Report on the Sixth International Symposium on Isotopomers; ISI 2012

18-22 June 2012, Carnegie Institution of Washington

with support for student travel expenses provided by

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by

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The ISI 2012 met in Washington, DC, 18-22 June 2012, bringing together researchers and their students spanning an unusually wide range of disciplines including quantum and physical chemistry, cosmochemistry, atmospheric chemistry, chemical oceanography, biogeochemistry, organic and inorganic geochemistry. The diversity of subject matter was matched geographically with 92 attendees hailing from Canada, China, Finland, France, Germany, India, Israel, Japan, the Netherlands, Russia, Switzerland, Taiwan, the United Kingdom, and the USA.

Although diverse, the group was united in its commitment to use the light stable isotopes of H, C, N, O, and S, with their equilibrium, kinetic, and intramolecular fractionations, to understand the material cycles and their dynamics between atmosphere, biosphere, hydrosphere, and lithosphere that make life possible on Earth.

A distinct benefit of a small meeting like ISI 2012 is the opportunity for everyone to talk to each other. The historic rooms of the Carnegie Institution of Washington offered a cozy and warm atmosphere for participants in ISI 2012 to talk science and life in a casual, relaxed, and in-depth fashion. Graduate students and postdoctoral researchers were particularly appreciative of being able to spend five days together with old and new colleagues in comfortable quarters. Many commented that they had gained a lot more in building their life-long working relationships with colleagues at this meeting than at larger meetings.

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The entire community of isotope researchers owes a debt of gratitude to Prof. Naohiro Yoshida, Tokyo Institute of Technology, for his leadership in establishing the International Symposium on Isotopomers as a definitive outpost on the frontier of knowledge. And we, the members of the scientific committee, are grateful for his encouragement and wise counsel.

Clumped Isotopes

The new discipline of "Clumped Isotopes" was well-represented at the Symposium. The word "clump" is used in an isotopic context to describe the substitution of two, or more, rare, heavy isotopes into the same molecule (Eiler, 2007, EPSL **262**, 309 – 327; Wang et al. 2004, GCA **68**, 4779 – 4794). Beginning with a molecule free from substitutions of rare isotopes, such as $^{12}CH_4$, and setting its abundance equal to 1, there follow in succession single-substituted molecules of $^{13}CH_4$ and $^{12}CDH_3$, with abundances of approximately 10^{-3} to 10^{-4}, double-substituted molecules $^{13}CDH_3$ and $^{12}CD_2H_2$ with abundances of 10^{-6} and 10^{-7}, respectively, and the triply-substituted molecules $^{12}CD_3H$ and $^{13}CD_2H_2$ with abundances less than 10^{-8}.

Reflecting the growing-pains of a developing discipline, there were as many contributions towards technical issues as there were applications at ISI 2012. Among the technical concerns were the problems of adequate mass resolution and the observed dependence of $\Delta^{47}CO_2$ on $\delta^{47}CO_2$. The importance of mass resolving power may be immediately grasped by observing that the molecules $^{13}C^{18}O^{16}O$ and $^{12}C^{17}O^{18}O$, both with integer mass 47, cannot be resolved with current gas source, electron impact isotope ratio mass spectrometers. A new generation of high mass-resolution mass spectrometers, Thermo-Scientific's "Ultra" and Nu Instruments "Panorama", are alleviating the problem, however. The Ultra is currently capable of resolving the $^{13}CDH_3$ peak from $^{13}CH_5^+$. The Panorama is under construction and offers the promise of even higher mass resolving power.

Applications of clumped isotope methods at ISI 2012 included (1) the first reported measurements of $^{17}O^{18}O$ and $^{18}O^{18}O$ in the atmosphere, (2) the analysis of modern marine carbonates to calibrate the temperature dependence of clumping of ^{13}C and ^{18}O in carbonate ion, (3) a comparison of growth temperatures derived from fluid inclusion measurements with temperatures based on analysis of clumping in carbonate ions of stalagmitic calcite, and (4) the use of clumped isotope carbonate geothermometry to deduce the evolution of hydrocarbon reservoirs. New theoretical contributions enable the prediction of clumping fractionation effects with improved accuracy.

Mass-Independent Fraction Effects In Multi-Sulfur And Oxygen Isotopes

Research on anomalous fraction effects in both oxygen and sulfur isotopes extracted from atmospheric, oceanic, and lithospheric samples or produced experimentally in the laboratory were presented in breath-taking diversity and profusion, reflecting the activities of a dynamic research community. Considering that anomalous O-isotope fractionations are now known from samples of oxygen dissolved in deep ocean water, from tropospheric CO_2, from nitrate and sulfate aerosol particles frozen in polar ice, from the tooth enamel of Cenozoic rodents, and from sulfate extracted from carbonate minerals 635 million years old, one may appreciate the role of ozone, with its capacity to transfer ^{17}O anomalies to that which it oxidizes, in providing a proxy for the absorption of solar ultraviolet light by O_2 and O_3 over the past millennia. Laboratory and *gedanken* experiments of the vaporization of SiO, the formation of ozone on liquid helium-cooled surfaces, thermal decomposition of carbonate, magnetic isotope effects, and reservoir isolation and mixing mechanisms give insights into alternative pathways for the generation of O-isotope anomalies. Continuing theoretical investigations of ozone are providing insights into symmetry-dependent isotope effects at quantum levels. Results presented at ISI 2012 confirm ozone to be the most fascinating molecule in Earth's atmosphere (although a strong case was made at the Symposium for the beguiling power of N_2O, see below).

The discovery of large mass-independent anomalies in sulfur isotopes of rocks and minerals more than 2.5 billon years old has inspired an explosive development in the measurement of isotopologue-specific adsorption cross-sections of SO_2 and OCS gases, candidates for inclusion as constituents of the Archean atmosphere, as well as direct observations of ultraviolet light photolysis of representative gas samples. Photoexcitation, photodissociation, self-shielding, as well as magnetic effects all have been proposed as mechanisms responsible for the production of mass-independent fractionations in sulfur isotope systems. Combinations of some or all of these mechanisms may eventually be shown to be determinative in specific environments. High-precision analyses of small, anomalous sulfur isotope fractionations in mid-oceanic basalts suggest additional geologic and biologic effects related to core-mantle segregation, the extraction of continents, subduction, and weathering.

Nitrous Oxide---N_2O

Nitrous oxide (N_2O, "laughing gas") is a linear molecule whose central site, flanked by N and O, prefers the substitution of ^{15}N. The molecule has a strong greenhouse effect and it contributes to catalytic losses of ozone in the stratosphere. Its abundance in the atmosphere has been growing since the advent of the Industrial Revolution. Mass spectrometric analysis of bulk $^{15}N/^{14}N$, $^{18}O/^{16}O$ isotope ratios and measurements of the preference of ^{15}N for the central site in the molecule are used to identify sources, sinks, and trace pathways through the atmosphere. This remarkable molecule is produced by soil microbes and its abundance is strongly affected by agricultural practices. Time series analyses over decades of N_2O's isotopic composition are revealing trends in abundance and isotopic composition in the atmosphere. Controlled agricultural experiments are

enhancing understanding of the complex soil cycle of N_2O. With a variety of investigations ranging from field-based atmospheric and agricultural studies to laboratory measurements of photolysis reactions, a need for calibrated interlaboratory reference materials is recognized. Participants at ISI 2012 agreed upon a strategy of round-robin sample exchange for the purpose of interlaboratory calibration.

High-resolution Spectroscopy

Mass-spectroscopy was the method chosen by most ISI 2012 investigators for measurement of isotope substitutions. There is an important development of growing significance, however in the use of non-mass spectrometric spectroscopies for isotopic analyses. Nuclear magnetic resonance spectroscopy (NMR) has successfully been used to measure site-specific $^{13}C/^{12}C$ ratios in organic molecules. Furthermore, NMR can provide site-specific analyses of $^{2}H/^{1}H$ ratios in organic molecules. Quantum cascade laser absorption spectroscopy has been shown to measure to high precision in N_2O samples bulk $^{15}N/^{14}N$ as well as $^{15}N/^{14}N$ site preferences. A tunable difference frequency generation spectrometer was used to measure ratios of the methane isotopologues $^{13}CH_3D/^{12}CH_3D$ and $^{13}CH_3D/^{12}CH_4$ at mid-infrared wavelengths. These methods all require cross-calibration with mass spectrometric measurements, a task well-suited to the talents of members of the ISI 2012 research community.

The next ISI: 2014.

The value of bringing together isotope practitioners, their graduate students, and post-doctoral fellows from a wide variety of disciplines, theoretical, atmospheric, agricultural, geochemical, and cosmochemical has once again been demonstrated. Everyone is looking forward to the next International Symposium on Isotopomers for inspiration in enhancing stable isotope theory, experiments, and applications. ISI 2014 will be held in Japan (location to be determined) and will be hosted by Prof. Naohiro Yoshida, Tokyo Institute of Technology.