Geochemical and $^{87}Sr/^{86}Sr$ and $\delta^{44/40}Ca$ Compositions of Ediacaran Carbonates from the Indian Shield: Understanding Preservation of Local versus Global Biogeochemical Signatures during Periods of Extreme Environmental Changes

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Abstract

The Neoproterozoic Era represents extreme environmental conditions with three major glaciation events. Associated with these glaciation and deglaciation periods are high amplitude positive and negative $\delta^{13}C$ excursions which have been observed in the rock records, suggesting perturbations in oceanic biogeochemical cycles. However, whether these isotopic records reflect primary depositional signature and open ocean condition are debated. The Marwar Basin of the Indian Shield preserves one such record of the Ediacaran time period. The magnitude of negative $\delta^{13}C$ excursion from the Marwar Basin is comparable with the Shuram excursion.[1] We report elemental compositions of sixty-eight carbonate samples collected from five spatially distributed sections from the Bilara carbonates of the Marwar Basin. Selected samples from two of these sections were analyzed for their radiogenic Sr ($^{87}Sr/^{86}Sr$) and stable Ca ($\delta^{44/40}Ca$) isotopic compositions. Elemental compositions were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, X series II) while $^{87}Sr/^{86}Sr$ and $\delta^{44/40}Ca$ (reported relative to NIST SRM 915a) values were measured using a Thermal Ionization Mass Spectrometer (TIMS, Triton Plus), both at the CEaS, IISc Bangalore, India. The Bilara Group carbonates are sub-divided into two populations based on non-redox REY anomalies and the Y/Ho ratio. Super-Chondritic Y/Ho (40-52) and positive La anomaly (1.01-2.65) of some samples suggest deposition under open ocean conditions and connectivity to the global ocean. While heterogeneity in $\delta^{13}C$ values is evident in samples with low Y/Ho (<40), samples with high Y/Ho (> 40) preserve low $\delta^{13}C$ values. No significant correlation has been observed between $\delta^{13}C$ and Ce anomaly (Ce/Ce*) suggesting absence of any paleo-redox gradient. The lowest $^{87}Sr/^{86}Sr$ (˜0.7079) observed in the carbonates is comparable with Ediacaran seawater confirming retention of primary depositional signatures in these samples. These carbonates show heavy $\delta^{44/40}Ca_{SRM915a}$ compositions (1.44successions[2]. Our study confirms primary origin and open ocean nature of the late Neoproterozoic $\delta^{13}C$ excursions in the Marwar Basin. [1] Ansari et al., (2018) Precambrian Research, [2] Silva-Tamayo et al., (2010) Precambrian Research

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1. Introduction

- The Neoproterozoic era represents extreme environmental changes with major glaciation and deglaciation events
- Associated with these glaciation and deglaciation periods are high amplitude positive and negative $\delta^{13}C$ excursions which have been observed in the rock records, suggesting perturbations in oceanic biogeochemical cycles. However, whether these isotopic records reflect primary depositional signature and open ocean condition are debated
- This study focuses on the geochemistry, radiogenic Nd-Sr and stable Ca isotope composition of carbonates from the Marwar Basin of the Indian Shield (Fig.1)
- The magnitude of negative $\delta^{13}C$ excursion from the Marwar Basin carbonates is comparable with the Shuram excursion

> - What was the extent of connectivity of the Marwar Basin to the global open ocean?
> - Do the Marwar carbonates reflect primary depositional signature?
> - What are the possible mechanisms behind anomalous Neoproterozoic Ca isotope cycle?

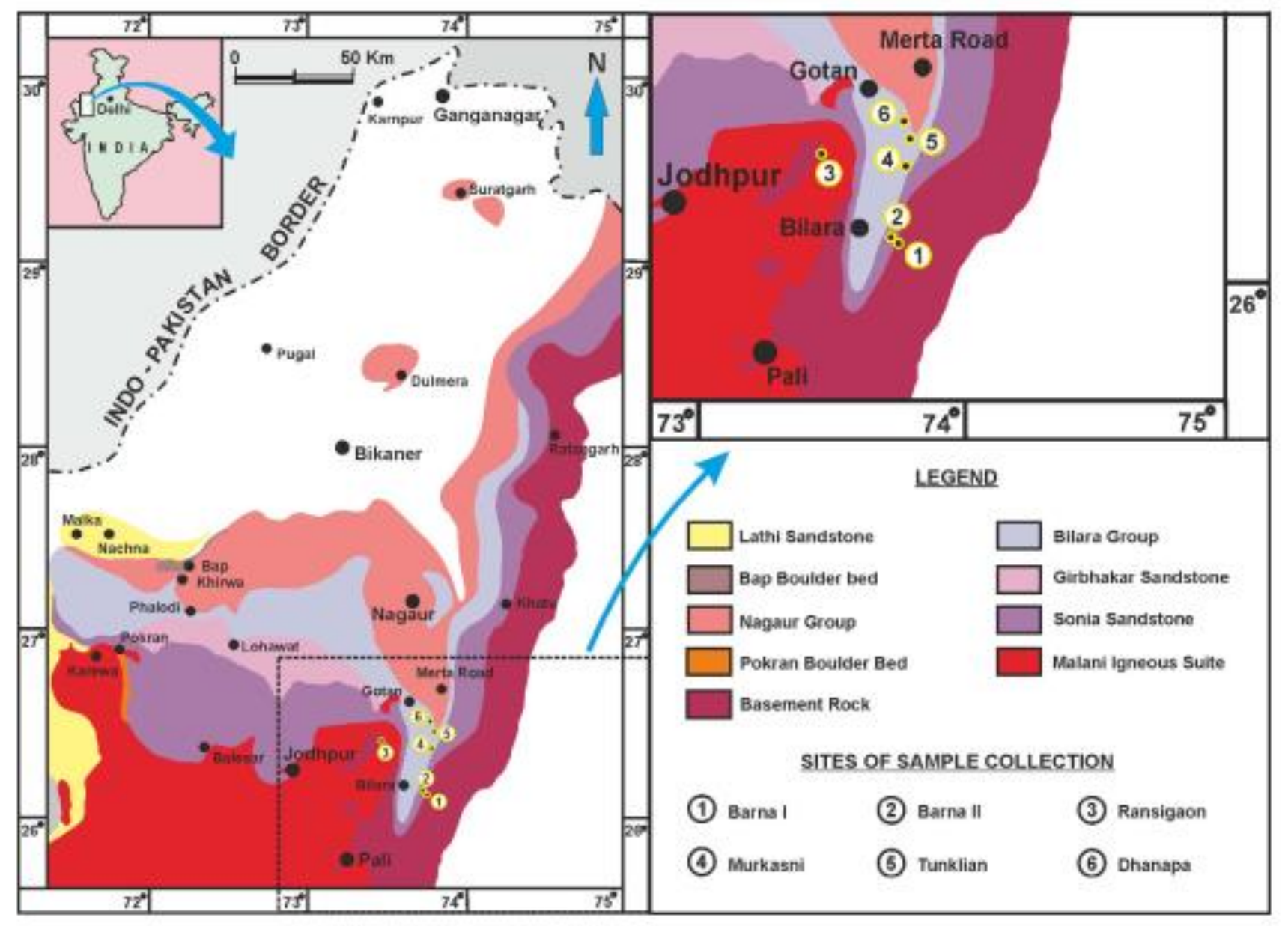
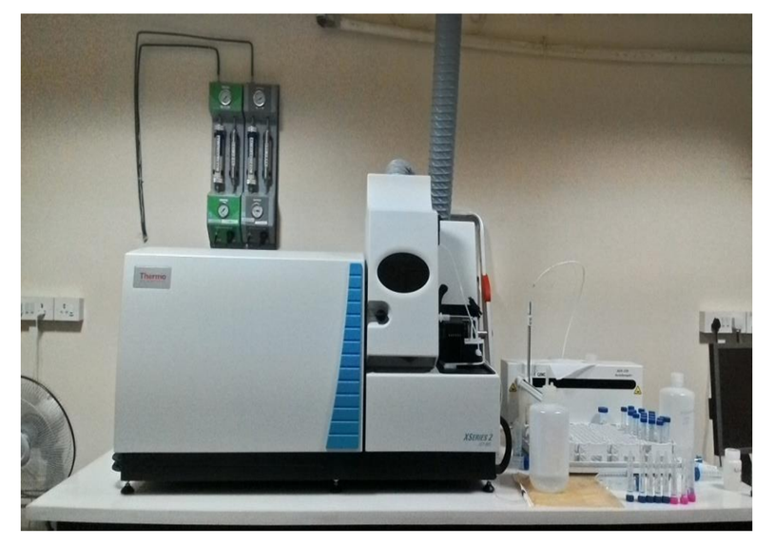


Fig: 1: A generalized geological map of the study area Marwar Basin of the Indian Shield (after Ansari et al., 2018) showing the sample locations

This study presents geochemical, radiogenic Nd-Sr, and stable Ca isotope data of Bilara Group of carbonates from the Marwar Basin of the Indian Shield

2. Analytical techniques



- Elemental concentrations were measured using Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Thermo Scientific, X Series II) at the Centre for Earth Sciences (CEaS), IISc.
- Nd isotopic ratios were measured using a Thermal Ionization Mass Spectrometer (TIMS, Triton Plus) at CEaS, IISc following established protocols.[10]

3. Results and Discussion

Marwar Basin: A shuram excursion site

Fig.2: Representative field occurrence of Bilara Group carbonates from the Marwar Basin, Indian Shield (Ansari et al., 2018)

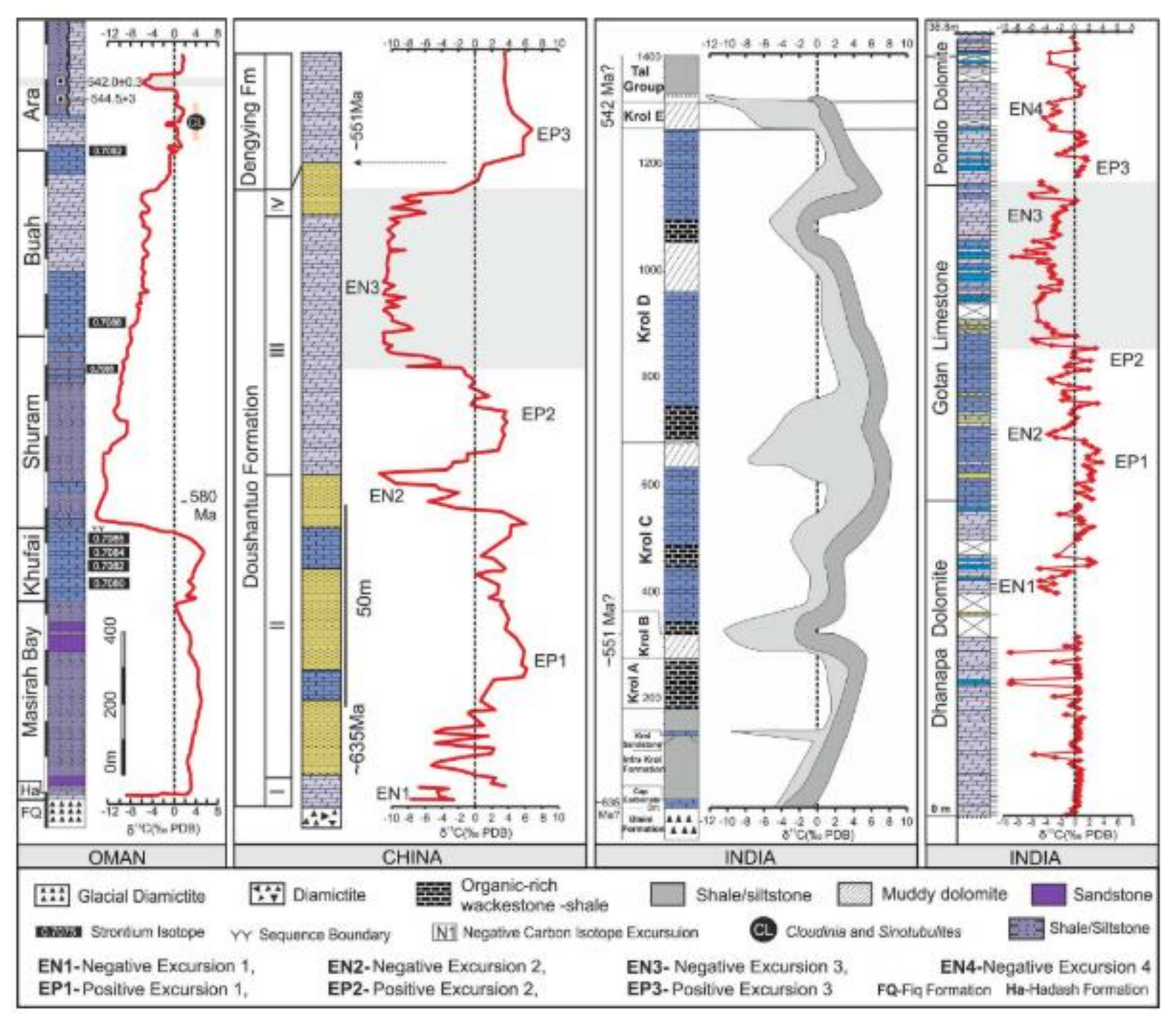


Fig. 3: The magnitude of negative $\delta^{13}C$ excursion from the Marwar Basin is comparable with other Shuram excursion sites (Ansari et al., 2018)

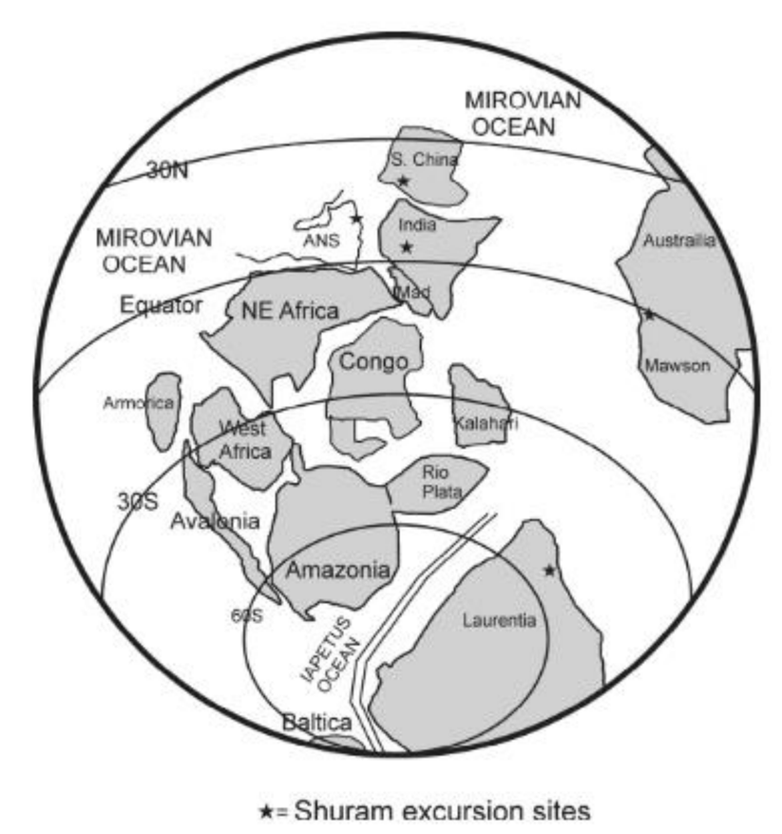


Fig.4. Paleogeographic map showing distribution of landmass around 565 Ma and Shuram excursion sites (After Meert and Lieberman, 2008, Ansari et al., 2018)

Does the Marwar carbonates reflect open ocean condition?

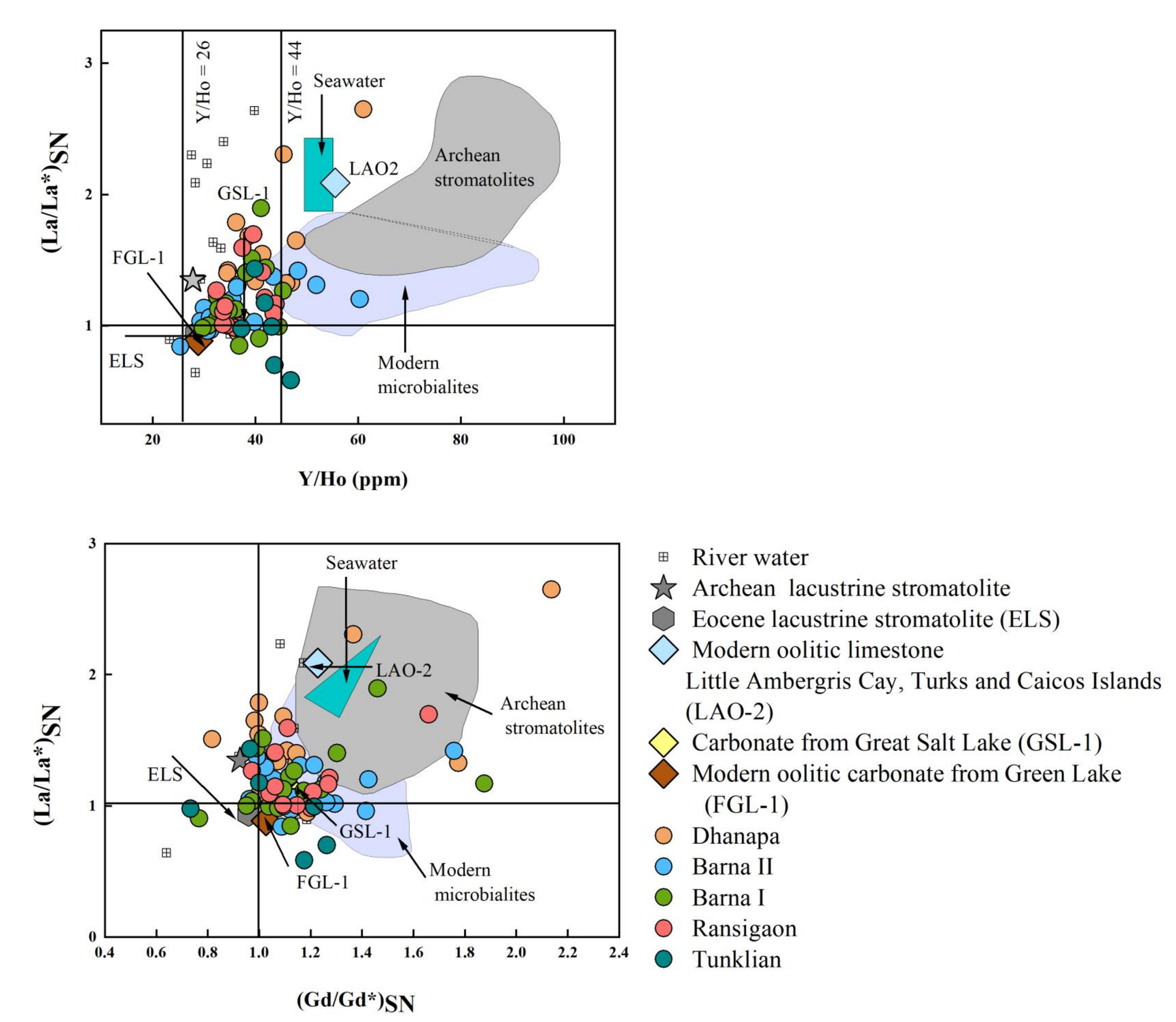


Fig.5: Analysis of sixty-eight carbonate samples from five locations of the Marwar Basin show presence of Y/Ho> 40 and positive La , Gd anomaly (La/La, Gd/Gd*) >1 suggesting open ocean condition*

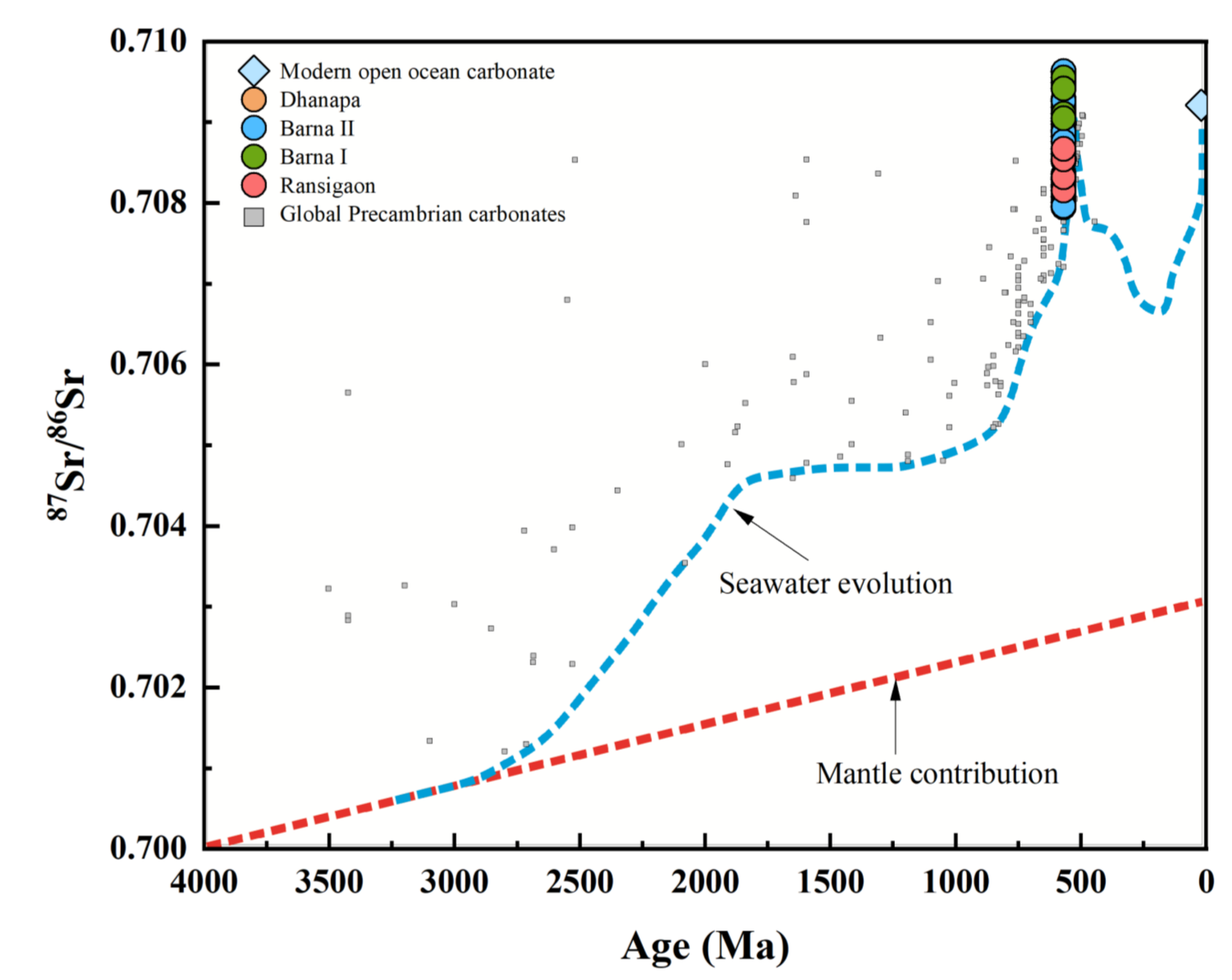


Fig. 6: $^{87}Sr/^{86}Sr$ composition of Marwar carbonates are similar to contemporaneous seawater suggesting connectivity to the open ocean

- REY signature and Sr isotopic composition of Marwar carbonates suggests connectivity to the open ocean

$\delta^{13}C$ variation in the Marwar Basin

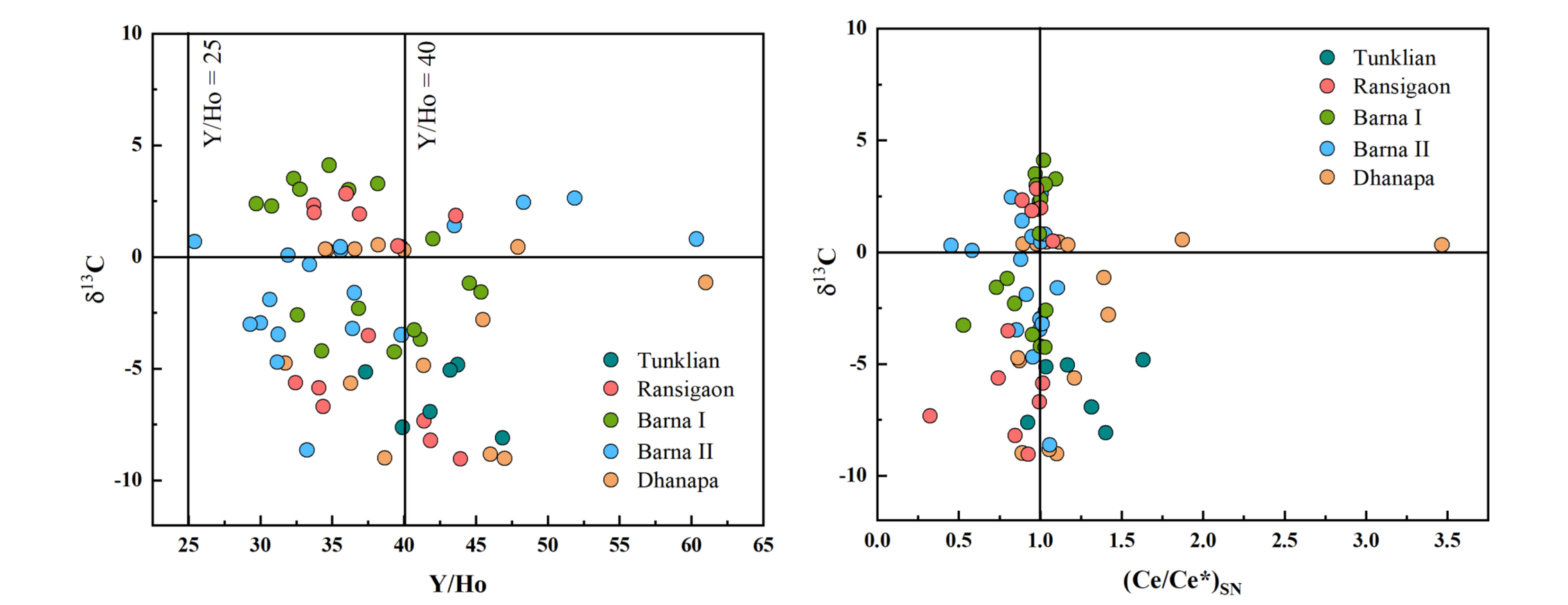


Fig. 7: $\delta^{13}C$ vs. Y/Ho and $\delta^{13}C$ vs. Ce/Ce plot of Marwar carbonates. $\delta^{13}C$ composition less than -7 ‰ has been observed in samples with Y/Ho>40 confirming global open nature of the Shuram excursion event. $\delta^{13}C$ composition do not show any variation with Ce anomaly confirming absence of any paleo-gradient in the Marwar Basin*

- The co-variation between REY and $\delta^{13}C$ composition confirm high amplitude negative $\delta^{13}C$ excursion in the Marwar Basin reflects open ocean condition

$\delta^{44/40}Ca$ composition of the Marwar carbonates: Signature of a post-glacial ocean?

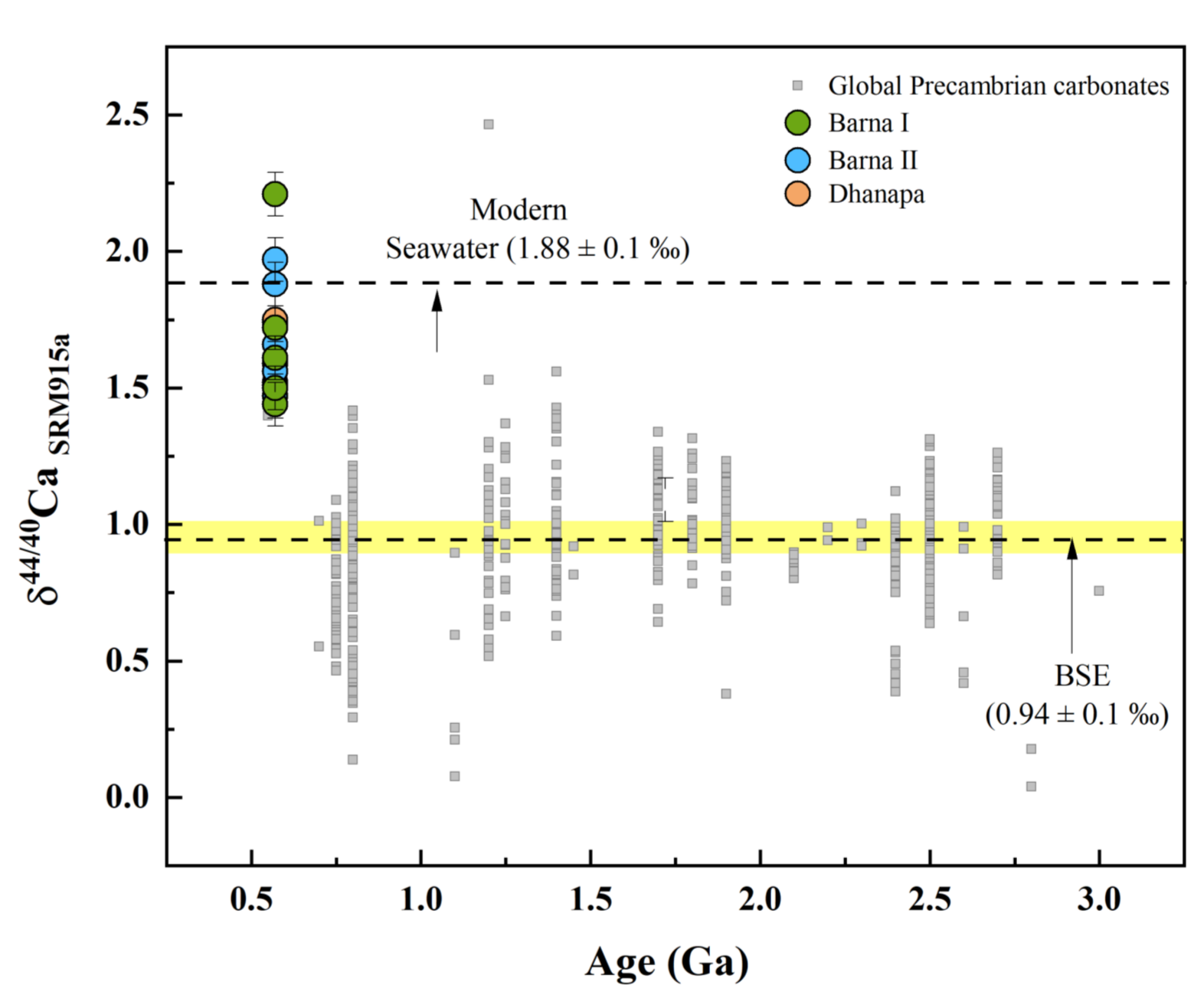
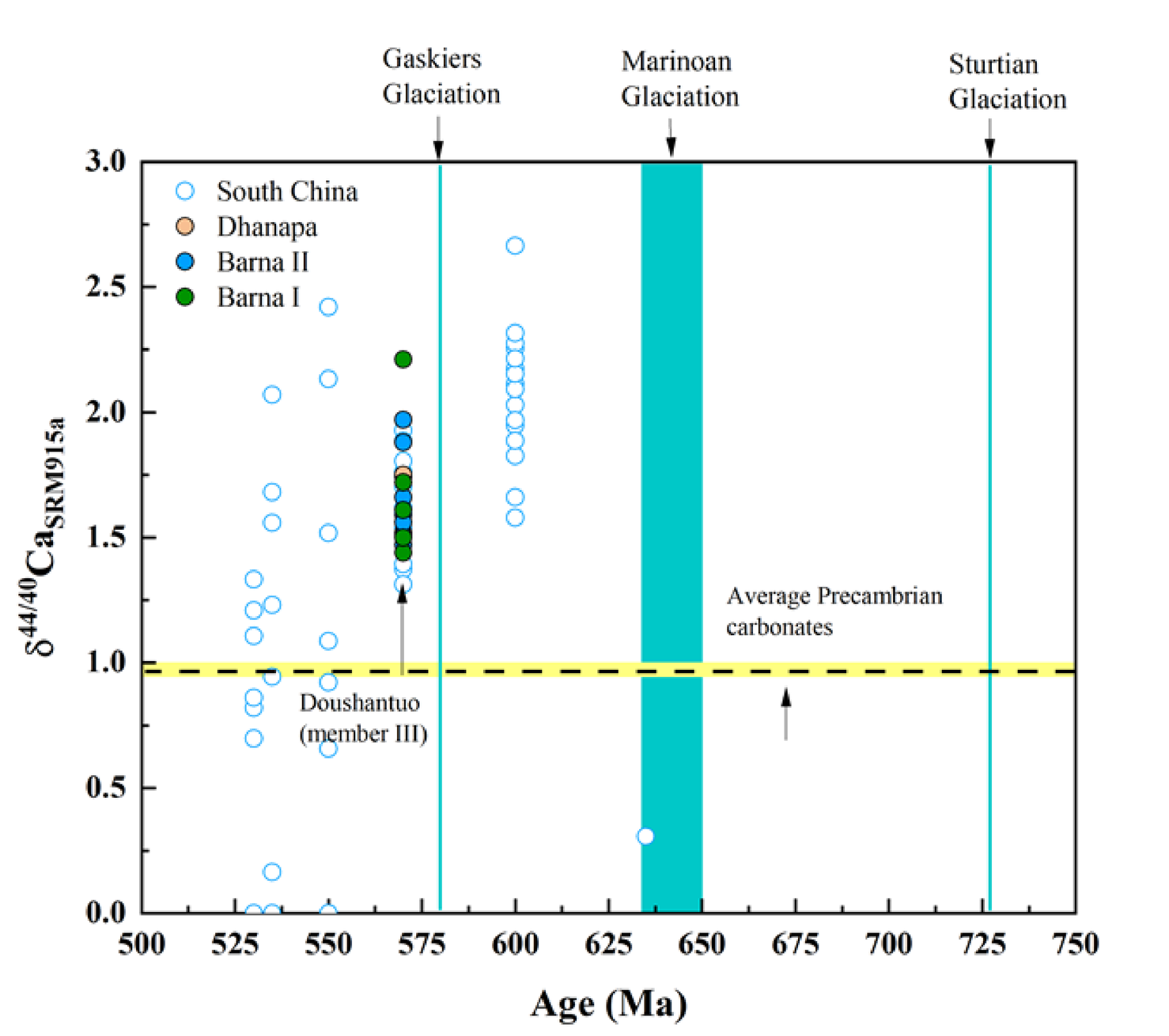


Fig. 8: Marwar carbonates show anomalously high $\delta^{44/40}Ca$ composition



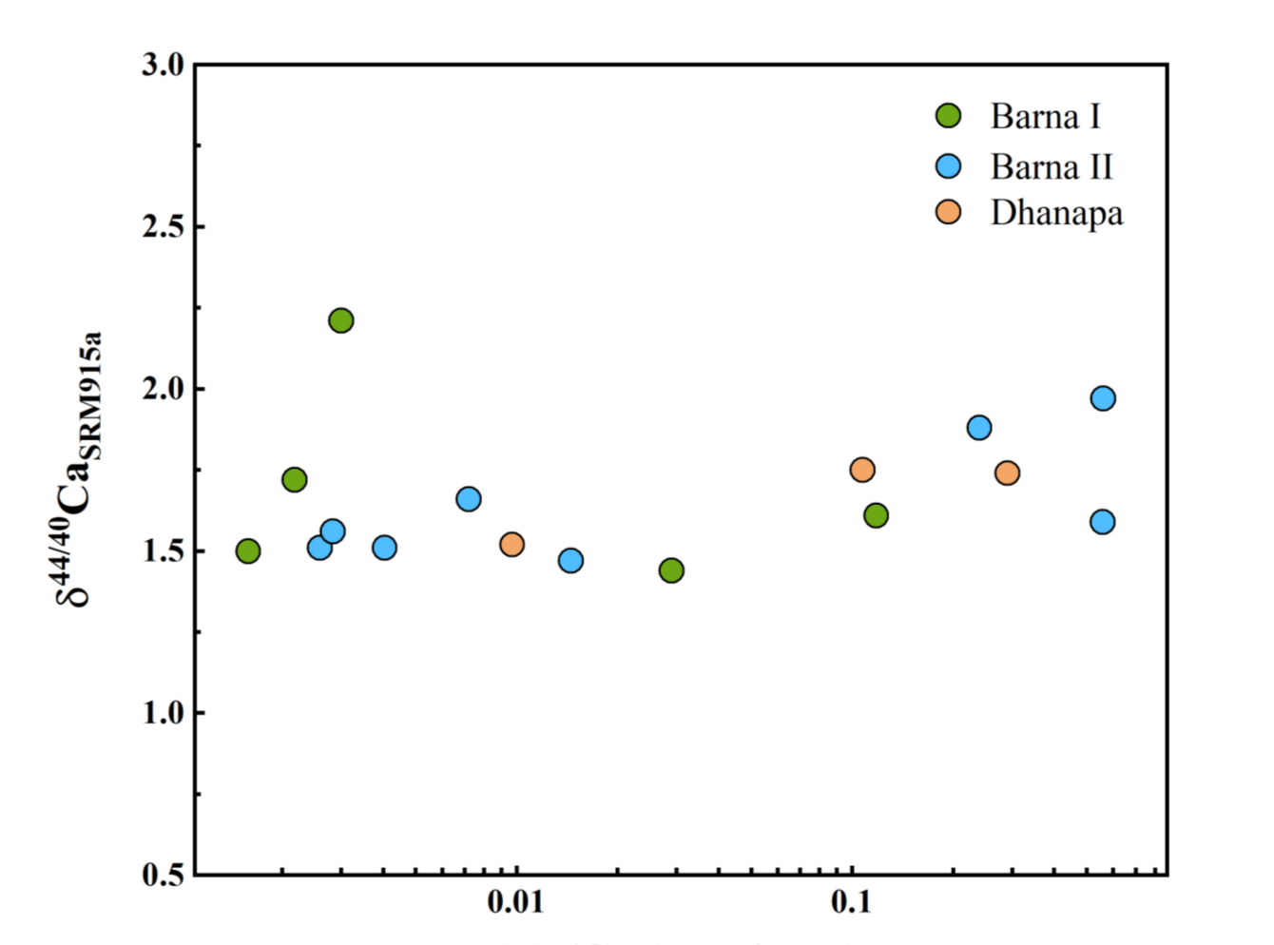


Fig. 9: $\delta^{44/40}Ca$ composition of Marwar carbonates do not show significant variation with Mg/Ca ratio indicating minerology is not the controlling factor

- Very high $\delta^{44/40}Ca$ composition (1.44-2.21‰) of Marwar carbonates are similar to Doushantuo Formation, South China (Sawaki et al., 2018)
- High amount of calcium carbonate precipitation in the aftermath of Neoproterozoic glaciation possibly led to observed heavy $\delta^{44/40}Ca$ composition

Nd isotope evidence of post-glacial water-mass mixing

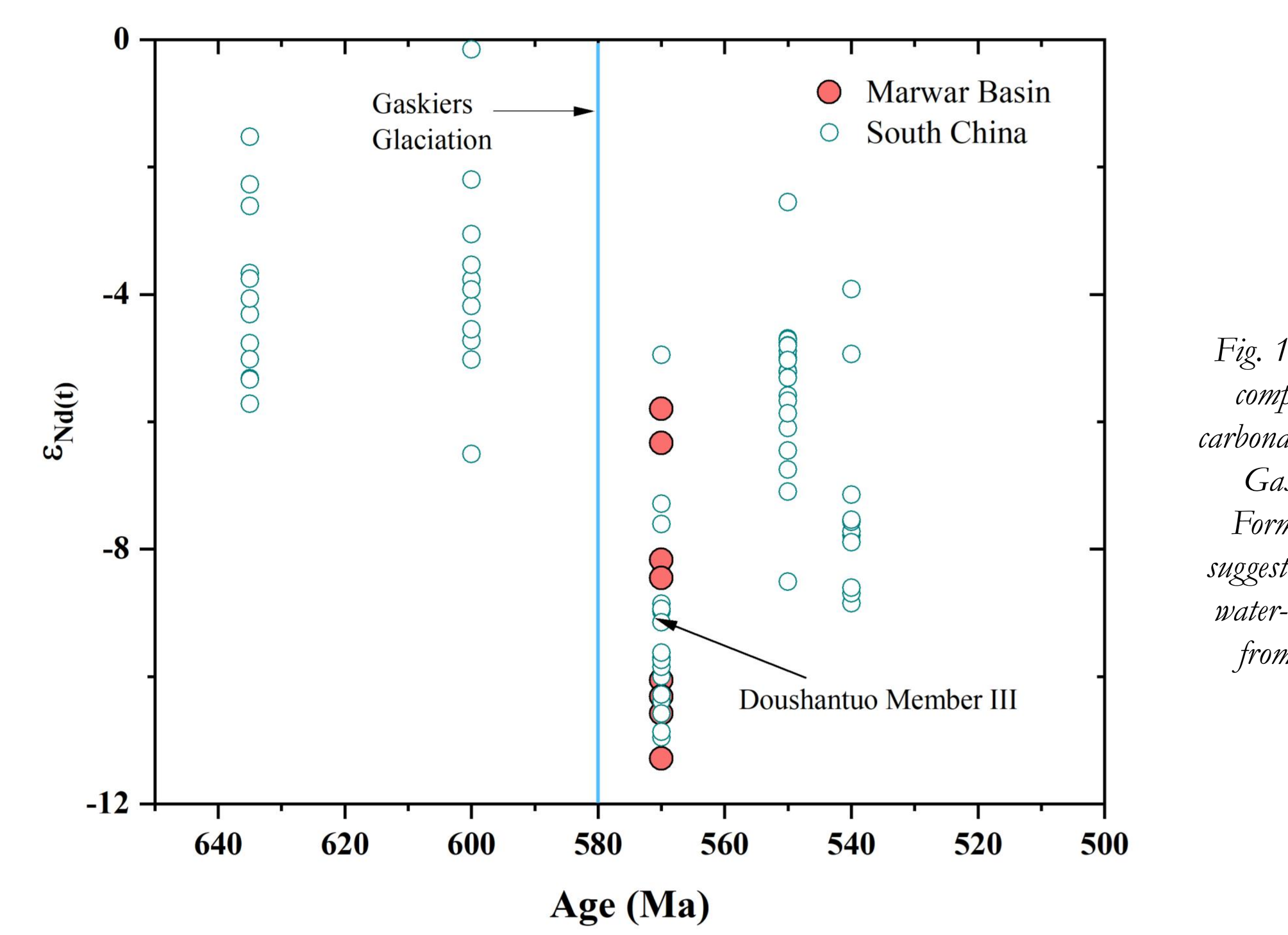


Fig. 11: Initial Nd isotope composition of Marwar carbonates are similar to post-Gaskiers Doushantuo Formation (member III) suggesting connectivity of the water-mass (S. China data from Wei et al., 2020)

- Initial Nd isotope composition of Marwar carbonates of the Indian Shield show similarity with post-Gaskiers Doushantuo Formation (member III) suggesting water-mass mixing
- Paleogeographic reconstruction during the Ediacaran show India to be of closer proximity with S. China further supporting post-glacial water-mass mixing

4. Conclusion

- The REY and Sr isotope systematics confirm primary and open ocean nature of the high amplitude negative C isotope excursion observed in the Marwar carbonates
- High amount of calcium carbonate precipitation led to observed anomalously high $\delta^{44/40}Ca$ composition of Marwar and Doushantuo (S. China) carbonates
- Initial Nd isotope composition of Marwar and Doushantuo (member III) carbonates show similar values suggesting water-mass mixing

References: 1.Ansari et al., 2018; 2.Basu et al., 2021; 3.Shields and Veizer, 2002; 4. Blattler and Higgins 2017; 5. Sawaki et al., 2018; 6. Wei et al., 2020