



## **Early diagenesis of trace metals (V, Mo, U) in sediments of the Peruvian upwelling area: response to oxygen dynamics in the water column**

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The upwelling area in the eastern equatorial Pacific off Peru is one of the most pronounced oxygen minimum zones (OMZs) of the modern ocean. Modeling scenarios predict an expansion of the OMZs in the course of global change in the coming decades. As a consequence, the Peruvian continental margin represents a key locality for studies on biogeochemical dynamics in the future ocean.

We present pore water and sediment data for redox-sensitive metals (Fe, Mn, V, Mo, and U) that have been collected along a transect across the Peruvian margin at 11°S. The results are used to evaluate the behavior of trace metals in a wide range of biogeochemical and hydrodynamic settings.

In the core of the OMZ, where permanently anoxic conditions prevail, redox sensitive metals exhibit diagenetic behaviors largely consistent with previous studies. Vanadium and Mo are released from Fe oxihydroxides and subsequently recycled through diffusion across the benthic boundary or trapped through formation of authigenic V phases and sequestration of Mo by authigenic pyrite. Some U is delivered through diffusion across the benthic boundary, reduction and precipitation of  $UO_2$  and incorporation into phosphorites. The utmost part of the buried U, however, is delivered in particulate form, most likely as bioauthigenic U which cannot be recycled in the suboxic waters overlying the anoxic sediments. In contrast to sediments in the core of the OMZ, sediments on the shelf experience frequent oxygenation episodes related to the passage of internal waves and the regular recurrence of El Niño events. These oxygenation episodes lead to the re-oxidation and remobilization of authigenic U and V. In contrast to that, the authigenic accumulation of Mo is favored by the occasional occurrence of slightly oxidizing conditions. This is most likely due to enhanced formation of sulfur intermediates necessary for pyrite formation and the increased stability of pyrite, the major Mo sink, under oxidizing conditions, compared to authigenic V and U phases. Redox oscillations in the Peruvian OMZ thus lead to a discrimination of U against Mo, a mechanism that should be considered in the interpretation of U/Mo systematics in paleo redox studies. Overall our results provide valuable constraints on how trace metal inventories of marginal sediments may respond to expanding shelf anoxia and to short term perturbations of sediment redox conditions.