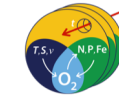


Influence of centennial to millennial scale climate change on low-latitude oxygen minimum conditions

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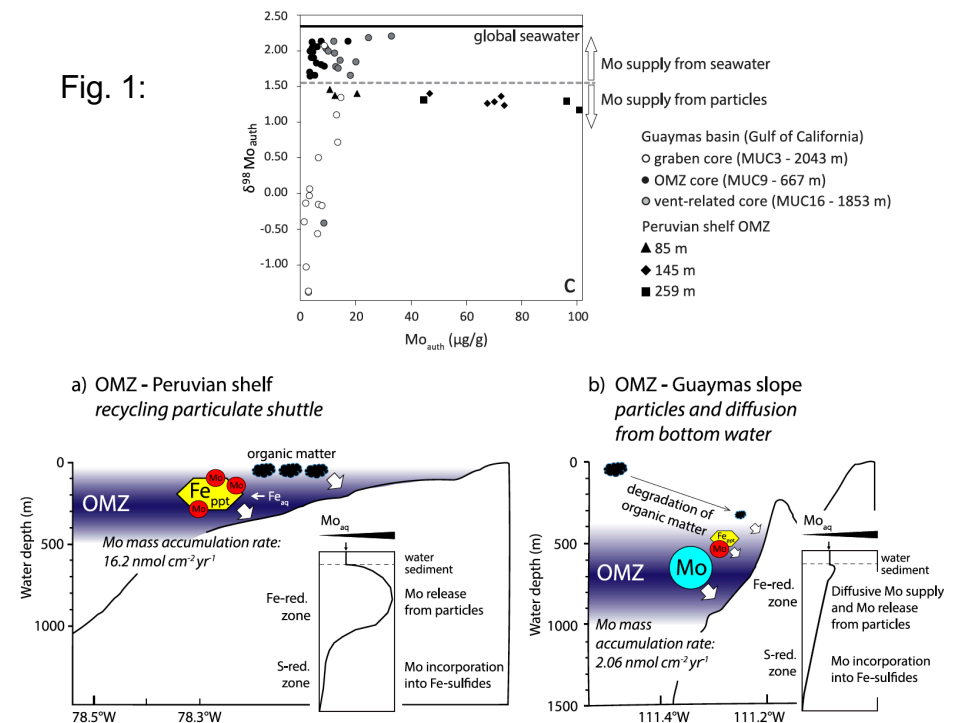
Variations in the stable isotope composition and concentration of the redox sensitive metals molybdenum (Mo) and iron (Fe) are extensively studied as tracer for past sedimentary redox conditions. In general, oxic sediments have light Mo isotope compositions. In contrast, euxinic sediments often show isotope compositions close to seawater. Mo redox proxy signals in anoxic sediments and the mechanisms causing them are not very well understood. Fe forms poorly soluble (oxyhydr)oxide and sulphide minerals under oxic and anoxic-sulphidic conditions, respectively. By contrast, under ferruginous conditions in the sediment, Fe (oxyhydr)oxides are reductively dissolved and Fe may be transported across the sediment-water interface. Variations in Fe content and associated changes in the Fe isotope compositions provide information about the water column redox structure.

In order to understand redox changes in tropical oxygen minimum zones (OMZs) we needed to gain further insight into processes controlling Mo and Fe biogeochemistry of anoxic sediments in these settings. We therefore compared OMZ sediments from the Gulf of California with those from the Peruvian OMZ, because of systematic differences in the settings. The major finding was that Mo isotope compositions in these settings is strongly depend on how Mo is delivered to the sediment. If diffusive Mo delivery dominates (Guaymas Basin), Mo concentrations are low and the isotope values are close to the $\delta^{98}\text{Mo}$ signal of seawater. If Mo is delivered by particles (Peruvian shelf), Mo concentrations are high and Mo isotope values are lighter due to particle adsorption processes (Fig. 1). Our findings deemphasize the role of dissolved Mo speciation in pore waters but highlight the importance of the mode of Mo delivery for the Mo concentration and isotope composition preserved in the paleo-record (Eroglu et al., 2020).

Another major finding was that once Mo is fixed in sulphides, its content and isotope signature is no longer affected by diagenetic processes.

In contrast, we can show that Fe speciation ratios can change on a centennial to millennial timescale due to differences in reaction rates of Fe minerals with sulfide during sedimentary submersion. As a result, paleo-data can falsely imply ferruginous or even euxinic conditions

Fig. 1:



Eroglu et al., 2020