



Reconstructing past seawater $\delta^{88/86}\text{Sr}$ from calcium-sulfates (gypsum and anhydrite)

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Records of the stable-Sr isotope composition of past seawater, $\delta^{88/86}\text{Sr}_{\text{sw}}$, have recently been demonstrated to be good proxies for the evolution of the marine 'carbonate factory', the ultimate sink of carbon from the ocean-atmosphere system [e.g., 1-3]. Nevertheless, these records are incomplete, and they generally do not overlap in age. Thus, despite their proven significance, these records have not been validated by data from any independent archives. The Ca-sulfate minerals, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and its burial transformation product, anhydrite (CaSO_4), are relatively abundant in ancient evaporitic sequences and they contain Sr in typically high concentrations of 1000-2000 ppm. In a previous study, we show that gypsum is always ^{88}Sr -enriched relative to its precipitating solution by around 0.2‰ and that it is possible to detect significant variations in past $\delta^{88/86}\text{Sr}_{\text{sw}}$ ($\geq 0.1\text{‰}$) from ancient gypsum/anhydrite samples from the geological record.

Here, we study Phanerozoic Ca-sulfate samples of four different ages: Ordovician, Triassic, Cretaceous, and Messinian. Preliminary $\delta^{88/86}\text{Sr}$ results are in the range of 0.29 – 0.67‰. Most of the results cluster between the calculated gypsum composition expected for the two known extreme cases of seawater $\delta^{88/86}\text{Sr}$ values inferred from Ca-carbonate archives: the high- $\delta^{88/86}\text{Sr}$ Precambrian seawater [3], and Late Permian seawater - the Phanerozoic minimum [2]. Thus, our preliminary Phanerozoic data are generally in accordance with the suggestion that the long-term Precambrian seawater $\delta^{88/86}\text{Sr}$ is higher than the Phanerozoic long-term background [3]. Furthermore, our preliminary data point to significant seawater $\delta^{88/86}\text{Sr}$ variations during the Phanerozoic, with lower values in the Ordovician and Triassic relative to Cretaceous and Messinian samples. Such variations may suggest major changes in the 'carbonate factory' in the ocean between the Triassic and Cretaceous. It is further suggested that such variations in the mineralogy and/or flux of marine carbonates may result from evolutionary changes in marine calcifiers.

[1] Paytan et al. (2021) A 35-million-year record of seawater stable Sr isotopes reveals a fluctuating

global carbon cycle. *Science* 371(6536), 1346-1350.

[2] Vollstaedt et al. (2014) The Phanerozoic $\delta^{88/86}\text{Sr}$ record of seawater: New constraints on past changes in oceanic carbonate fluxes. *Geochim. Cosmochim. Acta* 128, 249–265.

[3] Wang et al. (2023) The evolution of the marine carbonate factory. *Nature*, 1-5.

[4] Kirichenko et al. (n.d.), First Insights into Strontium Isotope Fractionation in Gypsum and Its Geochemical Implications. Under review in *Geochim. Cosmochim. Acta*.