The effects of iron and manganese shuttles on thallium and vanadium isotopes in Black Sea sediments

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The rise of atmosperic oxygen is crucial to the evolution of life, particularly early animals that require low levels of oxygen. We are exploring variations of thallium ($^{205}Tl/^{203}Tl$) and vanadium ($^{51}V/^{50}V$) isotopic ratios in organic-rich sediments to fingerprint low but non-zero bottom water oxygen concentrations in the oceans—specifically sites with burial of Mn oxides [1]. Organic-rich facies can record the seawater isotope values. Tl isotopes are strongly fractionated by adsorption onto Mn oxides (12 – 18 for $\varepsilon^{205}Tl$), and V isotopes are fractionated by Fe-Mn crust and nodules (0.9 – 1.8 ‰ for $\delta^{51}V$) [2, 3]. In fact, these oxides exhibit the largest control on Tl and V isotopic systematics in modern oceans. Fe-Mn oxides also cause the largest fractionations for molybdenum (Mo) isotopes, which can be transported through a ‘shuttle’ mechanism from the water column to the sediment. Such processes are known from the Baltic Sea with the result of more negative Mo isotope compositions in sediments and corresponding complications for Mo data from similar ancient settings if used to interpret global redox conditions [4]. By analogy to Mo isotopes, Fe-Mn shuttling to the sediments could shift the Tl and V isotope records of seawater compositions preserved in marine sediments.

To test our hypothesis, we measured V and Tl isotope compositions in Black Sea sediments deposited under diverse bottow-water oxygen conditions. All these sediments (–2.54 ± 0.73) documented the same $\varepsilon^{250}Tl$ values as the oxic surface water (–2.20 ± 0.30) of the Black Sea[5], suggesting a lack of contributions to sediments by Mn-oxides shuttling. Additional analysis will test the potential for a shuttle signal in the V isotope system using these sediments. These results are important as we continue to constrain the systematics of novel isotope systems and their relevance to interpertations of the ancient record.

[1] Owens et al. (2019); [2] Nielsen et al. (2013) *GCA*, 117, 252-265; [3] Wu et al. (2019) *GCA*, 265, 371-38; [4] Scholz et al. (2018) *CG*, 491, 27-38; [5] Owens et al. (2017) *GCA*, 213, 293-307.