## The Mechanism of the Sedimentary Bedrock Selenium Pump

SERGIO CARRERO<sup>1</sup>, BHAVNA ARORA<sup>2</sup>, CURTIS BEUTLER<sup>3</sup>, SHARON E. BONE<sup>4</sup>, SHARON BORGLIN<sup>2</sup>, WENDY BROWN<sup>3</sup>, JOHN N CHRISTENSEN<sup>2</sup>, WENMING DONG<sup>2</sup>, AMANDA N HENDERSON<sup>3</sup>, LANGLANG LI<sup>5</sup>, ALEXANDER W NEWMAN<sup>3</sup>, LUCIEN STOLZE<sup>2</sup>, NICHOLAS E THIROS<sup>2</sup>, TETSU K TOKUNAGA<sup>2</sup>, JIAMIN WAN<sup>2</sup>, ERICA R WOODBURN<sup>2</sup>, YIMING ZHANG<sup>6</sup>, CARL I STEEFEL<sup>2</sup>, NICHOLAS L SWANSON-HYSELL<sup>7</sup>, KENNETH H WILLIAMS<sup>2</sup>, JILL BANFIELD<sup>7</sup> AND **BENJAMIN GILBERT**<sup>2,5</sup>

<sup>1</sup>Institute of Environmental Assessment and Water Research
<sup>2</sup>Lawrence Berkeley National Laboratory
<sup>3</sup>Rocky Mountain Biological Laboratory
<sup>4</sup>SLAC National Accelerator Laboratory
<sup>5</sup>University of California, Berkeley
<sup>6</sup>UC Berkeley
<sup>7</sup>University of California Berkeley
Presenting Author: bgilbert@lbl.gov

Selenium (Se) is an essential nutrient that is toxic to animals and humans at ppm concentrations. In the Upper Colorado River Basin, selenium is released into water bodies by weathering from sedimentary bedrock. Climate change, including warming and variation in precipitation type, timing and amount, is expected to alter weathering patterns and solute exports. The anticipated changes in selenium exports are difficult to predict, however, in part because the pathway for selenium mobilization from bedrock to river water is unknown. We used microscale rock analyses, time- and depth-dependent water chemistry data and geochemical and hydrologic modeling to discover and describe a two-step redox pathway for Se release from weathering shale in the East River watershed, Colorado. Weathering of seleniumbearing sulfide minerals occurs in a zone defined hydrologically (by water table fluctuation) and geochemically (between redox transitions marked by barite and pyrite precipitates). Reduced selenium is transformed into insoluble Se(0) in transiently oxidizing saturated conditions following snowmelt and water table rise. Elemental selenium is further transformed to soluble selenate in oxidizing partially-unsaturated conditions, and mobilized to groundwater upon the successive water table excursion. This model, in which multiple water table excursions transform and mobilize selenium into groundwater, explains the different ground water and river dynamics of Se compared to S and other solutes. This work provides a new conceptual model for selenium release from sedimentary bedrock and a geochemical reaction network that could be integrated into watershed-scale ecohydrogeological predictions for redoxsensitive contaminant exports in a changing climate.