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### REE in Neoproterozoic phosphorite and dolomite from South China: Implications for paleoenvironmental change

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The earliest metazoan fossils and large amount small shell fossils occurred respectively in the basal upper unit of the Weng'an phosphorite deposit, Neoproterozoic Doushantuo Fm (DST) and in the phosphorite of the basal Cambrian Meishucun Fm (MSC). We analyzed the REE as well as stable isotopes of samples from the DST, Dengying (DY) and MSC Fms, in Guizhou, SW China, in an attempt to trace the paleoenvironment change. Phosphorite, dolomite and shale are dissolved or leached by HCl+HNO<sub>3</sub>, and some of the dolomitic phosphorite samples are leached by acetic acid and then by HCl. HF is not used to avoid REE in silicate detritus.

The phosphorite-bearing dolomitic shale from the lower unit of the Weng'an phosphorite deposit (TSD Fm) show no or minor Ce anomaly, consistent with [1]. For the upper unit, Chen et al. [1] have shown similar negative Ce anomalies and REE patterns, but our results show the Ce anomalies becoming more negative up section. In lower part of the upper unit dolomite has more negative Ce anomaly than coexisting phosphate. In the upper part of the same unit dolomite and phosphate have similar Ce anomaly. This is also the case for phosphate and dolomite of the MSC Fm. Taken together, the results show a systematic general increase in negative Ce anomaly from the Neoproterozoic TSD Fm to DY Fm and then keeping the strong negative Ce anomaly to the basal Cambrian MSC Fm (Fig.1). We argue that this trend of Ce anomaly reflects evolution of oxygen availability in the shallow water of the ocean and thus reflects oxygen increase in the atmosphere, which may have resulted in the bloom of the biosphere during the period studied.

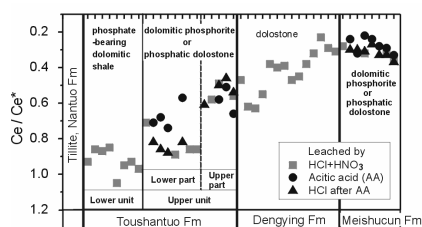


Fig.1 Ce anomaly of the TSD, DY and MSC Fms.

#### Reference

[1] Chen D.F., Dong W.Q., Qi L., Chen G.Q. Chen X.P. (2003) *Chem. Geol.* **201**, 103-118.

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### Carbonate-associated sulfate as a paleoceanographic proxy: An update

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Carbonate-associated sulfate (CAS) preserved at ppm levels within limestone and dolostone is being used with increasing frequency as a tracer for ancient seawater. Several detailed studies, including our work in South Florida, have shown that both skeletal grains and bulk mud samples faithfully record the sulfur isotope composition of overlying seawater. Primary values are observed even at a site of appreciable early diagenetic carbonate precipitation, suggesting a mass balance dominated by the initial input. A number of recent studies have confirmed the utility of CAS as a paleoceanographic proxy through comparisons to coeval evaporite data. Most recently, our data from interbedded gypsum and dolomite have extended this confirmation to platform rocks of Proterozoic age. Among the most intriguing Precambrian findings is evidence for comparatively low CAS concentrations and rapid S isotope variation, which suggest a sulfate-deficient Proterozoic ocean that mirrored the limited availability of atmospheric oxygen. However, while S isotope ratios may be buffered to primary seawater values, lower ancient CAS concentrations relative to those of modern sediments may also reflect diagenetic loss.

For more than two decades the Claypool et al. curve and analogous evaporite-based compilations have defined the paradigm for S isotope variation in marine sulfate during the Phanerozoic. These curves have historically been limited in their resolution by the lack of continuous gypsum records, and consequently, finer-scale isotopic variability in the ocean and its relationship to atmospheric oxygen have remained largely unknown. CAS, along with biogenic barite, is greatly improving the continuity of S isotope curves, with CAS permitting parallel determinations of C and Sr data from the thick cratonic carbonate sequences that pervade the geologic record. Our ongoing work is further exploring the integrity of CAS in bulk, fine-grained samples, including the importance of emphasizing pure, organic-poor lithologies. Studies of the carbonate transformations recorded in the Pleistocene Key Largo Limestone and deeper cores in Florida Bay are addressing mineralogical controls. We are also refining our ability to measure low-level CAS concentrations and CAS oxygen isotope ratios.