

Vanadium isotopes of the Yangtze river system, China

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Investigation of redox variations in recent and paleo-oceans has been of particular scientific interest to elucidate the rise and variations of the atmospheric O₂ level (e.g., [1]) by analyses of isotopic signatures of e.g., Fe, Mo, U, V. The oceanic vanadium cycle can be simplified to consist of one major source represented by rivers and two major sinks (sediments, mid-ocean ridge systems). The balance between these V pools is sensitive to the ocean water O₂ level and chemistry. Yet, the isotope signature of the modern V cycle is poorly investigated.

To characterize the V isotope composition of the major V source to the oceans, we determined for the first time V isotope signatures of 13 selected rivers (dissolved and particulate fractions of source water, tributary rivers, and the Yangtze River) in the Yangtze River Basin, China. A large variation of dissolved V (ca. 0.07 to 6.0 µg/L) and particulate-bound V (ca. 0.03 to 17 µg/L) was found for the sample suite. The obtained $\delta^{51}\text{V}_{\text{AA}}$ values of the dissolved V pool span a range of -0.79 ‰ (± 0.18 ; all 2SD) to -0.13 ‰ (± 0.22), whereas particulate-bound V extends to lower $\delta^{51}\text{V}$ signatures between -2.16 ‰ (± 0.30) and -0.14 ‰ (± 0.11).

Notably, dissolved V from the river sources and small tributaries scatters between ca. -0.45 ‰ to -0.75 ‰, and agrees well with the predicted average $\delta^{51}\text{V}$ value of -0.6 ‰ ± 0.3 for continental run-off [2]. For the lower Yangtze River, however, the dissolved $\delta^{51}\text{V}$ signatures increase from the Three-Gorges Dam towards the estuary from -0.79 ‰ to -0.13 ‰, suggesting V isotope fractionation due to adsorption to abundant particulate Fe oxides, but may also reflect an input of anthropogenic V. The low $\delta^{51}\text{V}$ of particulate V largely follow this trend, and thus indicate ongoing V isotope fractionation during riverine V transport to the ocean.

[1] Lyons, T.W., Reinhard, C.T., Planavsky, N.J. (2014) *Nature* 506, 307-315. [2] Wu, F., Owens, J.D., Huang, T., et al. (2019) *Geochimica et Cosmochimica Acta* 244, 403-415.