

Analysis of distribution and sources of Mo and W in the hydrosphere based on concentration and isotope ratios

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Mo and W are both group 6 elements and have similar chemical properties. However, the two elements behave in a different way in the hydrosphere. Mo is an essential element, but W has toxicity for mammals. In the modern ocean, Mo and W are distributed uniformly from surface water to bottom water^[1,2]. However, the concentrations are totally different (Mo/W = 2000 mol/mol)^[1,2]. Recently, stable isotope ratios of Mo and W are used for marine geochemical study:

However, there are still few analyses for W. This study is aimed to provide with simultaneous data of dissolved Mo and W throughout the hydrosphere: total 136 samples from the North Pacific Ocean, the Indian Ocean, the East China Sea, the Sea of Japan, Osaka Bay and Uji-River were analyzed. Mo and W were concentrated and measured following the method developed in our laboratory^[1] (fig).

In the ocean samples, Mo concentration is 104.3 ± 5.7 nmol/kg (ave \pm sd, $n = 100$) and $\delta^{98}\text{Mo}$ is 2.40 ± 0.03 ‰ ($n = 92$), W concentration is 48.0 ± 2.9 pmol/kg ($n = 97$) and $\delta^{186}\text{W}$ is 0.533 ± 0.034 ‰ ($n = 98$), these data are congruent with the precedence study (Mo concentration: 104.4 ± 5.8 nmol/kg, $\delta^{98}\text{Mo}$: 2.37 ± 0.02 ‰, W concentration: 52.8 ± 3.9 pmol/kg, $\delta^{186}\text{W}$: 0.55 ± 0.12)^[1].

In the marginal seas' samples ($n = 31$), Mo concentration is 105.7 ± 3.1 nmol/kg and $\delta^{98}\text{Mo}$ is 2.36 ± 0.03 ‰, being identical with the oceanic values. However, W concentration is 71.6 ± 59.4 pmol/kg, $\delta^{186}\text{W}$ is 0.443 ± 0.063 ‰, and these data are significantly different from the oceanic values. Particularly in Osaka Bay, W concentration is from 195.7 to 319.5 pmol/kg, $\delta^{186}\text{W}$ is 0.282 ± 0.038 ‰. When $\delta^{186}\text{W}$ is plotted against the inverse W concentration, Osaka Bay's data occur below the mixing line between the data of the open ocean seawater and the Uji-River water. We propose that anthropogenic W has significant contribution in Osaka Bay and the marginal seas.

[1] Fujiwara et al. Chem. Geol. 555, 119835 (2020).

[2] Firdaus M. L. et al. Oceanogr. 64, 247–257 (2008).

$$\delta_{\square}^{98}\text{Mo}(\text{‰}) = \left[\frac{(\frac{98}{100}\text{Mo}/\frac{95}{100}\text{Mo})_{\text{sample}}}{(\frac{98}{100}\text{Mo}/\frac{95}{100}\text{Mo})_{\text{NIST SRM 3143}}} - 1 \right] \times 1000 + 0.25$$

$$\delta_{\square}^{186}\text{W}(\text{‰}) = \left[\frac{(\frac{186}{184}\text{W}/\frac{184}{184}\text{W})_{\text{sample}}}{(\frac{186}{184}\text{W}/\frac{184}{184}\text{W})_{\text{NIST SRM 3163}}} - 1 \right] \times 1000$$