

Origin of Difference in Solubility between Tellurium and Selenium into Water at Earth's Surface

Although both tellurium (Te) and selenium (Se) are found in relatively low abundance in the crust, it is possible that the high toxicities of these elements can induce environmental problems. For example, Se contamination has been found in soils, groundwater, and surface waters, which has triggered many studies on the environmental geochemistry of Se. There has been much less studies on Te due to its even lesser quantities in the crust, but Te contamination has also been found in areas associated with mine tailings. Irrespective of the possible problems related to the environment, however, the details of Te behavior in a soil-water system are still unknown. Thus, the comparison of the environmental behavior of Te with that of Se belonging to the same group in the periodic table is important in environmental geochemistry. In addition, it is expected that such comparison will shed light on the differences in their chemical properties, which may help us understand the solubilities of Se and Te in water. Such consideration can be linked to the distribution coefficient of Se between water and ferromanganese oxides in a marine system, which is much larger than that of Te by a factor of 10^5 despite their similar chemical nature.

Among various solid-water systems on earth's surface, the present study [1] focuses on the distributions of Te and Se in a soil-water system, and their speciation in both soil and water phases, which enables us to understand their distribution behaviors on the atomic scale. The samples examined were prepared by the addition of Se(IV), Se(VI), Te(IV), or Te(VI) in synthetic soil-water systems at various soil-water ratios [2]. We conducted an X-ray absorption fine structure analysis (XAFS; experiments were conducted at **BL01B1**) to determine directly the Te and Se species (oxidation state and host phase) in the soil phase, while a high-performance liquid chromatography system connected to ICP-MS (HPLC-ICP-MS) was used to determine the oxidation states of Se and Te in water.

Among these analyses, we conducted an extended X-ray absorption fine structure analysis (EXAFS) to obtain information on the local structures of Se and Te in soil samples. **Figure 1** shows the radial structural function (RSF) for EXAFS spectra of Se in the reference materials and soil samples when added as Se(IV) and Se(VI) into a soil-water system. For the sample added with Se(IV), two peaks were observed at 1.25 and 3.10 Å (**Fig. 1(a)**; phase shift uncorrected). These peaks were also found in the RSF of Se(IV) sorbed on ferrihydrite (reference

sample; **Fig. 1(b)**) and correspond to the Se-O and Se-Fe shells, respectively. The similarity of the two RSFs shows that Se(IV) in soils is sorbed on the Fe(III) hydroxide phase. In particular, the presence of Fe in the second shell indicates that Se(IV) forms inner-sphere complexes at the surface of Fe(III) hydroxide. In contrast, the RSF of the sample added with Se(VI) did not exhibit a prominent peak for the Se-Fe shell (**Fig. 1(c)**), which was almost identical to that of Se(VI) sorbed on ferrihydrite (**Fig. 1(d)**). The absence of a peak for the Se-Fe shell suggests that an outer-sphere surface complex of selenate is formed at the surface of Fe(III) hydroxide. For Te(IV) and Te(VI), prominent peaks that can be ascribed to the Te-Fe shell were found near 3.20 and 2.70 Å (phase shift uncorrected) in the RSFs of Te(IV) and Te(VI), respectively. The presence of Fe in the second shell showed that both Te(IV) and Te(VI) formed inner-sphere surface complexes at the surface of Fe(III) hydroxide.

The EXAFS analyses showed that the outer-sphere complex is important for the Se(VI) sorbed on Fe(III) hydroxide in soils, while Se(IV), Te(IV), and Te(VI) form inner-sphere complexes. This structural information, in turn, is closely related to the solubilities of the elements in water. In terms of the distribution between soil and water, the Se distribution in water was much higher than that of Te under wide redox

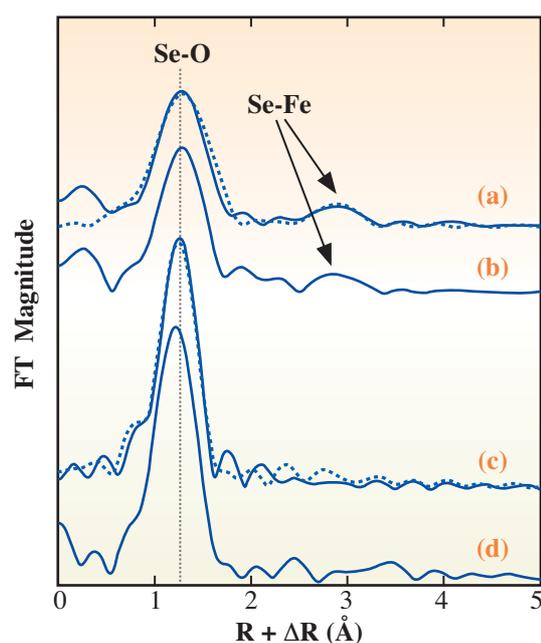


Fig. 1. Radial structural functions of Se(IV) species sorbed on (a) ferrihydrite (iron hydroxide) and (b) soil, and Se(VI) species sorbed on (c) ferrihydrite and (d) soil.

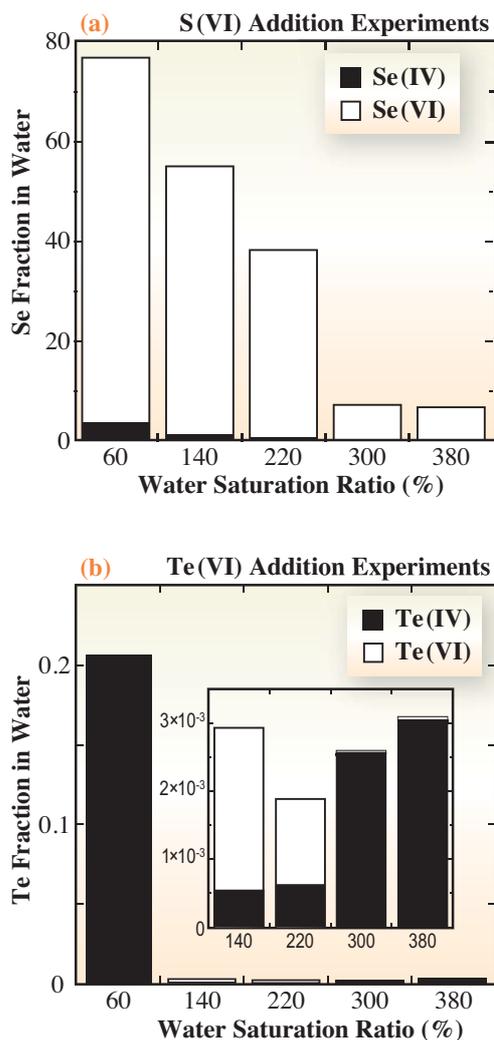


Fig. 2. Dissolved fraction of (a) Se and (b) Te in water in distribution experiments of Se and Te in soil-water system. Initial concentrations of Se and Te were 150 mg/kg in the system. The horizontal axis indicates the volume ratio of water to soil. When the ratio was large, Eh decreased (= more reducing) owing to the small content of oxygen dissolved in water.

conditions (Fig. 2). 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, the much smaller distribution of Te in water was primarily due to the larger affinities of Te(IV) and Te(VI) to Fe(III) hydroxide than Se(VI), which originates from the formation of the inner-sphere complexes of Te(IV) and Te(VI) at the surface of Fe(III) hydroxide.

This difference can be finally ascribed to the stability of the oxyanion of Se(VI) compared with those of Se(IV), Te(IV), and Te(VI). Based on the effective ionic radius at sixfold coordination ($r/\text{\AA}$), the ionic potential ($IP; =z/r$; z : charge of the ion) of Se^{6+} was 14.3\AA^{-1} , which is much larger than those of Se^{4+} (8.0\AA^{-1}), Te^{4+} (4.1\AA^{-1}), and Te^{6+} (10.7\AA^{-1}). The ion with a larger IP forms stable oxyanions, which may not form

an inner-sphere complex at the surface of Fe(III) hydroxide without the bonding of Se-O-Fe or Te-O-Fe.

Finally, the difference between Se and Te found in this study can be used to explain the large difference in abundance between Se and Te in marine ferromanganese oxides relative to those in seawater (Fig. 3). The enrichment factor of Te in ferromanganese crusts relative to the mean abundance in seawater is larger than that of Se by more than four orders of magnitude. This is most likely due to the formation of outer- and inner-sphere complexes of Se and Te, respectively, when reacted with the ferromanganese oxides. The high stability of Se(VI) oxyanions induces a large Se abundance in seawater, which is not the case for Te(IV) and Te(VI) that prefer to form hydroxides rather than oxyanions.

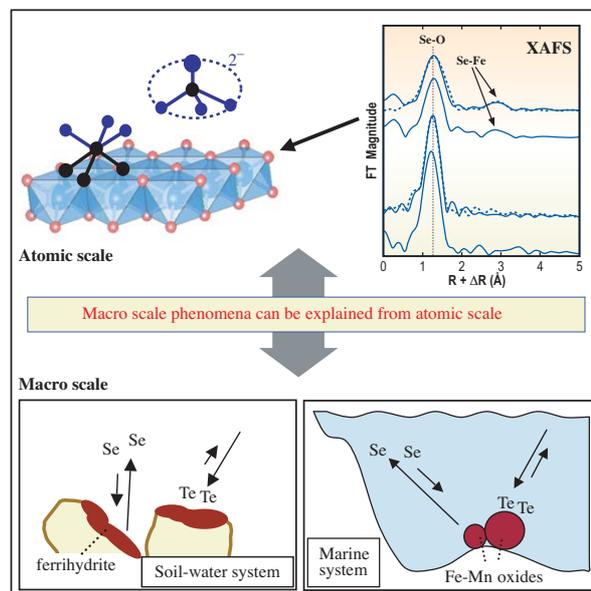


Fig. 3. Schematic showing that difference between solid-water distributions of Se and Te in soil-water and marine systems may be caused by difference between structures of Se and Te species sorbed on ferrihydrite (outer- or inner-sphere complex). Understanding the interactions of metal ions and solid on the atomic scale reveals the macroscopic phenomena observed at earth's surface.

Yoshio Takahashi

Department of Earth and Planetary
Systems Science, Hiroshima University

E-mail: ytakaha@hiroshima-u.ac.jp

References

- [1] T. Harada and Y. Takahashi: *Geochim. Cosmochim. Acta* **72** (2008) 1281.
- [2] Y. Takahashi *et al.*: *Environ. Sci. Technol.* **38** (2004) 1038.