

Origin of the difference in the distribution behaviors of Tellurium and Selenium in a soil-water system

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The distribution behavior of tellurium (Te) between soil and water in a synthetic system was studied at various soil-water ratios so that we can examine the effect of systematic variation of redox condition on the distribution of Te. The speciation of Te both in soil and water phases were conducted by X-ray absorption fine structure (XAFS) spectroscopy and a high-performance liquid chromatography connected to an ICP-MS (HPLC-ICP-MS), respectively. The results were compared with a similar data set for Se, which was simultaneously obtained in this study. The oxidation states and host phases of Te and Se in the soil samples were given by XAFS, while the oxidation states in water were given by HPLC-ICP-MS. It was found that both Te and Se in soil are mainly associated with Fe(III) hydroxides under oxic conditions. From the EXAFS analyses, the outer-sphere complex is the main species of Se(VI) sorbed on Fe(III) hydroxides in soils, while Se(IV), Te(IV), and Te(VI) form inner-sphere complexes. Under reducing condition, it was found that Te(0) and Se(0) species were formed and that Se was more readily reduced to Se(0) than Te, as is predicted from their Eh-pH diagrams. The reduction process from hexavalent to zerovalent species was different between Se and Te, that is, the direct reduction from Se(VI) to Se(0) was observed for Se, while Te was reduced stepwise from Te(VI) to Te(0) via Te(IV).

In terms of the distribution between soil and water, Se distribution to water was much higher than that of Te under wide redox conditions. For Se, selenate is the predominant species in water even under reducing condition due to the much higher solubility of Se(VI) than Se(IV). Furthermore, a much smaller distribution of Te in water was primarily due to the larger affinities of Te(IV) and Te(VI) to Fe(III) hydroxides than Se(VI). The difference between Se and Te can finally be ascribed to the high stability of oxyanion of Se(VI), which is not the case for Te(IV) and Te(VI) with smaller pK_a values which prefer to form hydroxides rather than oxyanions.

[1] Harada & Takahashi (2008) *Geochim. Cosmochim. Acta* **72**, 1281-1294.

Absolute dated terrestrial climate record of temperature and precipitation in the Eastern US

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Stalagmite samples from Buckeye Creek Cave (37°59'N, 80°24'W) provide a high resolution, absolute dated record of mid-latitude climate change in the eastern US. $\delta^{18}\text{O}$ values in our samples reflect a combined signal representing both temperature and precipitation during glacial and interglacial intervals. A cross-correlation analysis using the Blackman-Tukey method demonstrates significant coherence with local summer (JJA) insolation in the precessional band ($p=0.05$). The sense of shift in the $\delta^{18}\text{O}$ record is consistent with warmer temperatures during insolation maxima. Because the record contains glacial and interglacial intervals and has a range of 2‰ (~5.5 °C at +0.35‰/°C), it is reasonable to conclude that temperature effects determine the isotopic composition of the samples. However, temperature cannot fully explain the record as Holocene samples show values comparable to insolation minima during marine isotope stages 6 and 8. This relationship can be explained by a wetter Holocene relative to stages 6-8. $\delta^{13}\text{C}$ values corroborate $\delta^{18}\text{O}$ behavior as they are notably more positive during stages 6-8. $\delta^{13}\text{C}$ variation is most likely an abiotic non-linear response to prior precipitation within the vadose zone [1] during dry intervals. Mg/Ca ratios from Holocene samples support this conclusion as Mg/Ca is correlated with $\delta^{13}\text{C}$ (see [2]). In addition to the more negative Holocene values, our record contains abrupt negative shifts in $\delta^{18}\text{O}$ during maxima in local summer (JJA) insolation. We interpret these rapid shifts as the onset of enhanced precipitation due to an increase in precipitable moisture associated with warmer temperatures or a change in atmospheric circulation.

[1] Denniston R., DuPree M., Dorale J., Asmerom Y., Polyak V. & Carpenter S. (2007) *Quaternary Research* **68**, 45-52.

[2] Fairchild I. J., Borsato A., Tooth A. F., Frisia S., Hawkesworth C., Huang Y., McDermott F. & Spiro B. (2006) *Earth-Science Reviews* **75**, 105-153.