Stratigraphic trends in cerium anomaly in authigenic marine carbonates and phosphates: diagenetic alteration or seawater signals?

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Modern marine authigenic carbonates, barytes and phosphates incorporate seawater rare earth element (*REE*) patterns, which display an enrichment in heavy *REE* and a pronounced relative depletion in cerium (a negative cerium anomaly). The Ce anomaly relates to the decrease in solubility which accompanies the oxidation of Ce(III) to Ce(IV), while the size of the Ce anomaly may correlate with the oxidation potential, age (German and Elderfield, 1990), pH (Tricca *et al.*, 1997) and/or depth of a water body (Piepgras and Jacobsen, 1992). Several authors have attempted to use Ce anomaly to proxy ocean anoxia through time by measuring *REE* concentrations in authigenic minerals. However, all such studies have run against apparently irreconcilable problems of *early* diagenetic alteration.

Although, *late* diagenetic alteration of *REE* distributions is considered uncommon in carbonates (Banner *et al.*, 1988) due to the high fluid/rock ratios required, recycling of *REE* and reduced forms of Fe, Mn and Ce related to organic decay may reset Ce anomalies in authigenic minerals during *early* diagenesis. Elderfield and Pagett (1986) reported that although apatitic icthyoliths in marine sediments retained superficially similar *REE* patterns to seawater, those deposited in 'shallow, nearshore, anoxic sediments underlying high productivity environments' recorded positive Ce anomalies, while those from 'cores of deep ocean sediment undergoing oxic diagenesis' exhibited negative Ce anomalies. Presumably, all these icthyoliths possessed originally a seawater derived Ce anomaly. The authors conclude that authigenic minerals will only preserve a negative Ce anomaly if no suboxic or anoxic diagenesis has taken place, and this appears to have become the prevailing view among marine geochemists. However, if this is true, how can we explain the preservation of marked Ce anomalies in ancient, often sulphidic sediments and robust stratigraphic trends (data herein). It appears that these '*exceptions*' have managed to retain a seawater Ce anomaly despite the ubiquitously anoxic or suboxic nature of shallow marine diagenesis.

We report Ce anomaly and *REE* data for two separate sedimentary sections from the Neoproterozoic (Tsagaan Gol, W Mongolia) and the early Cambrian (Meishucun, Yunnan, S China). For Tsagaan Gol, calcite was measured from >95% pure limestones and for Meishucun, we measured carbonate fluorapatite from dolomitic phosphorites. Both studies reveal robust stratigraphic trends in Ce anomaly. Unlike the Elderfield and Pagett study, pronounced Ce anomalies were found in samples deposited in shallow waters, whereas those from laminated, more organic rich (also Fe, Mn, *REE* rich), deeper water samples showed little fractionation among the light *REE*. Instead of concluding that diagenesis was oxic in shallow waters and anoxic in deeper waters, we interpret this relation as suggesting the existence of redox stratification in late Precambrian/Cambrian seawater.

In the case of Tsagaan Gol, that the *REE*, Fe and Mn are really contained within the calcite phase has been confirmed by sequential leaching procedures using Königswasser, HNO_3, HCl, acetic acid and alpha-hiba reagent buffered to a pH of 4.5, which reveal no change in Ce anomaly of the leachate. Initial results of this work are published in Shields *et al.* (1997). In this presentation, we describe a second more detailed data set from Tsagaan Gol, which although based on unrelated samples from a second sampling excursion shows the same features as the first.

We argue that correlation of Ce anomaly with other primary parameters implies that trends in Ce anomaly in this study reflect changes in seawater chemistry:

1. Preservation of primary Sr isotope ratios, and Sr contents up to 3000 ppm in these samples confirm that the diagenetic system was closed to isotopic

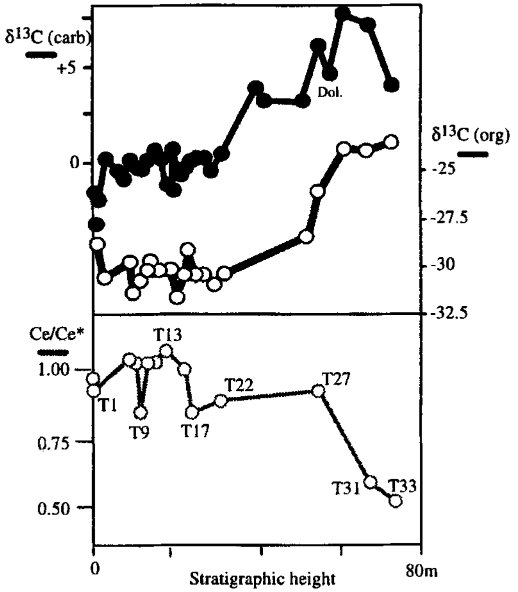

FIG. 1. Stratigraphic trends in Ce anomaly mirror apparently seawater C-isotopic changes.

exchange within metres of the sediment-water interface.

2. Covariation of $\delta^{13}C$ carb. and $\delta^{13}C$ org. indicates retention of an original seawater carbon isotope trend. Good correlation between this distinct trend and Ce anomaly leads us to believe that both these geochemical parameters reflect changes in coeval seawater.

3. Primary sedimentological features also indicate that there were changes in seawater oxidation potential upsection. Ce anomalies are not found in laminated samples but only in micrites, which commonly contain Catagraphia (Maslov), interpreted to be remains of photosynthesising bacteria.

4. If the lack of Ce anomalies in deep water samples were the result of early diagenetic migration of Fe or Mn bound *REE*, we should expect no change in $^{143}Nd/^{144}Nd$. However, Ce anomalies display perfect correlation ($r^2 = 100$) with Nd isotope ratio. Lack of correlation between $^{143}Nd/^{144}Nd$ and 1/Nd, and the agreement of a sample from a separate section forty kilometres distant, imply that the system was not subjected to simple mixing between seawater and some other end member. Therefore, the correlation is likely to be primary; both $^{143}Nd/^{144}Nd$ and Ce anomalies reflect local seawater.

We take this evidence together as indicating that the Tsagaan Gol section was deposited in an area marked by redox stratification, which caused extreme chemical gradients in local seawater with depth, for Fe, Mn, *REE* concentrations, $\delta^{13}C$, $^{143}Nd/^{144}Nd$, and Ce anomaly. Extreme switches in all these geochemical parameters upsection are related to the passing of the locus of deposition through to oxic waters.

Ce anomalies deserve an important place in palaeoceanography, especially when combined with other petrographic and geochemical proxies. However, their easy migration under even suboxic conditions will always be a thorn in the sides of those who wish to use them for palaeoceanographic interpretation. More work is required before the behaviour of *REE* during diagenesis, especially carbonate diagenesis, is sufficiently understood.

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