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Evidence of lighter ocean during ~1.8 Ga ago from Clumped and stable isotope ratios in carbonate and chert

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Clumped-Isotope-Thermometry on dolomite and $\delta^{18}O$ signature in associated chert from Paleoproterozoic Vempalle formation exposed near the south-western margin of Cuddapah basin, eastern Dharwar revealed environment for the proliferation of microbial mat. Previous studies documented the presence of stromatolite layers in the sedimentary sequence, suggesting early organic evolution of life in an isolated basin within a marine setting. The stromatolitic layer is characterized by lamination comprising an alternate display of dolomite and chert, with frequent gypsum-lamina[1].

Sedimentological studies and isotopic compositions suggest the deposition of this sequence on a carbonate-ramp with varying contributions of hydrothermal-fluid and siliciclastic/terrigenous sediments[1]. The frequent occurrence of gypsum layers in cherty-dolostone indicates the desiccation of a sea with variable hydrothermal input.

Drill-core samples are utilized to confirm the outcrop-based observation and verify the record in subsurface undisturbed lithologies. The set of samples is further analyzed for trace-element concentration to draw a relationship with fluid temperature and distribution of elements like Li, Al, Mg, and Ca.

The $\delta^{13}C_{Carb}$ varies from -0.34‰(VPDB) to 0.59‰(VPDB), which is consistent with the global record of marine-carbonates analyzed from Paleoproterozoic sediments. The $\delta^{18}O_{Carb}$ is lighter with a range of values from -9.1‰(VPDB) to -5.5‰ (VPDB). The clumped-isotope-based temperature estimates for these carbonates (26 samples) showed a bimodal-distribution with two major clusters having a range in temperature values between 13-79ºC(7 samples) and 79-140 ºC(16 samples). A few showed very high-temperature values from 145-230ºC(3 samples). The $\delta^{18}O_{Water}$ responsible for the precipitation of carbonates of lower and higher temperature populations ranges from -11.4‰ to -3‰(VSMOW) and -3‰ to 5.2‰(VSMOW), respectively. The isotopic signature recorded in the sample showed variable evaporation-precipitation conditions, with heavier composition suggesting the presence of hydrothermal-water, which is further confirmed by their higher abundance of Li and Pb. The $\delta^{18}O_{Chert}$ varies from 12.59‰(VSMOW) to 17.3‰(VSMOW) with a lighter composition reflecting higher temperature confirming variable hydrothermal input during the formation of chert. The temperature obtained from $\delta^{18}O_{Chert}$ at equilibrium conditions, assuming lighter water-composition deduced from clumped-isotope measurement, varies between 38-63ºC, which lies within the range of expected values[2] during chert precipitation.

References:

1. *Banerjee et al.,2023;Chemical Geology*,*621*,121356.

2. Marin et al.,2010;Geochimica et Cosmochimica Acta,74(1),116-130.