A Distinct Magnetic Isotope Effect Measured in Atmospheric Mercury in Epiphytes

Sulata Ghosh and A. L. Odom (FSU, Geochemistry)

Introduction
Part of a study to determine the isotopic composition of mercury deposited from the atmosphere has involved the use of epiphytes as monitors. Here we have made high precision mercury isotopic measurements of samples of Spanish moss collected along the eastern Coastal Plain of the U.S. from northern Florida to North Carolina.

Experimental
Samples were dissolved in aqua regia. A CETAC HGX-200 hydride generator was used to produce a stream of cold vapor Hg that was introduced into the plasma of the Thermo-Finnigan Neptune MC-ICPMS. Mercury isotopes were measured by a standard-sample bracketing technique against the Hg standard SRM NIST3133 and recorded as $\delta^{\text{A}}\text{Hg}$ values. For example $\delta^{\text{A}}\text{Hg} = \{(^{\text{A}}\text{Hg}/^{202}\text{Hg})_{\text{sample}}/(^{\text{A}}\text{Hg}/^{202}\text{Hg})_{\text{NIST3133}}\} - 1 \times 1000 \text{ \%/oo}$

Results and Discussion
The $\delta^{\text{A}}\text{Hg}$ values indicate that the total isotopic fractionation for even-A isotopes relative to $^{202}\text{Hg}$ are proportional to atomic mass number, while the values $\delta^{199}\text{Hg}$ and $\delta^{201}\text{Hg}$ reflect a mass independent effect. When corrected for mass dependent fractionation, the odd-A isotopes $^{199}\text{Hg}$ and $^{201}\text{Hg}$ have non-zero residuals, and these are negative for all samples. These residuals are expressed as $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$. A plot of $\Delta^{199}\text{Hg}$ versus $\Delta^{201}\text{Hg}$ values obtained reveals a striking pattern.

All samples plot closely along a straight line passing through zero and having a slope of 1.11 (the ratio of the nuclear magnetic moments of $^{201}\text{Hg}/\Delta^{199}\text{Hg}$). The magnetic isotopic effect (MIE) as developed in theory by Buchachenko (1976) predicts nearly equal isotope separation of $^{199}\text{Hg}$ and $^{201}\text{Hg}$ from the odd-A isotopes because of their nearly equal nuclear magnetic moments and zero spin of the nuclei of even-A isotopes. Isotope fractionation by MIE is a kinetic effect influencing the recombination rates of free radical pairs and hence the partitioning of magnetic and non-magnetic nuclei between products and reactants.

Conclusions
Mercury deposited from the atmosphere is depleted in those isotopes with odd neutron numbers in nearly equal proportions as expected if isotope fractionation is due to the MIE. Recent laboratory experiments (Bergquist and Blum, 2007) have shown that Hg$^{2+}$ aqueous solutions from which Hg$^0$ vapor has been removed by phot-reduction is enriched in the odd-A isotopes. These findings seem to support the idea that natural evasion of mercury from waters by photolysis is a major source of atmospheric mercury.

Acknowledgements
U.S. EPA through STAR Grant R-83060301 and NSF Award No# 0106789.

References