

# MO AND U ISOTOPES IN A FERRUGINOUS LAKE: AN ANALOGUE FOR THE PROTEROZOIC OCEAN

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## Abstract

Authigenic trace metal enrichments, as well as Mo and U isotope systematics, have attracted attention as a tool for reconstruction of ocean redox structure through Earth's history [1]. However, the main controls on such redox proxies need to be verified in modern analogues of past ocean environments. Due to the highly oxygenated modern atmosphere, analogues for ancient anoxic oceans are rare, particularly for times when conditions were likely to be enriched in dissolved iron [2]. We have measured the Mo and U isotopic composition in tributaries, sediments, water column and sinking particles in a meromictic and ferruginous lake (Lake Pavin, France) to understand the behaviour of U, Mo and their isotopes in an environment akin to the Precambrian ocean.

*Keywords: Anoxia, Ocean history, Anoxic basin, Black Sea*

## Results and Discussion

The lake is characterised by low Mo and U concentrations in the water column compared to the open ocean, exhibiting Mo and U depletion below the redox/chemocline down to approx. 75 to 80 m depth, and increasing dissolved Mo and U concentrations towards the bottom of the lake (max. 90 m depth). Molybdenum isotopes ( $\delta^{98}\text{Mo}$ ) show large and systematic variations within the stratified water column.

The upper oxic lake layer is characterised by  $\delta^{98}\text{Mo}$  in the range of +1.20 to +1.52‰. These isotope compositions are significantly heavier than  $\delta^{98}\text{Mo}$  in tributaries (0.5‰), the source of Mo to the lake, demonstrating that dissolved Mo is isotopically fractionated in oxic waters. The likely cause is adsorption of Mo to Mn and/or Fe (oxyhydr)oxide particulates, which involves preferential uptake of light Mo isotopes, thereby leaving the remaining dissolved Mo pool isotopically heavy.

In the anoxic part of the lake, the dissolved Mo pool has  $\delta^{98}\text{Mo}$  in the range of +0.71 to +0.27‰. The difference between the oxic surface and the anoxic deep lake is most likely due to Fe-Mn cycling across the chemocline. Dissolved, reduced Fe and Mn diffuse upwards from the anoxic waters and are oxidised in the upper oxic portion. Consequently, the Lake Pavin chemocline is characterised by high concentrations of Mn and Fe (oxyhydr)oxides that preferentially sorb the light Mo isotopes.

Sinking and dissolution of these Mn and Fe (oxyhydr)oxides in the anoxic part of the lake is most probably responsible for low  $\delta^{98}\text{Mo}$  in the anoxic bottom of Lake Pavin. Due to very low U concentrations the  $^{238}\text{U}/^{235}\text{U}$  ( $\delta^{238}\text{U}$ ) could not be determined in oxygenated waters. However, dissolved U in the anoxic water column below 75 meters depth has  $\delta^{238}\text{U}$  in the range of +0.2 to -0.28‰, averaging -0.2‰. This isotopic composition is similar to  $\delta^{238}\text{U}$  measured in the tributaries, indicating little net U isotope fractionation in this part of the water column.

Anoxic Lake Pavin sediments show contrasting behaviour with depth beneath the sediment-water interface. In the top ~10 cm both U (~4 ppm) and Mo (~20 ppm) concentrations are higher than below (~2 and ~10 ppm, respectively). This abundance variation is accompanied by shifts in U and Mo isotopic composition:  $\delta^{98}\text{Mo}$  and  $\delta^{238}\text{U}$  are around +0.15‰ and 0.0‰, respectively, in the upper sediments, and -0.5‰ and -0.2‰, further down.

The changes in  $\delta^{98}\text{Mo}$  and  $\delta^{238}\text{U}$ , as well as the Mo and U concentrations in anoxic Lake Pavin sediment, imply significant changes in redox conditions during the deposition of the investigated sediments. Mo and U concentration and isotope systematics in the deeper sediments suggest little authigenic enrichment and more oxic conditions during deposition, whereas the top 10 cm show both authigenic U and Mo enrichment and isotope fractionation. The upper sediments also suggest that Mo and U incorporation into sediments under ferruginous ocean conditions may lead to lower  $\delta^{98}\text{Mo}$  and higher  $\delta^{238}\text{U}$  compositions compared to the overlying waters.

## References

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