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Unravelling the Gordian's knot of bulk carbonates – The Lake Van example

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Bulk carbonate oxygen and carbon isotope ($\delta^{18}O$ and $\delta^{13}C$) analysis is a commonly applied analytical method in palaeolimnology. However, in some cases interpretation of the isotopic signal of bulk carbonates, is far from straightforward when relying on traditional approaches. In case of terminal, alkaline Lake Van, positive bulk $\delta^{18}O$ values appear in both, cold arid periods such as the Younger Dryas and in warm wet periods such as the Last Interglacial (MIS 5e). Taking a systematic approach and applying XRD, SEM imaging and isotope mass spectrometry we found that Lake Van´s carbonate inventory consists of various primary and secondary phases, each characterised by isotopic signals reflecting the differences of their origin. Next to primary inorganic carbonates precipitating within the surface water (aragonite and low-Mg calcite) and benthic biogenic carbonates (ostracods), sediments contain early diagenetic dolomite, and, likely microbially-related, aragonite encrustations of organic remains and ostracod valves.

Here we focus on the isotopic composition of the inorganic and biogenic primary carbonates of Lake Van and their respective applications as proxies for palaeohydrology (e.g., palaeosalinity). Our interval of interest covers the last glacial/interglacial period, ca. 150 kyr. Inorganic (< 63 μm) and biogenic (> 63 μm) carbonates were isolated by wet-sieving. Samples containing diagenetic dolomite (strongly influencing bulk isotopic composition) were excluded from the study.

The apparent inconsistencies of the bulk isotope record are primarily controlled by variations in the aragonite/calcite ratio. Aragonite is enriched in ^{18}O and ^{13}C relative to calcite, yet, the differences in aragonite-water and calcite-water fractionation factors alone are minor, and insufficient in explaining changes observed in the amplitude of the $\delta^{18}O$ and $\delta^{13}C$ signals in the Lake Van profile. It seems likely, that aragonite and calcite particles forming the bulk sediment precipitated under different geochemical conditions (spring versus summer) inheriting differing isotopic compositions. This is of particular importance as many studies account only for differences in isotopic fractionation between aragonite and calcite ignoring processes which favour the precipitating polymorph.

Biogenic carbonates (ostracod valves) are present in most samples, but due to negligible volume they do not influence the bulk record. We performed geochemical ($\delta^{18}O$ and $\delta^{13}C$), taxonomic and morphological analysis on the valves in order to trace changes in deep water chemistry. Next, we compared these data with published ICDP PALEOVAN records. The genus *Candona* occurs only during intervals of low salinity. Valves of the species *Limnocythere inopinata* occurring throughout the record display hollow protrusions ("nodes") during intervals of increased salinity. Both, the amount of noded valves as well as the number of nodes per valve appears to increase with increasing salinity, suggesting that these morphological changes are related to the changes in palaeohydrology. Ostracod $\delta^{18}O$ and $\delta^{13}C$ are both ca. 1 ‰ heavier within Last Glacial (low stand) than Holocene (high stand) sediments, indicating a sensibility toward lake level changes.

Comparing signals from inorganic (surface) and biogenic (bottom water) carbonates allows a detailed and comprehensive insight into palaeohydrology, allowing for singling out seasonal changes.