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Triple oxygen isotopes in eggshell carbonate as a proxy of late Cenozoic CO_2 and primary productivity.

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The triple oxygen isotope composition of biominerals is a promising recorder of changes in global primary productivity (GPP), CO_2, as well as environmental and physiological influences. However, its application remains largely unexplored, particularly in regions where eggshell carbonate is a common component of Late Cenozoic paleontological and archaeological sites. Ratites (ostriches and their relatives), as nonobligate drinkers, derive most of their oxygen from atmospheric O_2 and leaves, meaning that their eggshell should strongly reflect the anomalous $\Delta'^{17}O$ signature of atmospheric O_2—ultimately linked to GPP and CO_2 levels. In this study, we ground-truth the relationship between GPP:CO_2 ratios and atmospheric $\Delta'^{17}O$ (O_2) by analyzing modern and Last Glacial Maximum (LGM) eggshells from southern Africa. We extend this approach to reconstruct GPP during the Middle and Late Miocene, leveraging an existing animal body water model that we refine using Bayesian inverse methods. We used two different methods to determine the triple oxygen isotope composition of CO_2 from eggshell: (1) Tunable Infrared Laser Direct Absorption Spectroscopy (TILDAS), and (2) sequential conversion of CO_2 to O_2 by reduction/fluorination, followed by extended-collection-time dual-inlet IRMS, anchoring carbonates to the VSMOW-SLAP scale using a two-point normalization based on the triple oxygen isotope composition of both NBS18 and IAEA603.

Our results indicate that the predominant signal in the triple isotopic composition of biomineral carbonate reflects global carbon cycling (i.e., the GPP:CO_2 ratio), suggesting that a widely available material can be used to reconstruct planetary primary productivity beyond the ice core record. We find that Middle Miocene GPP was significantly lower than today at 95% confidence. Comparison with a box-model of the atmospheric O_2 budget suggests that GPP levels during the Middle Miocene fell below 60% of modern values, assuming contemporaneous CO_2 levels of 441–472 ppm (95% confidence). These findings have potentially important implications for understanding past and future climate change. However, the inferred GPP level is somewhat dependent on the values of NBS18 and IAEA603 chosen to anchor our carbonates to the VSMOW-SLAP scale, as well as the range of plausible Middle Miocene CO_2 levels – uncertainties which are discussed.