Redox Speciation and Early Diagenetic Behavior of Molybdenum in Sediment Porewater at a Salt Marsh Flat

Deli Wang¹*, Robert C. Aller² and Sergio A. Sañudo-Wilhelmy³

¹ State Key Laboratory of Marine Environmental Science, Xiamen University, 422 Siming Nanlu, Xiamen, 361005, China

² School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY 11794-5000, USA

³ Department of Biological Sciences and Department of Earth Sciences, University of Southern California, Los Angeles, CA, 90089, USA

In order to elucidate the early diagenetic behavior of Molybdenum (Mo), this study examined both, in the field and in the laboratory, the redox speciation of dissolved Mo in sediment porewater taken from a back-barrier salt marsh environment in eastern Long Island (Flax Pond, NY). The vertical sediment porewater profile showed that total dissolved Mo in surface nonsulfidic porewater was 80 nM with dominant Mo (VI) as MoO_4^{2-} with and negligible Mo (V), while total dissolved Mo increased up to 150 nM at a depth of 3.5 cm with low sulfide content (sulfide: 11~100 μ M) where Mo (V) was observed with a concentration of as high as 20 nM. Total dissolved Mo decreased until ~70 nM at the depth of 7.5 cm in highly sulfidic deep sediment porewater (sulfide: >100 µM), where Mo (VI) dominated again probably as thiomolybdates as desorption of Mo from carrier phases and MoS₂ formation continue, and a portion was stabilized in solution as MoS₄²⁻. Anaerobic incubation of surface sediments mirrored the vertical sediment porewater profile: dissolved Mo was dominated as as Mo (VI) at the beginning, and addition of total dissolved Mo with high levels of Mo (V) occurred during anaerobic incubation with low sulfide conditions (sulfide:11~100 µM; Mo (V): as high as 160 nM). Finally, Mo (VI) was gradually reestablished under highly sulfidic conditions (sulfide: >100 µM). The results observed in this study demonstrated that Mo was remobilized with production of transient intermediates Mo (V) in low sulfide porewater, but precipitated as MoS₂ in highly sulfidic sediments, and a possible upward diffusion of dissolved Mo (V) may also likely occur across the sediment-water interface.