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Using rhenium, $\delta^{187}Re$, and RPO-^{14}C to trace the fate of rock organic carbon in the Critical Zone

KATHERINE E GRANT[1], MATHIEU DELLINGER[2], GEOFF M NOWELL[2], STEVEN PETSCH[3], VALIER GALY[4] AND ROBERT HILTON[5]

[1]Lawrence Livermore National Laboratory
[2]Durham University
[3]University of Massachusetts Amherst
[4]Woods Hole Oceanographic Institution
[5]University of Oxford

Presenting Author: grant39@llnl.gov

The rock organic carbon (OC_{petro}) reservoir is vast and contributes to the evolution of Earth's atmospheric O_2 and CO_2concentrations over geological timescales[1]. There is an estimated 1100 Pg C stored as OC_{petro} in the upper 1 m of sedimentary rocks at the earth surface[2]. It has been shown that in rapidly eroding environments, chemical weathering OC_{petro} can rapidly release CO_2 to the atmosphere[3], yet OC_{petro} oxidation rates are poorly constrained in settings with moderate to low erosion rates. Rhenium (Re) has emerged as a promising tracer, but we require improved constraint on Re mobility during OC_{petro} weathering, while rampled pyrolysis-oxidation RPO coupled to radiocarbon measurment can help illucidate the mixture of organic carbon in a sample. A combination of these techniques can shed light on the continuum of rock OC persistence during oxidative weathering.

Here we assess the fate of Re during OC_{petro} weathering in 2 well studied black shale weathering profiles [1], providing additional constraints from the rhenium isotope composition ($\delta^{187}Re$) and RPO activation energy distributions. We find that un-weathered (unaltered) samples range in [Re] from 78 to 670 ng/g. Weathered samples have lost between 59 and 99% of Re, and 45 to 95 % of OC_{petro}: confirmation of coupled Re and OC_{petro} oxidation. In un-weathered late Devonian aged samples, $\delta^{187}Re$ is similar to Miller et al. 2015 [4] with values from -0.2 to -0.3 ‰. Miocene aged black shales range from -0.18 to -0.04 ‰. Weathered samples have both heavier and lighter $\delta^{187}Re$ values, while RPO results show a loss of higher mean E peaks in weathered samples. We discuss the mechanisms behind the observed Re isotope fractionation and examine the implications for using Re isotopes combined with RPO activation energies to trace OC_{petro} oxidation.

[1] Petsch (2014) Weathering of Organic Carbon.[2] Copard, Amiotte-Suchet & Di-Giovanni (2007), *EPSL* **258**, 345-357. [3] Hemingway *et al*. (2018), *Science* **360**, 209-212.[4] Miller et al. (2015), *EPSL* **430,** 339-348.