

## Te And Sb Isotopic Variations as Potential Paleo-redox Indicators

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Various geochemical proxies have been developed to constrain redox conditions in ancient earth systems, each having a unique character in its response to redox changes, threshold(s) for redox transitions, and other geochemical characteristics. We have begun exploring the potential for Te and Sb stable isotope variations to serve as new proxies with unique properties. Redox transitions for both elements seem to occur under more oxidizing conditions than for U and S, though thermodynamic data are scarce. Under highly reducing conditions, both elements form immobile solids, with Sb probably locked up in sulfides and Te present as Te(0), sulfide, and/or telluride phases. Under oxidizing conditions, both elements are soluble and much more mobile, yet prone to strong adsorption.

We measure  $^{128}\text{Te}/^{130}\text{Te}$  and  $^{123}\text{Sb}/^{125}\text{Sb}$  isotope ratios following previous MC-ICP-MS methods [1, 2] with some improvements. We developed a new hydride generation method for Te and used an existing one for Sb [1], enabling good measurements on small masses (<10ng; much needed, given low crustal concentrations). A few previous experiments [1,2] combined with our new ones show that biological and naturally relevant abiotic reduction reactions of both Sb(V) and Te(VI) favor lighter isotopes, with fractionations in the 0.5‰ to 1.0‰ range. Our experiments also show that adsorption of both elements also induces significant fractionation, up to 0.5‰. Given our emerging understanding, we expect that under highly reducing conditions of the early earth, Sb and Te were present as solids, did not undergo redox cycling, and should show little isotopic variation. As each element's respective oxidative threshold was reached, its isotopic variation should have "lit up," as redox and sorption reactions began, providing clues to be read in the rock record today. We have begun to measure Sb and Te isotopic variation at various times from the present to >3 Ga. Much work remains, as the redox thresholds, isotopic systematics, and geochemical behavior are not yet fully defined.

[1] Rouxel et al. (2003) *Chem. Geol.* **200** 25–40

[2] Baesman et al. (2007) *Appl. Env. Microbiol.* **73** 2135–2143