Geophysical Research Abstracts
Vol. 14, EGU2012-4904, 2012
EGU General Assembly 2012

Nickel – chlorin relationship in Peru upwelling sediments: a water column source of Nickel for geoporphyrins?

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The exclusive occurence of Ni(II) and V(IV) in geoporphyrins of mature organic-rich sediments (black shales) and crude oils is a long-known phenomenon, however, when and where the metallation of these tetrapyrroles occur in the diagenetic sequence is still unknown. It was argued that the metal – tetrapyrrole association forms within the reducing sediments, however, the association of Ni with prophyrins in diagenetically „young“ organic material has not been investigated. The early binding of Ni with pigment tetrapyrroles may provide an indicator of productivity as pigment export from the upper water column.
Here we present chemical data from modern upwelling systems, which may shed light on the origin of this metal – tetrapyrrole association. We combined data from organic-rich upwelling sediments (Peru, Namibia, Chile and Gulf of California), which suggest an exclusive, linear and uniform relationship between Ni and organic carbon. This may be explained by the occurrence of diatoms, which dominate productivity in these systems, and which have the same, high Ni – organic carbon relation. This hypothesis is backed up by the observed stoichiometric relationship exclusively between Ni and chlorins (the degradation products of chlorophyll and precursor molecules of geoporphyrins) in Peruvian surface sediments. This suggests a mechanistic relationship between Ni – tetrapyrrole formation and accumulation, and primary productivity. Based on water column metal data from the literature we hypothesize that (i) Ni is essentially available in excess as Ni(II) for tetrapyrrole incorporation and (ii) the Ni – tetrapyrrole association may form early in the water column, perhaps related to diatom cell lysis. Further, Ni(II) does not need a reduction step [unlike V(V)] to be incorporated into tetrapyrroles. The ideal conditions to observe the early Ni – tetrapyrrole association that leads to accumulation in the sediment is the combination of stable water column anoxia reaching into the upper photic zone, the highest flux of organic matter world-wide and the shallow water depth, all of which are unique for the Peruvian upwelling system. The stoichiometric association of Ni with tetrapyrroles implies that the sequestration of Ni in sediments via sulfides is only a minor contribution to the Ni accumulation record. Taken together, Ni stability and water column abundance are prerequisites for the formation and preservation of Ni-tetrapyrroles.