Trace element behavior and redox facies analysis of core shales of upper Pennsylvanian Kansas-type cyclothems

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The black shale submembers of core shales of Pennsylvanian "Kansas-type" cyclothems are highly enriched in redox-sensitive trace elements (RSTEs) relative to overlying gray shale submembers as well as to many other modern and ancient organic-rich deposits. Controls on RSTE behavior in the study units can be elucidated from relationships of the Al-normalized concentrations of RSTEs to TOC and other trace elements. In low-TOC samples (<~10 wt%) most RSTEs exhibit strong positive covariation with TOC, but in high-TOC samples (>~10 wt%) two distinctly different patterns of RSTE enrichment are observed: (1) Mo, U, V, Zn, and Pb are highly enriched but weakly covariant with TOC; and (2) Cu, Ni, Cr, and Co are weakly enriched but strongly covariant with TOC. These patterns are inferred to represent different responses to euxinic conditions. The first pattern is characteristic of RSTEs of "strong euxinic affinity," i.e., those taken up in solid solution by Fe-sulfide or involved in other reactions catalyzed by free H₂S, and resident mainly in authigenic phases, whereas the second pattern is characteristic of RSTEs of "weak euxinic affinity," i.e., those not strongly influenced by the presence of free H₂S and resident mainly in the organic C or detrital fractions of the sediment. The redox facies of black shale samples were assessed based on levels of enrichment of four RSTEs of strong euxinic affinity (i.e., Mo, U, V, Zn). The majority of samples (69% of 185) exhibited complete agreement among all four redox indicators, a high level of internal consistency validating the procedure. Samples yielding a mixed redox signal showed a systematic sequence of RSTE enrichment: first V, then Zn and Mo, and finally U. This sequence may reflect (1) initiation of V enrichment under non-sulfidic anoxic conditions through semi-reduction from V(V) to V(IV); (2) complete reduction of V to V(III) and precipitation of authigenic phases containing V, U, Mo, and Zn under euxinic conditions; and (3) preferential loss of authigenic U from euxinic facies samples through post-depositional remobilization under conditions of rising or fluctuating benthic O2 levels. The multi-proxy trace-element procedure for redox facies analysis developed in this study is likely to be more reliable than commonly used single-proxy trace-element methods (e.g., Mo/Al, authigenic U, or V/(V+Ni)) or C-S-Fe systematics (e.g., S/TOC or DOP

Distribution and implication of silicon isotopic composition in marine and freshwaters

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Introduction

Recent progresses in silicon isotopic measurements using MC-ICP-MS technology have brought hopes among the biogeochemical scientific community in order to improve our knowledge on the silicon cycle (Cardinal et al., 2003).

Results and Discussion

The first silicon isotopic dissolved profiles obtained by this technique have confirmed the biological fractionation effect (De la Rocha et al., 2000) linked to the siliceous organism productivity both in marine (Antarctic Ocean) and fresh water (Lake Tanganyika) systems. This isotopic desequilibrium (δ^{29} Si = 0.94±0.11 in surface and 0.62±0.06 in deep) is controlled by the Rayleigh distillation equation and allows to reconstruct the dissolved silicic acid utilisation based on the fractionation factor recorded in biogenic opal material.

The fractionation observed in our studies between the dissolved Si pool in surface waters and the estimated diatom signature displays a δ^{29} Si strikingly similar to what was measured on cultured batch (De la Rocha et al., 1997). These in-vivo measurements thus confirm the small impact in changes of temperature, salinity, pH and diatom species in the fractionation process.

Spatial and temporal changes of the silicic acid utilisation will be discussed for the Tanganyika lake and Antarctic water samples along with the isotopic signature of silicon sources. **Conclusions**

Several questions still need consideration: A better constrain of the Si isotopic fractionation factor and the parameters controlling it; Determining the δ^{29} Si for silicic acid supply to the euphotic zone and its spatial variability; Deepening our perception of this tracer to provide valuable information on paleo-diatom rich productivities.

References

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