

## **Segregation of Cesium and Rubidium geochemical pathways in the upper continental crust**

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Cesium and rubidium are large-ion-lithophile and strongly incompatible elements known to follow a general geochemical pathway of potassium. Despite similarities in geochemical behavior, Cs and Rb concentrate in the upper continental crust (UCC) preferentially to K. The Cs/K, Rb/K and Cs/Rb ratios in the UCC are significantly higher than those in middle and lower continental crusts, MORB, and seawater. Soils yield Cs/K and Rb/K ratios several to tens of times greater than the UCC and Cs fixation in micaceous frayed edge sites (FES) is a suggested long-term, bio-unavailable retention mechanism. Illite, a potassium-depleted dioctahedral mica, and hydroxy-interlayered dioctahedral vermiculite are the common soil minerals known for high Cs and Rb selectivity and irreversible adsorption in crystallite wedges and FES [1].

Analyzing 4000+ samples from 22 basins and sub-basins throughout the world, we found that illite is a global sink for Cs on the Earth's surface. The Cs/K and Cs/Rb ratios in illite were found unique to a geologic section and location. Using mass balance and realistic assumptions, illite was estimated to be responsible for up to 20% of Cs in UCC and it is the major, or even the only sink for Cs in sedimentary basins. The entire Cs present in the Earth oceans can be irreversibly adsorbed by illite frayed edges with an average concentration of 17.7 ppm Cs (as found in our study) in just several cm of illite-rich sediment covering the sea floor, or by < 15 mg of illite suspension in 1 m<sup>3</sup> of seawater. As the Cs equilibration with FES on illite or inner-sphere fixing in vermiculite is complete within hours, any Cs+ contact with illitic material may result in its immediate fixation.

The order of cation hydration enthalpy Cs > Rb > K > Na, is the order of cation selectivity in illite, which is also the order of the cations relative depletion in global seawater with respect to the UCC. We believe that Cs adsorption by illite crystallite edges is the mechanism controlling Cs variability in sedimentary basins and the segregation of Cs and Rb geochemical pathways in UCC.

[1] Wampler et al. (2012), *Environ. Sci. Technol.* 46, 3837–3843.