Tungsten in ancient seawater: did early microbes like heavy metal?

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Both molybdenum (Mo) and tungsten (W) are essential heavy metals, as all life forms require one or the other. Tungsten, the heaviest element in nature with a known bioessential role in prokaryotes, is thought to be among the first metals utilized by Earth's earliest living organisms [1]. Both tungsten and molybdenum share similar chemistries, however their evolution in seawater was probably remarkably different, and the sedimentary record of tungsten has received little attention to date. Today, tungsten is present in oxic oceans as the stable and soluble tungstate (WO_4^{2-}) oxyanion, but at much lower concentrations than Mo. Sinks in the modern oceanic tungsten cycle appear to be dominated by ferromanganese deposits and sulfidic marine sediments. Here, we set out to provide constraints on the ancient marine tungsten cycle to test the possible antiquity of tungsten metalloenzyme utilization and evaluate biological co-evolution. We show that tungsten had variable concentrations, and its bioavailability likely varied throughout geologic time. Tungsten concentrations in the shale record show broad increases between ~2.3–2.15 Ga and ~1.1–0.8 Ga, but remained near crustal levels at other times in Earth's history, including the Archean. Similarly, the record of iron-rich deposits does not support a higher tungsten concentration in Archean oceans. Tungsten appears to have been more abundant relative to Mo during parts of the mid-Proterozoic, which might have implications for Mo-dependent metalloenzymes and early eukaryotic evolution.

[1] Pushie et al. (2014), *Metallomics* 6, 15-24.