

## Authigenic uranium formation and preservation in two contrasting settings: Santa Barbara Basin and Middle Atlantic Bight, and a comparison with molybdenum

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U and Mo are among a group of redox sensitive elements which are highly soluble in oxygenated ocean water, but become much less soluble in reducing sediments. In the case of Mo, this reduction in solubility causes enrichment of Mo in sediments underlying sulphidic anoxic waters. Another mechanism causing Mo enrichment in sediments under more oxygenated waters is co-precipitation with Mn-oxides. In the case of U, authigenic precipitation is caused by chemical or microbial reduction at a lower redox potential than required formation of authigenic Mo under sulphidic conditions. The difference in redox potential at which U and Mo are reduced can therefore be exploited to reconstruct the redox state of ocean sediments in the past. Bottom water oxygen (BWO) and organic carbon flux (OCF) are the main determinants of the redox state of sediment. We present results from the Santa Barbara basin (SBB) and the Middle Atlantic Bight (MAB) to compare the behaviour of U and Mo (SBB only) under different BWO (<3 to 200  $\mu\text{M}$ ) but similar OCF ( $\sim 2 \text{ g/cm}^2 \text{ ka}$ ) conditions.

In the SBB, sediment authigenic U mass accumulation rates (MAR) range between 150-250  $\mu\text{g/cm}^2 \text{ kyr}$ , which is also typical for anoxic basins such as the Black Sea, the Cariaco Trench and Saanich Inlet. In the MAB, on the other hand, sediment authigenic U MAR is a factor of 5 to 10 lower (average  $\sim 30 \mu\text{g/cm}^2 \text{ kyr}$ ), which is typical for hemipelagic environment. Both diffusion across sediment-water interface and input of metals associated with sinking particulate matters could potentially contribute to U enrichment in the sediment. To quantify this contribution, we measured the flux of U attached to sinking particles by

sediment traps. In SBB, the particulate U flux to sediment amounts to 90  $\mu\text{g/cm}^2 \text{ kyr}$ , is preserved at sediment-water interface under low BWO, and accounts for 40 to 60% of total sediment authigenic U. The particulate U flux to the sediment is only  $\sim 2 \mu\text{g/cm}^2 \text{ ka}$  in the MAB, most of it is further re-oxidized at sediment-water interface under high BWO, and the contribution to total U MAR is negligible. Our data indicate that lower BWO is the main reason for much higher U MAR in the SBB than in the MAB. At the same time, a depth transect of cores within the SBB indicates that the U MAR response increases by less than a factor of two as BWO is reduced further from 25  $\mu\text{M}$  to < 3  $\mu\text{M}$ . Under elevated BWO of the MAB, OCF is the dominant control on U MAR.

Our results from within the SBB show that enrichment of Mo in the absence of Mn precipitation is very sensitive to variations in BWO between <3-10  $\mu\text{M}$ . The threshold level in sulphide concentrations required for authigenic Mo formation is  $\sim 1 \mu\text{M}$ . Total sediment authigenic Mo MAR increases from  $\sim 80 \mu\text{g/cm}^2 \text{ ka}$  under 10 to 25  $\mu\text{M}$  of BWO, to 600 to 1000  $\mu\text{g/cm}^2 \text{ ka}$  under 3 to 5  $\mu\text{M}$  of BWO. It increases further to over thousands of  $\mu\text{g/cm}^2 \text{ ka}$  in other anoxic marine basins containing > 1  $\mu\text{M}$  sulphide in the water column. We also measured a Mo flux of 87  $\mu\text{g/cm}^2 \text{ ka}$  for sinking particles collected in a sediment trap. This source of particulate Mo can account for most of total sediment authigenic Mo in sediments at BWO > 10  $\mu\text{M}$ , but only 10 to 20% of total sediment authigenic Mo MAR at BWO < 5  $\mu\text{M}$ . The SBB data demonstrate that authigenic Mo formation is not observed when BWO is above 10  $\mu\text{M}$  even under very high OCF.