

Do particulate $^{231}\text{Pa}/^{230}\text{Th}$ ratios depend on water depth?

JAN C. SCHOLTEN¹ AND J. FIETZKE²

¹Marine Environment Laboratories, International Atomic Energy Agency, 4 Quai Antoine 1^{er}, 98000 Monaco (j.scholten@iaea.org)

²IFM-GEOMAR, Wischhofstr. 1-3, 24148 Kiel, Germany (jfietzke@ifm-geomar.de)

The natural radionuclides ^{230}Th ($T_{1/2} = 75.6$ ky) and ^{231}Pa ($T_{1/2} = 32.1$ ky) are widely used as tracers for paleoceanographic process studies. Both isotopes are produced in seawater by radioactive decay of uranium isotopes (^{234}U , ^{235}U) and due to their particle reactivity they adsorb on sinking particles and are removed to the sediments. Since ^{231}Pa is less particle reactive than ^{230}Th i.e. ^{231}Pa has a longer residence time (τ) in the water column compared to ^{230}Th ($\tau = ^{230}\text{Th}$: 20-40y; $\tau = ^{231}\text{Pa}$: 80-200y) ^{231}Pa is preferentially removed in areas of higher particle flux like e. g. ocean margins (boundary scavenging); and the variable $^{231}\text{Pa}/^{230}\text{Th}$ ratios stored in the sediment record are believed to reflect changes in the paleofluxes (or paleoproductivity) during the geological past. Further processes which may influence $^{231}\text{Pa}/^{230}\text{Th}$ ratios are the composition of sinking particles, i.e. the higher affinity of ^{231}Pa to adsorb on biogenic opal compared to ^{230}Th , and the dissolved $^{231}\text{Pa}/^{230}\text{Th}$ in water masses.

In a study of $^{231}\text{Pa}/^{230}\text{Th}$ ratios in surface sediments from the southeast Atlantic off Namibia we find $^{231}\text{Pa}/^{230}\text{Th}$ ratios higher than the production ratio (P) of both isotopes ($P_{\text{Pa}/\text{Th}} = 0.093$) at the ocean margin and lower ones in the open ocean, a distribution typical of boundary scavenging. For this data set we observe a strong negative correlation ($r^2 = 0.82$) between $^{231}\text{Pa}/^{230}\text{Th}$ ratios in surface sediments and water depths. Also for previously published data from the Pacific and Arabian Sea we find negative correlations between $^{231}\text{Pa}/^{230}\text{Th}$ ratios in surface sediments and water depths, however, these correlations are less strong. We will discuss to what extent changes in the fractionation between ^{231}Pa and ^{230}Th with depth, high opal content, and/or boundary scavenging may cause $^{231}\text{Pa}/^{230}\text{Th}$ ratios to depend on water depth off Namibia.

Trace element behavior in sulfidic porewaters of the Oder estuary, SW Baltic Sea

F. SCHOLZ¹ AND T. NEUMANN¹

¹Institut für Mineralogie und Geochemie, Universität Karlsruhe, 76131 Karlsruhe, Germany (thomas.neumann@img.uka.de)

The diagenesis of trace elements in anoxic sediments of the Achterwasser lagoon, which is part of the Oder estuary in the Baltic Sea, is examined and evaluated in the context of pyrite formation.

Certain trace elements show the same distribution pattern within the pore water regime suggesting a similar diagenetic behavior. The release of Zn, Cu and Cd into the pore water occurs prior to the reduction of Fe and Mn, indicating that they are released from organic matter in the thin oxic surface layer of the sediments. While a considerable part of these elements is recycled into the water column another part diffuses downcore and is removed as soon as H_2S appears in pore water. Since degrees of trace element pyritization (DTMP) for Zn and Cd range well below 1%, it is inferred that they become trapped as monosulfide. Copper appears as both monosulfide and impurity in pyrite (DTMP: 12%).

The accumulation of V, Cr, Co and As in the pore water starts concomitantly to that of Mn and Fe suggesting that these elements are liberated through reductive dissolution of Mn- and Fe-oxyhydroxides. Increasing concentrations of dissolved V, Cr, Co and As with depth demonstrate that the fixation of these elements is not quantitatively controlled by the process of pyrite formation. While pyritization of Co and As is intense with median DTMP values of 35% and 17%, respectively, Cr (DTMP: 4%) is less and V (DTMP: <1%) almost not incorporated into pyrite.

The coinstantaneous increase of DOP and DTMP with depth suggests that, in analogy to Fe pyritization, addition of trace metal sulfide complexes on preexisting pyrite grains may be responsible for increasing DTMP values for Co, Cu and Zn. Arsenic does not form sulfide complexes but rather As(III) oxyanions under reducing conditions, suggesting that again adsorption of complexes is responsible for increasing pyritization with depth.