

## Sr isotopes ( $\delta^{88/86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ) in cold seep environment of Niger and Nile Delta Fans

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In cold seep areas, carbonates form as a result of the anaerobic oxidation of methane, which increases alkalinity in pore waters. Upon formation, cold seep carbonates incorporate dissolved alkali earth elements, such as Ca and Sr. The Ca and Sr isotopic compositions of authigenic carbonates and associated pore waters can hence provide information into fluid sources and biogeochemical processes at cold seeps. Over the last decades, radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in sediment interstitial fluids have been used for identifying deep fluid sources in seepage areas. However, recent studies have demonstrated that significant fractionation of stable Sr isotopes can occur in marine carbonates, which led to a revisited view of the oceanic budget [1].

Here, we report paired  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88/86}\text{Sr}$  values on a series of authigenic carbonate crusts and associated pore waters from fluid seepage areas of the Niger and Nile deep-sea fans. Sr isotopes were measured on a Neptune MC-ICP-MS using Zr for mass bias correction to acquire simultaneously radiogenic and stable ( $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88/86}\text{Sr}$ ) values [2, 3]. Our results indicate that  $\delta^{88/86}\text{Sr}$  values for most carbonate samples exhibit very small fractionation relative to seawater or pore water signatures, contrary to biogenic carbonates that shows a 0.1‰/amu lower than seawater [1]. Exceptions are found for a few samples collected from mud volcano settings, which are characterized by distinctively low  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\delta^{88/86}\text{Sr}$  values. We will discuss the Sr isotope systematics in comparison with other proxies.

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## What role did methane seeps play in the formation of the Doushantuo cap carbonate?

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Extremely negative  $\delta^{13}\text{C}_{\text{carb}}$  values, less than -30‰, have been reported for the cap carbonate of the Ediacaran Doushantuo Formation (ca. 635 Ma) and used to support the hypothesis that methane hydrate destabilization contributed significantly to formation of the enigmatic cap carbonate and negative carbon isotope anomalies following Neoproterozoic ice ages (1, 2). Here, we show distinct differences between the methane-related carbonate and bulk cap carbonate.

Negative  $\delta^{13}\text{C}_{\text{carb}}$  values of <-30‰ obtained from isopachous cements and recrystallized carbonate crusts have been found only in the Yangtze Gorges area (YGA), South China. These microsamples were reported from secondary, pore-filling carbonate minerals tied to methane seep activity, rather than reflecting the bulk composition of the cap carbonate. We investigated the Doushantuo cap carbonate at three localities, the Jiulongwan (inner-shelf, YGA), Zhongling (outer-shelf), and Long'e (basin) sections, and find that the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values for the cap vary from -2‰ to -10‰ and -5‰ to -12‰, respectively, and show a positive  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  correlation, with a negative trend from the shallow to deep sites. Interestingly, all the microsampled  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data from the methane-seep sections in the YGA (1, 2) show two distinct trends in the  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  cross-plot, a positive correlation the same as the bulk cap carbonate and negative correlation attributed to methane oxidation. Similar to the Upper-Cretaceous Tepee Buttes in Colorado (3), the latter shows a nice relationship from early to late diagenetic carbonate phases – starting with very light, methane-dominated carbon.

We conclude that the methane-related carbonate can be distinguished clearly from the bulk Doushantuo cap carbonate by coupled C and O isotopes.

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