Geophysical Research Abstracts
Vol. 20, EGU2018-12504, 2018
EGU General Assembly 2018

Developing the tools for the future anthropogenic pollutions : the potential of kinetic isotopic signatures

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The unprecedented rise in global population from the second half of the XXth century is putting pressure on the Critical Zone (CZ). One common aspect to the various anthropogenic effects is to speed up and scale up many naturally occurring cycles and processes. Here, I propose to use one consequence of changing the kinetics of chemical reactions, namely inducing kinetic isotopic fractionation, to better fingerprint and quantify the changes caused by human activities. Kinetic isotopic fractionation can be distinguished from isotopic fractionation related to reaching a thermodynamic equilibrium that generally affects natural processes in the CZ. Still, natural kinetic isotopic fractionations are widespread, such as Dexcess during evaporation for the water cycle, or a large fraction of the biological 12C enrichment for the carbon cycle. This is nevertheless mainly restricted to light elements and the theoretical framework establishing a difference in the mass-dependent fractionation laws that describe the partitioning of isotopes are different for kinetic and equilibrium reactions is barely applied to CZ. These laws can be expressed a single power law relating the fractionation factors for 3 isotope ratios, with the power coefficient being slightly different for kinetic and equilibrium reactions. On the light side of the periodic table, such small differences induce a maximum of 0.21 permil per amu for Mg. But this quickly drops to a mere 0.04 permil per amu for non-radiogenic Nd. Nevertheless, such effects are now detectable with sate-of-the-art mass-spectrometry. In particular, I will show that purified Nd commercially available (either purchased as solution or metal) against the JNdi-1 reference standard solution display a range of 0.3 permil per amu. This confirms that man-made samples have a distinct Nd isotopic signature since the range of stable Nd isotopic composition of natural terrestrial material is 3 times smaller than that of synthetic man-made purified Nd, albeit the very low number of natural terrestrial material characterized for its stable Nd isotopic composition. However, this purification process and anthropogenic Nd is associated with kinetic isotopic fractionation.