Sorption and interfacial redox of Sn(II) under anoxic conditions: Magnetite vs. anatase

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The long-lived fission product ^{126}Sn is of substantial interest in the context of nuclear waste deposition in deep underground repositories. However, the redox state (di- or tetravalent) under the expected anoxic conditions is still a matter of debate. We therefore investigated the stability of Sn(II) in the presence of a highly redox-reactive mineral, magnetite ($Fe^{II}Fe^{III}{}_2O_4$), in comparison to a non-redox-reactive, anatase (TiO_2).

Sorption experiments were performed at < 2 ppm O_2, and redox state and local structure was monitored over time by X-ray absorption spectroscopy (XAS).

We found a rapid (< 30 min) oxidation of Sn(II) to Sn(IV) in the presence of magnetite. Although solubility calculation predicted the precipitation of SnO_2, the local structure determined by XAS showed two Sn-Fe distances of about 3.15 and 3.60 Å in line with edge and corner sharing arrangements between octahedrally coordinated Sn(IV) and the magnetite surface, indicative of inner-sphere complexation. The structure of the complex remained largely unchanged up to an equilibration time of 1 month.

After 30 min reaction with anatase, Sn(II) was conserved. However, even with the redox-inert anatase, Sn(II) oxidized to Sn(IV) over time, forming an Sn(IV) inner-sphere complex with Sn-Ti distances at 3.24 and 3.53 Å. Therefore, our results clearly indicate that Sn(IV) is the most relevant oxidation state to be considered even under reducing conditions, and that inner-sphere complexation is a relevant retention mechanism.

Evidence of lime-CO_2 evolution and priming effect of agricultural liming

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Agricultural liming contributes significantly to atmospheric CO_2 emission from soils [1] and enhances the turnover of soil organic matter (SOC), termed priming effect (PE) [2]. We believe that these impacts of liming acid soils should be factored in our existing soil organic matter (SOM) models but data on magnitude of lime-contributed CO_2 and priming effect in a wide range of global acid soils are still few.

Using two acid soils in Japan: (1) an acidic Kuroboku Andisol from Tanashi, Tokyo Prefecture (35°44' N, 139°32' E), and (2) Kunigami Mahji Ultisol of Nakijin, Okinawa Prefecture (26°38' N, 127°58' E), we employed a unique methodology to separate and quantify lime-contributed ($^{13}CO_2$), and SOC-originated ($^{12}CO_2$) CO_2-C evolution using $Ca^{13}CO_3$ (^{13}C 99%) as lime and tracer.

Our experimental data have confirmed that (1) lime contributes heavily to CO_2 evolution, and (2) liming acid soils increases SOC turnover. On the average, lime-CO_2 was 76.84% (Kuroboku Andisol) and 66.36% (Kunigami Mahji Ultisol) of overall CO_2 emission after 36 days, indicating that the mineralization of lime-carbonates is the major source of CO_2 emission from acid soils during agricultural liming. The calculated PE of lime (Kuroboku Andisol, 51.97-114.95%; Kunigami Mahji Ultisol, 10.13-35.61%) was entirely ^{12}C turnover of stable SOC since the soil microbial biomass (SMBC), a labile SOC pool, was suppressed by liming in our experiment.

Liming can influence the magnitude of CO_2 evolution from agricultural ecosystems considering global extent of acid soils and current volume of lime utilization. The measured PE of liming in SOC is large and can significantly alter atmospheric CO_2 evolution from agricultural ecosystems.

[1] Biasi *et al.* (2008) *Soil Biol. Biochem.*, **40**, 2660–2669. [2] Kuzyakov *et al.* (2000) *Soil Biol. Biochem.*, **32 (11-12),** 1485–1498.