

Mercury isotope fractionation during bio-accumulation in lichens

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Recently, mercury (Hg) isotope mass-independent fractionation (MIF) were reported in various lichens [1] and interpreted as the evidence for the atmospheric Hg to be a complementary reservoir to aquatic Hg [2] with respect to $\Delta^{199-201}\text{Hg}$. Recent data from the literature on more "direct" samples for atmospheric Hg [3, 4] suggest small Hg MIF, even slightly positive $\Delta^{199-201}\text{Hg}$, in contrast to significant negative $\Delta^{199-201}\text{Hg}$ values measured in lichens. This raised the question of the integrity of Hg isotopes measured in lichens relative to atmospheric matter, with the possibility of MIF during bio-accumulation.

A large amount of lichen tufts (*Evernia Prunastri*) was retrieved from trees in a small forest south of Nancy (France), rinsed with distilled water and dried at room temperature for a few days. Aliquots of bulk samples (1 g) were plunged into solutions (50 ml) containing various amounts of dissolved elements to simulate rain water. Lichens and solutions were in contact between 1 and 60 minutes (n=6).

Mass balance for Hg was calculated using Hg in lichens and Hg in the remaining solutions. Both were very similar suggesting that all Hg lost from the solution was pumped out by lichens (no wall adsorption). The $\delta^{202}\text{Hg}$ measured in lichens changed from -3.5‰ (initial value) to -0.5‰, interpreted as a progressive adsorption of solution Hg (0‰). However, Hg in the remaining solution shifted its $\delta^{202}\text{Hg}$ up to +1.5‰, decreasing with time, suggesting kinetic fractionation occurred when adsorption started. Isotopic equilibrium was not reached after 60% of total solution Hg was adsorbed by lichen ($\Delta^{202}\text{Hg}_{\text{sol-lichen}} \leq 1\text{‰}$).

Some lichens were exposed to sunlight (6 to 10 weeks) after being in contact with the NIST 3133 Hg, increasing their [Hg] variously from 0.15 to 18 $\mu\text{g/g}$. In all cases, no significant MIF were measured in both light exposed and non-exposed lichens, suggesting that bio-accumulation of Hg(II) by lichen do not result in MIF.

[1] Carignan et al. (2009) *Environ. Sci. Technol.* **43**, 5660-5664. [2] Bergquist & Blum (2007) *Science* **318**, 417-420. [3] Gratz et al. (2010) *Environ. Sci. Technol.* **44**, 7764-7770. [4] Sherman et al. (2010) *Nature Geosci.* **3**, 173-177.

Effect of initial Al concentration, pH and silicic acid on the formation and stability of tridecameric Al polymer

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Tridecameric Al polymer (the Keggin-type Al_{13} polycation)

Al^{3+} and its hydrolytic species which elute from soil due to the soil acidification have strongly toxic effect to plant and living organisms. In Al^{3+} hydrolytic species, tridecameric Al polymer (Keggin type Al_{13} polycation, $[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$) show the strongest toxicity. Surprisingly, Hunter and Ross detected Al_{13} in organic horizon of forested Spodosol in USA [1]. Much attention has been paid to the formation conditions of Al_{13} . According to the equilibrium calculation, at the total Al concentration of $10^{-5} \text{ mol/dm}^3(\text{M})$ which is the concentration level of soil solution, the occurrence of Al_{13} is sufficiently considered [2]. However, the detection of Al_{13} species such a low Al concentration is extremely difficult. Therefore, in this study, we developed the detection method of Al_{13} by ^{27}Al MAS NMR after adsorption onto chelate resin from solution with various Al concentration. Furthermore, we also studied the stability of Al_{13} on the solid surface and elution of Al species from solid surface and the effect of silicic acid to the formation and stability of Al_{13} .

When Al_{13} is formed in the soil environment, it is possible to adsorb on the surface of microbes and humic substances. In this study, the chelate resin was used as a model compound of the surface of microbes and humic substances because of similarity of functional group. For the concentration limit for the formation of Al_{13} , we could detect Al_{13} species after the adsorption onto chelate resin above 10^{-4} M . The pH range where Al_{13} can form in solution is very narrow [3], however, we also revealed that when Al_{13} adsorbed onto the resin, the pH range where it can exist clearly expanded. When the silicic acid coexisted in initial solution, the formation of Al_{13} distinguishably retarded.

[1] D. Hunter and D. S Ross, (1991) *Science* **251**, 1056. [2] G. Furrer et al., (1992) *Geochem. Cosmochim. Acta* **56**, 3831. [3] A. Etou et al., (2009) *J. Colloid Interface Sci.* **337**, 606.