

## Resolving the opal paradox in the glacial Eastern Equatorial Pacific: Implications for the biological pump of Carbon

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The modern Eastern Equatorial Pacific (EEP) is a major oceanic source of carbon to the atmosphere and could have potentially played a key role in lowering CO<sub>2</sub> levels during glacial times. However, available records of nutrient supply, carbon export and opal accumulation from the EEP show contradictory trends over the last glacial cycles and hence the efficiency of the biological pump in the area and its role in glacial CO<sub>2</sub> draw down remains unclear. Here we report a new silicon isotope record that explains the low opal accumulation during glacial times in the EEP. It allows us to propose a new model which reconciles existing records of glacial-interglacial variability in upwelling intensity, nutrient availability, carbon productivity and opal accumulation from the EEP. Specifically, we suggest that the paradoxically low opal accumulation rates in the glacial EEP is a result of the alleviation of iron limitation during the dustier glacial periods and the consequent decrease in Si:C uptake ratio by diatoms, and does not reflect a decline in rain rate ratio and biological CO<sub>2</sub> pump as suggested previously. Therefore, we argue that the EEP could have been an important contributor for the reduced atmospheric P<sub>CO2</sub> during glacial periods.

## Two high resolution snap shots of Pliocene climate change from U-Pb dated South Africa speleothems

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The Plio-Pleistocene locality of Cooper's D (South Africa) has produced a large fossil faunal assemblage, including several hominin specimens. Beneath and in between the fossil bearing sediments are well preserved speleothems. These speleothem layers are crucial in understanding this site: direct age determinations using MC-ICP-MS U-Pb dating can constrain the chronology of the hominins and stable light isotopes analysis can provide insights into the palaeoenvironments in which our early human ancestors lived.

For U-Pb dating of such young speleothems to be possible, U concentrations must be at least ~1ppm. U is not evenly distributed throughout speleothems and samples are pre-screened using a  $\beta$ -scanner. Once U-rich layers are identified, sub samples, typically <1cm<sup>2</sup>, are cut out and prepared using standard ion exchange chemistry. U and Pb isotopes are measured with a Nu-Instruments MC-ICP-MS.

Two 3-4 cm pieces from the base of both dated stalagmites were micro-milled at 0.5mm spacing and analysed for carbon and oxygen isotopes. The  $\delta^{18}\text{O}$  values range from -6.00 to -3.00 ‰ (VPDB). The oxygen isotope curve for both samples can be related to distinct growth horizons within the stalagmites. These layers are whiter in colour than the surrounding material and also more calcitic. The combination of enriched  $\delta^{18}\text{O}$  and calcite suggests that these were more arid periods. The interceding periods, more aragonitic in nature with more negative (depleted)  $\delta^{18}\text{O}$  values would therefore relate to wetter, possibly warmer periods. One of these more depleted layers is also rich in U, which may result from slow weathering of bedrock, with reduced leaching, in the preceding arid phase. The carbon isotope curves are more complex, recording high frequency and large changes in  $\delta^{13}\text{C}$  from -6.00 to 1.00 ‰ (VPDB). The composition of vegetation above the cave, with varying amounts of C4 type plants, must contribute heavily towards the C signal and can broadly be correlated to more arid or moist phases.

The mechanism behind these shifts and their timing is not immediately clear and a number of possibilities explored.