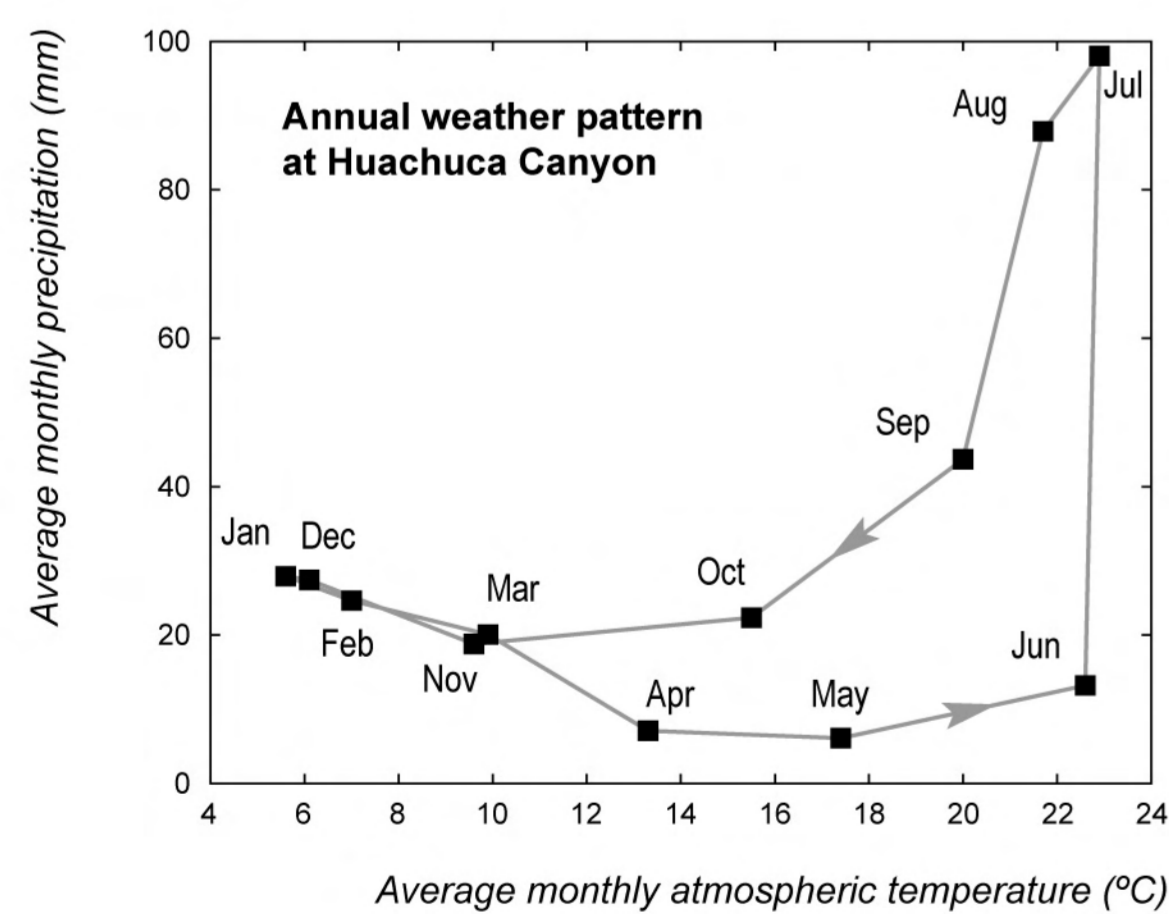


Figure 3: Historical weather data at nearby Fort Huachuca covers most of the 20th century. Precipitation patterns are dominated by the North American Monsoon, with abundant rainfall in July and August, coinciding with the warmest monthly average temperatures. Pedogenic carbonates are expected to precipitate during the wet season, or up to a few weeks thereafter, and the $\Delta 47$ measurements are expected to reflect ground temperatures over this period.

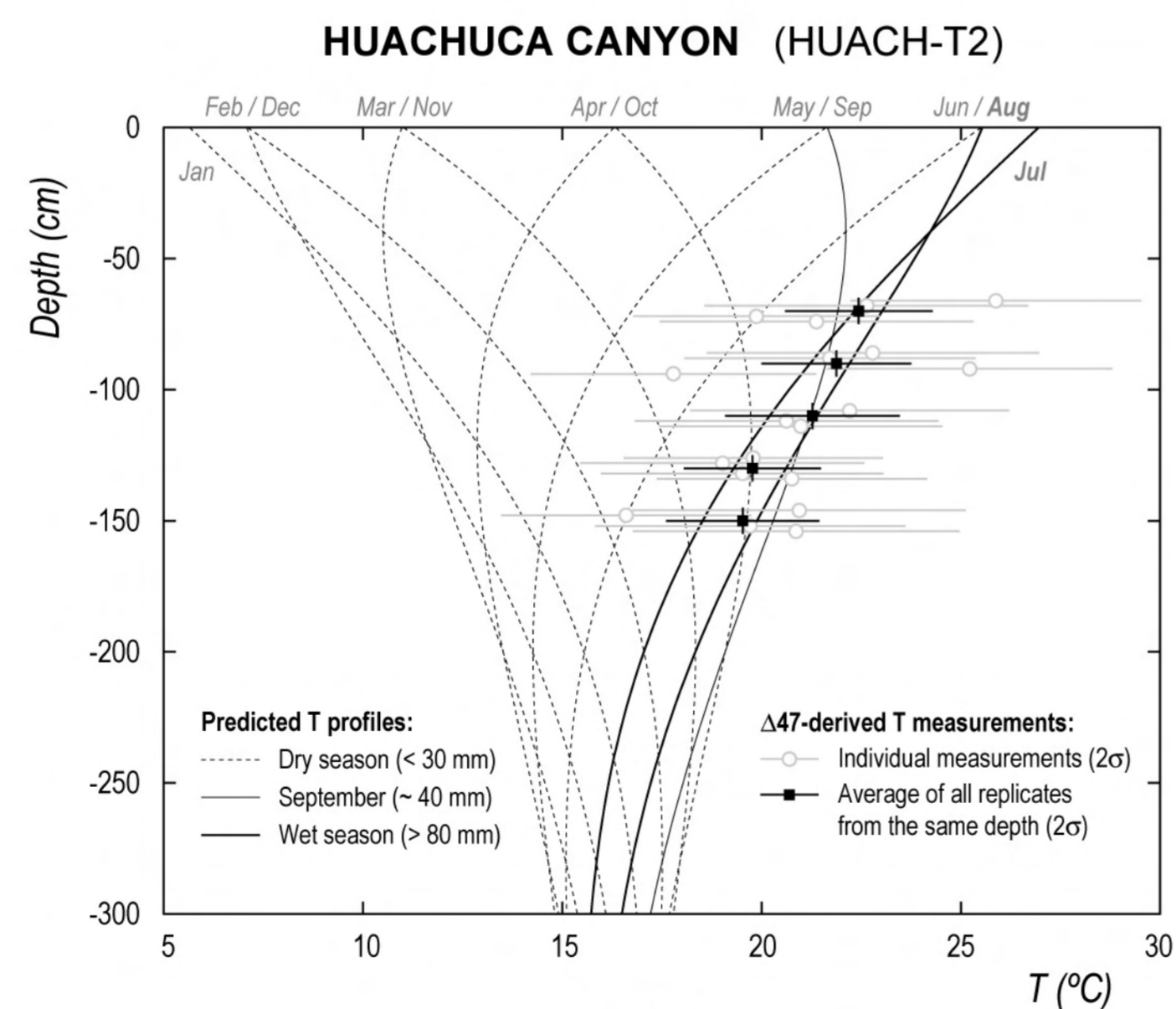


Figure 4: Ground temperature varies with depth and with time. Here, monthly temperature profiles modeled for Huachuca Canyon are plotted against depth. The model parameters are [1] summer radiative heating (the maximum excess of shallow ground T relative to the atmospheric T, due to solar radiation); [2] thermal diffusivity, which governs the phase shifting and attenuation of thermal oscillations with depth. The model plotted here assumes 4°C of summer radiative heating, the value observed by Bartlett et al. (2006) in the same regional setting. $\Delta 47$ measurements agree well with the model temperatures, suggesting that carbonates precipitates near thermodynamic equilibrium at this site.

Abstract

The carbonate "clumped-isotopes" thermometer (Ghosh et al., 2006a) constrains the crystallization temperatures of carbonate minerals by comparing the abundance of ^{13}C - ^{18}O bonds in these minerals to a stochastic abundance derived from the bulk isotopic composition of C and O atoms. This overabundance is noted $\Delta 47$ and increases as crystallization temperature decreases. Unlike previous ^{18}O -based carbonate paleo-thermometers, this method does not require knowledge of the parent water's composition. It was calibrated using synthetic carbonates, and has subsequently been applied to paleo-pedogenic rhizoliths of Miocene age (Ghosh et al., 2006b).

Further applications of this method to natural carbonates require a systematic investigation of modern systems such as soils or speleothems, by measuring $\Delta 47$ in carbonates whose precipitation temperature is known a priori. The main objective is to test whether such systems precipitate near thermodynamic isotopic equilibrium, and to understand, quantify (and eventually correct) deviations from that equilibrium caused by kinetic isotope fractionation. Here we report early results from Holocene soils and modern to Late Pleistocene speleothems.

SPELEO

Speleothem precipitation:

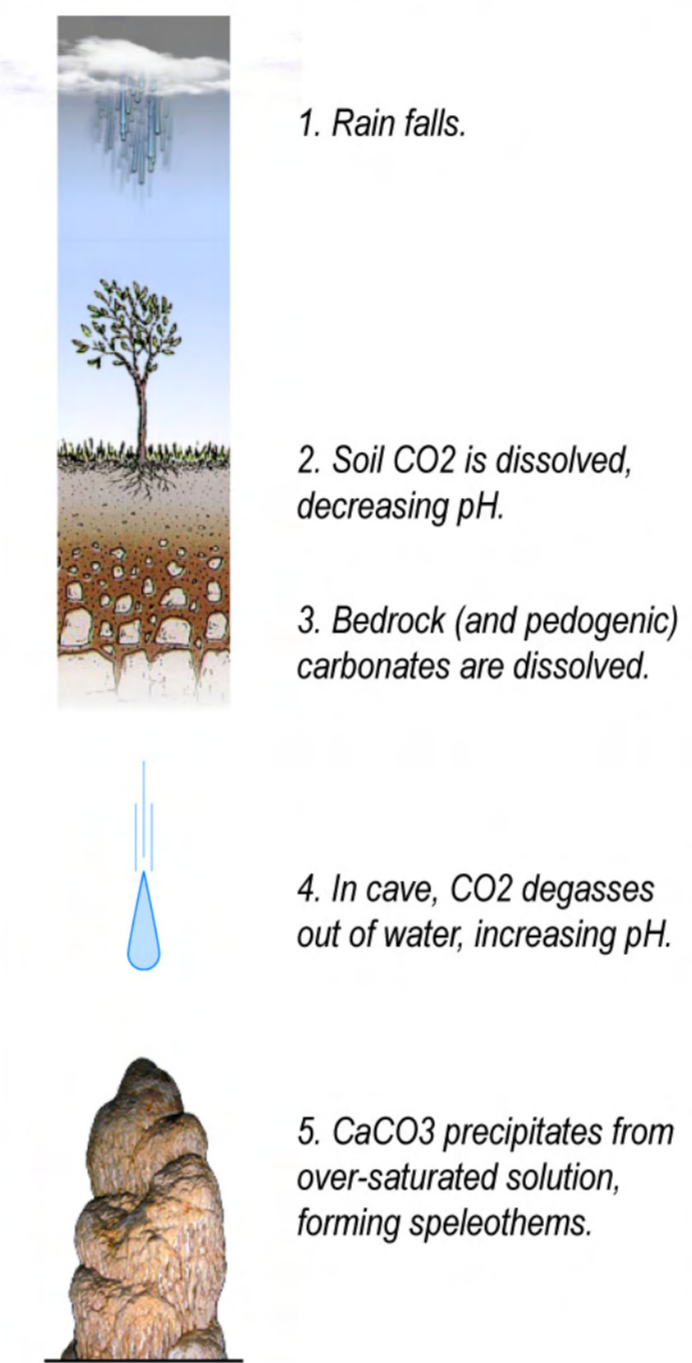


Figure 5: Physical processes leading to speleothem formation. Rainwater absorbs soil CO_2 , decreasing pH, so that pedogenic and/or bedrock carbonates are dissolved. As water percolates through karstic networks, the solution becomes saturated in Ca^{2+} ions. When water reaches a cave, CO_2 degasses out of the solution, sharply decreasing Ca^{2+} solubility, which results in rapid precipitation of CaCO_3 . Over time, this process generates speleothems, whose laminae can be dated (up to 500 ka) using U/Th.

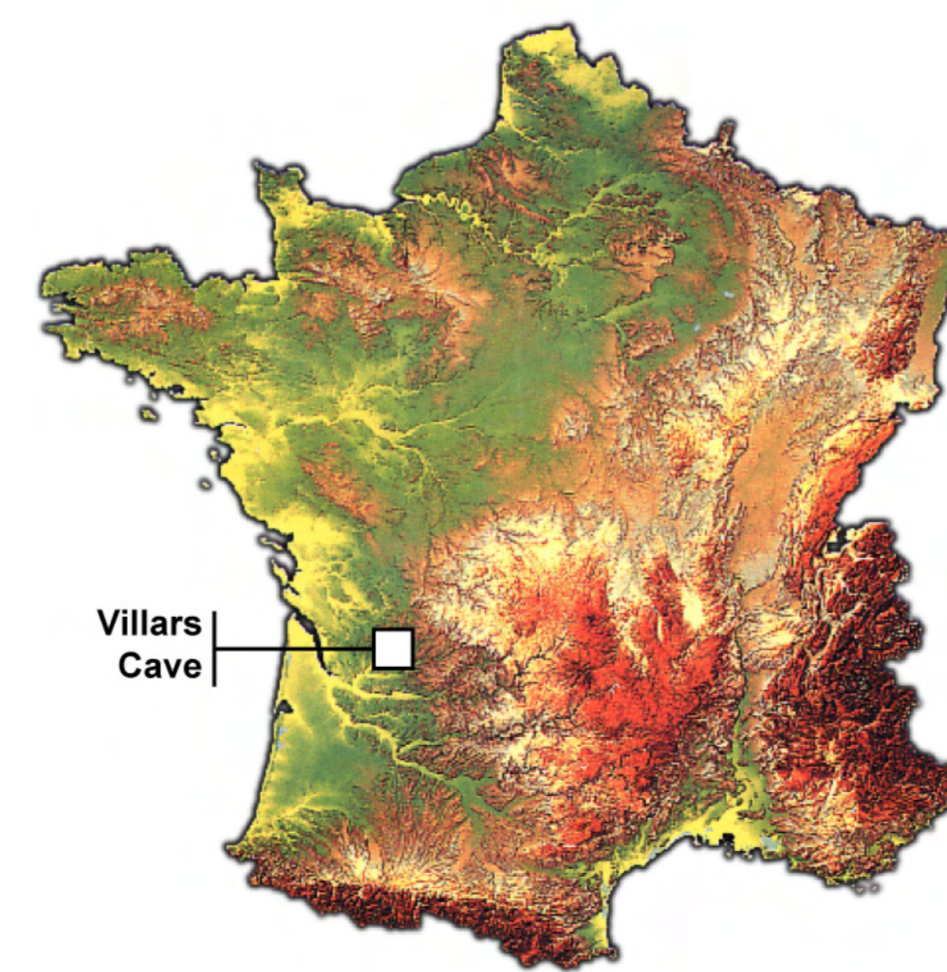


Figure 6: The Villars cave, where we sampled a flowstone (a specific type of speleothem) is located in SW France. Its annual temperature oscillations are negligible ($<0.2^\circ\text{C}$), as are those of drip water $\delta^{18}\text{O}$. Modern calcite was sampled from the top of the flowstone, as well as 4 older samples from MIS stages 5-6 (cf next figure).

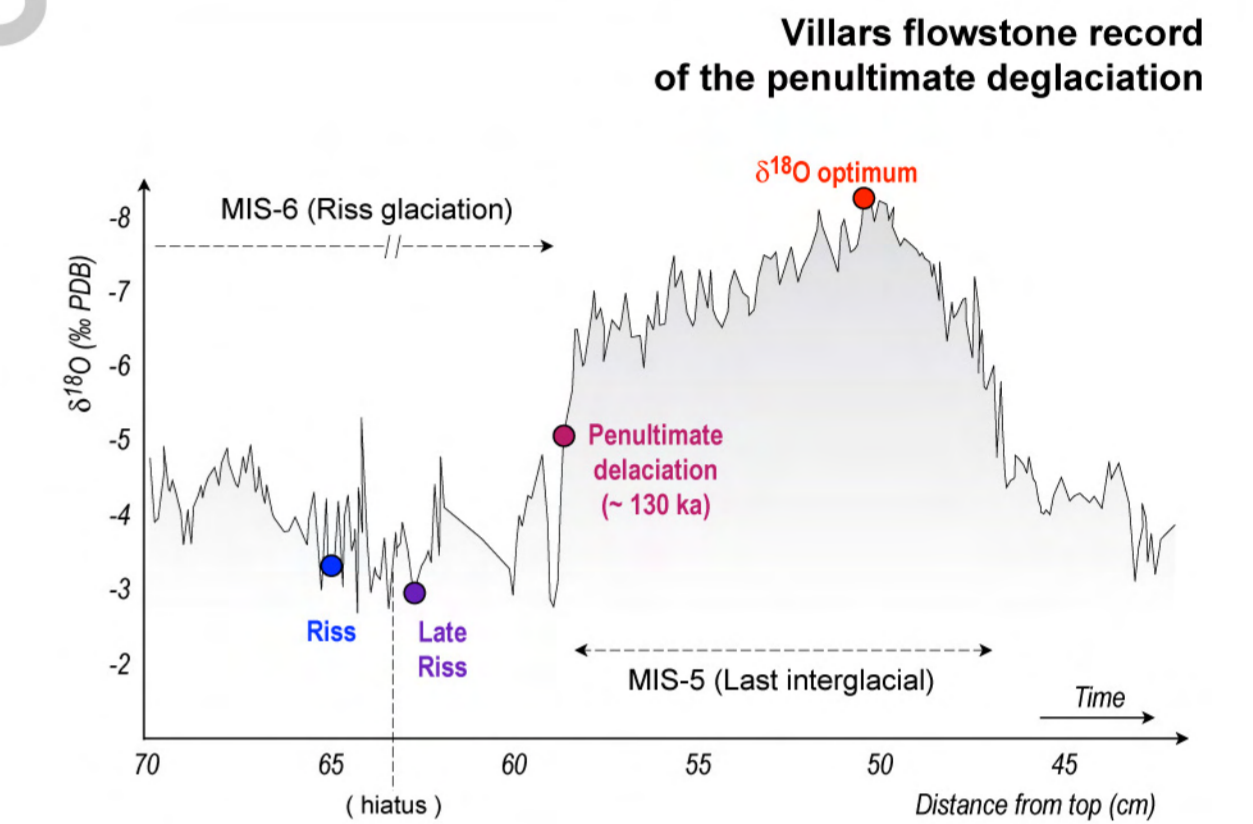


Figure 7: The Villars flowstone recorded the penultimate deglaciation (~130 ka), as evidenced by significant $\delta^{18}\text{O}$ variations. This is only a proxy of climate change, however, incorporating variations in mean annual temperatures and rainwater composition. Quantitatively reconstructing paleo-temperatures requires combining $\Delta 47$ and fluid inclusion $\delta^{18}\text{O}$ measurements (cf next figure).

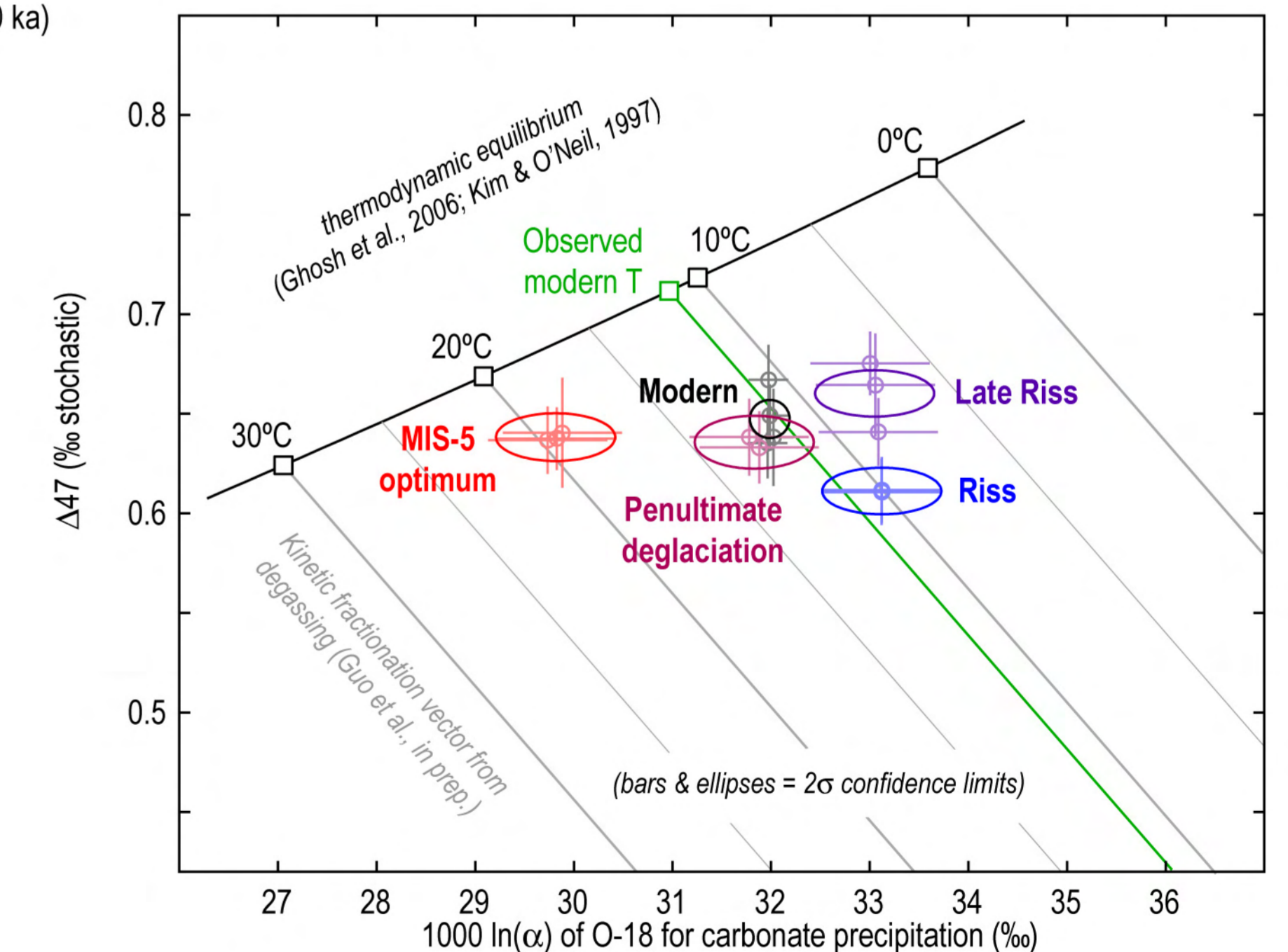


Figure 8: Quantitative speleothermometry (?) All Villars samples display evidence of kinetic isotope effects, likely due to rapid degassing of CO_2 . The modern sample, for which both $\Delta 47$ and $\delta^{18}\text{O}$ fractionation between calcite and drip water can be measured, lies far from thermodynamic equilibrium. For older samples, calcite/water isotopic fractionation was reconstructed using a new fluid inclusion technique (Vanhof et al., in prep.). According to these measurements, all older samples also precipitated far from equilibrium. On this graph, according to Guo et al. (in prep.), kinetic isotope effects due to degassing will be parallel to the direction plotted in grey. If corrected for such an effect, data for the modern sample is entirely consistent with the observed modern temperature and $\delta^{18}\text{O}$, and older samples yield realistic temperatures (in contrast with previous, uncorrected errors in excess of 10°C).