

## Trace metal signatures of recent TOC-rich sediments: Implications for C/T black shale formation

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Organic carbon-rich sediments are characterized by very specific trace metal signatures. In particular redox-sensitive and stable sulfide forming metals, like Ag, As, Cd, Co, Cr, Cu, Mo, Ni, Re, Sb, U, V, and Zn are significantly enriched in such sediments. The accumulation of trace metals may only be understood when potential metal sources (seawater, fluvial runoff, plankton) and the special situation in the depositional environment are considered.

In order to obtain paleoenvironmental information on ancient TOC-rich sediments, modern settings (coastal upwelling areas, silled basins) need to be investigated. In this contribution new data will be presented for cores obtained from the Namibian and Peruvian upwelling areas, the Black Sea, and Plio-/Pleistocene Mediterranean sapropels.

Modern upwelling sediments are enriched by more than a factor of 10 (relative to average shale) in Cd, Mo, U, Re, and Ag. Anoxic basin settings essentially accumulate the same elements, but additionally Sb, Cu, and V are trapped. The degree of enrichment in specific metals presumably not only depends on the trapping efficiency of anoxic systems, but also on metal availability in the water column. The potential use of Bi and Tl as paleoproxy elements will be discussed, as both metals are found enriched in OC-rich sediments.

Ancient black shales, like those from the C/T boundary, are generally metal-rich and show a very specific accumulation pattern. Elements like Zn, Ag, V, Sb, Co, Cu, As, Re, Ni, and Mo are (in decreasing order) present in concentrations exceeding those from modern upwelling settings by factors of 15 to 2. Several conclusions may be drawn from this fact: 1) Large parts of the C/T oceans must have been characterized by severe oxygen depletion and at least in part sulfidic conditions in the water column. 2) Productivity was not necessarily extremely high. 3) Information provided by major element composition has to be considered when trying to interpret trace metal signatures.

Examples for Cretaceous settings will include new data from the Gubbio C/T type-locality, the previously drilled ODP Leg 207 Demerara Rise, and the Jurassic/Cretaceous Barents Sea. Furthermore the importance of TOC-rich sediments for global metal cycles will be discussed.

## Minor elements, HREE and $\delta^{18}\text{O}$ distribution in UHP garnets from the Dora-Maira massif (Western Alps): Evidence for Gneiss and Mg-quartzite interaction at UHP?

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Garnets from three different Dora-Maira rock-types have been studied, (1) nearly pure pyrope (GT1) from the magnesian coesite-bearing quartzites, (2) almandine/pyrope dominant garnets (GT2) from jadeite-quartzite veins which crosscut the Mg-quartzite body, (3) almandine/grossular dominant garnets (GT3) from the country-rock gneiss, sampled in the vicinity of the quartzites. In GT1, minor elements are mainly Fe, Na and P. Na and P are incorporated according to a  $\text{Na}^+ + \text{P}^{5+} = \text{Me}^{2+} + \text{Si}^{4+}$  substitution with  $\text{P}_2\text{O}_5$  contents up to 2000 to 2500 ppm. HREE concentrations obtained by LA-ICP-MS, vary by 2 orders of magnitude from core to rim. The  $\delta^{18}\text{O}$  ratio (Cameca 1270, Nancy), around 4 - 5 ‰ (SMOW), is constant within error throughout the analyzed crystals. In GT2, the situation is different since HREE concentrations appear remarkably constant within a given crystal and from one crystal to the other. In contrast with GT1, Na in GT2 is partly charge-balanced by yttrium incorporation. The  $\delta^{18}\text{O}$  ratio in GT2, around 5.5 - 6.5 ‰, is close to that encountered in GT3 (gneiss) between 6.5 and 8 ‰. In GT3, phosphorus content is close to detection limit ( $\text{P}_2\text{O}_5$  below 300 ppm). HREE concentrations are highly variable from one crystal to the other and unfortunately, the size of garnet crystals does not allow profiling. The decrease in HREE and P concentration from GT1 cores to rims suggest that these elements are preferentially incorporated into garnet. Garnet growth leads to progressive depletion of these elements in the matrix. There is no significant influx of HREE during UHP garnet growth. The homogeneity of the  $\delta^{18}\text{O}$  ratio within garnet crystals is also an indication of UHP growth in a closed metamorphic system. We show that jadeite-quartzite veins have geochemical characteristics intermediate between those of the country gneiss and of the pyrope quartzite. They are likely to originate from the Mg-quartzite and country gneiss interaction at UHP.