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The sea surface concentration of chlorophyll in the northern Gulf of Mexico was derived from satellite remote sensing for the period of July 2001 to June of 2002. High resolution (L1A data, with 1 km spatial resolution) Sea-viewing Wide Field of view Sensors (SeaWiFS) data were used to calculate chlorophyll with the OC4 algorithm for all the clear and partly cloudy days. The chlorophyll pattern shows strong seasonal variation. In offshore areas, a single annual phytoplankton bloom was observed with chlorophyll concentration increasing in fall and winter to reach a maximum of 0.35 mg m⁻³ in February, and decreasing in spring and summer to a minimum of 0.1 mg m⁻³ in July. In coastal regions from the Texas shelf through Mississippi Sound, phytoplankton blooms were observed in February and July. During the bloom in summer, patches of high chlorophyll surface waters were injected into offshore waters. The chlorophyll concentration decreased from ~10 mg m⁻³ near the mouth of the Mississippi River and on the Louisiana shelf to ~5 mg m⁻³ on the Texas shelf and the Mississippi Sound. The temporal and spatial distribution of the phytoplankton bloom in summer coincides with reported annual hypoxia events.

B61D MCC: 132 Saturday 0830h Mass Independent Isotope Fractionation: New Frontiers in Isotope Biogeochemistry I (joint with A, V, GC, PP)

Presiding: G Michalski, University of California, San Diego; B Alexander, University of California, San Diego; J Savarino, Laboratoire de Glaciologie et Gophysique de l'Environnement

B61D-01 0830h

Mass Independent Isotope Effects and Their Occurrence in Nature

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It has been nearly 20 years since the discovery of a chemically produced mass independent isotope effect by Thiemens and Heidenreich. Subsequent to that time there has been a great deal of progress in developing a physical chemical theory to account for the effect. In particular, recent work by R. Marcus and colleagues has advanced understanding of the effect considerably.

There are now many know examples of mass independent isotopic compositions in nature, in fact, with the exception of water, all atmospheric molecules possess mass independent isotopic compositions. This includes O₂, O₃, CO₂, H₂O₂, N₂O, CO, and atmospheric aerosol sulfate and nitrate. In addition, sulfur in aerosol sulfate is mass independently fractionated and it is now known that the anomalies are preserved in Miocene Volcanic samples, Namibian desert sulfate, Pre-Cambrian sulfate and sulfide (sulfur isotopes), and sulfates from the Antarctic dry valleys. Polar ice samples are also known to preserve the mass independent isotopic anomalies. In addition, secondary minerals from the SNC Martian meteorites possess both sulfur and oxygen isotopic anomalies which are used to understand atmospheric-regolith coupling. In all cases where mass independent isotopic compositions have been observed, understanding of the particular cycle has been advanced.

B61D-02 0845h INVITED

Mass Independent Isotope Effect in Ozone and in the Earliest Processed Solids in the Solar System

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The main concepts in a theory are described for the mass-independent isotope effect in ozone formation discovered by Thiemens. They include (1) the relative lifetimes of the symmetric (OOQ*, OOO*) and asymmetric (OOQ*) vibrationally excited ozone intermediates, Q is ¹⁷O or ¹⁸O, (2) the differences in zero-point energy in the two exit channels of a dissociating

OOQ* molecule, and (3) "weak" deactivating collisions. The first plays a major role under the usual ("scrambled") conditions and causes the mass-independent isotope effect. The second produces large and unusual mass-dependent isotopic effects observed by Mauersberger under "unscrambled conditions," but cancels exactly under the scrambled conditions. Their theoretical basis is described. The third plays a role under both sets of conditions. We also discuss whether analogous concepts, particularly the first, are applicable to the formation of the earliest processed solids in the solar system, the calcium-aluminum-rich inclusions in meteorites, for which a mass-independent isotope effect was first observed by Clayton.

URL: <http://chemistry.caltech.edu/faculty/marcus/index.html>

B61D-03 0925h

The Temperature Dependence of Positional Resolved ¹⁸O Fractionation in Ozone

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The formation of ozone by the well known Chapman reaction O + O₂ + M → O₃ + M shows a large and unusual isotope effect. Laboratory predictions of oxygen fractionation in ozone molecules containing singly substituted ¹⁷O or ¹⁸O match well with both tropospheric and stratospheric observations. Quantitative modelling and understanding of isotope transfer from ozone into other atmospheric species (CO₂, N₂O, etc.), however, remains difficult or even impossible, since the positional fractionation in atmospheric ozone either is not accurately known (for ¹⁶O¹⁶O¹⁷O vs. ¹⁶O¹⁷O¹⁶O) or, when accurate measurements exist, published values obtained by different techniques seem to be in striking difference (for ¹⁶O¹⁶O¹⁸O vs. ¹⁶O¹⁸O¹⁶O).

Here we present mass spectrometric measurements of a temperature study of ozone forming rate coefficient ratios and oxygen fractionation values in ⁵⁰O₃, ⁵²O₃ and ⁵⁴O₃. The results are combined with the findings of earlier symmetry specific diode laser absorption spectroscopic (TDLAS) measurements in order to predict the temperature dependence of [¹⁶O¹⁶O¹⁸O]/[¹⁶O¹⁸O¹⁶O]. By numerical simulation of the isotope kinetics of ozone sample preparation in other symmetry resolving studies employing fourier transform far infrared (FTFIR) spectroscopy it is demonstrated that the seemingly differences in dependence of [¹⁶O¹⁶O¹⁸O]/[¹⁶O¹⁸O¹⁶O] between TDLAS experiments in the mid IR and the FT experiments in the far IR are not caused by experimental artefacts, but are rather due to the different temperature conditions in the two sets of experiments.

Therefore, the temperature dependence of end member enrichment of atmospheric ⁵⁰O₃ seems now to be well characterized for the first time and it can be used in quantitative modelling of isotope transfer from ozone into other atmospheric molecules.

B61D-04 0940h INVITED

Isotope transfer from O₃ to CO₂ in light of the ozone isotope anomaly

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An increasing amount of information is presently becoming available about the anomalous oxygen isotopic composition of atmospheric ozone. Due to its active role in atmospheric chemistry, the ozone isotope anomaly is transferred to a number of atmospheric constituents. The well established transfer to CO₂ via O(¹D) is responsible for the strong ¹⁷O and ¹⁸O enrichments of CO₂ in the stratosphere. However, in stratospheric CO₂ the ¹⁷O enrichment is considerably larger than the ¹⁸O enrichment, opposite to the situation for ozone, which implies a preferential transfer of ¹⁷O. New laboratory experiments are being carried out to study this transfer, which may involve an additional anomalous fractionation process. At the same time, detailed position resolved investigations of the ozone isotopic composition also provide new information about

the isotope transfer, which primarily involves the terminal oxygen atom. In light of these new data we evaluate various possible scenarios for the CO₂ - O₃ isotopic exchange.

B61D-05 0955h

Oxygen Isotope Anomalies in Carbon Dioxide: From the Laboratory to the Stratosphere

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A number of studies have suggested that the oxygen isotope anomaly in stratospheric CO₂ (defined as Δ¹⁷O = δ¹⁷O - 0.516 * δ¹⁸O) can be used as a tracer of integrated chemistry and transport in the stratosphere,¹ of stratosphere-troposphere exchange,² of gross carbon exchanges between the terrestrial biosphere and atmosphere,³ and, through the impact of anomalously fractionated CO₂ on the O₂ reservoir, of gross global primary productivity on millennial timescales through ice core measurements of O₂.⁴ Bringing these applications to fruition, however, requires a more fundamental understanding of the source and mechanism(s) of the anomalous fractionation in CO₂ than is currently available. Several new suites of laboratory and field measurements that address the source(s) of the oxygen isotope anomaly in CO₂ will be presented. Measurements of Δ¹⁷O of CO₂ from whole air samples collected from the NASA ER-2 aircraft and their correlation with trace gases measured in situ while the samples were being collected, such as N₂O and O₃, provide important new information as to the source and mechanism(s) of the anomalous enrichment in the stratosphere. Laboratory investigations of the reaction CO₂ + O(¹D) in a crossed molecular beam, of photochemical kinetics and isotope measurements in irradiated CO₂ / O₂ mixtures, and of isotope effects in the photolysis of CO₂ at different wavelengths are providing additional information. These new laboratory and field data will be discussed and compared with previous studies.

References: (1) K. Boering, *et al.*, *Eos Trans. AGU*, 79(45), A42F-06, 1998; (2) M. Thiemens, *et al.*, *Science* 270, 969, 1995; Y. Yung, *et al.*, *JGR* 102, 10857, 1997; (3) K. Hoag, *et al.*, *Eos Trans. AGU*, 82(47), B12A-0109, 2001; (4) B. Luz, *et al.*, *Nature* 400, 547, 1999.

B61D-06 1030h INVITED

How Large is the Mass Independent O-17 Anomaly in the Atmosphere?

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The isotopic composition of atmospheric oxygen is controlled by biological mechanisms, the hydrological cycle and stratospheric photochemistry. The biological mechanisms include photosynthetic oxygen production of identical isotopic composition as the substrate water and oxygen uptake by various mechanisms with mass dependent fractionation. Fractionation in the hydrological cycle is also mass dependent. In contrast, stratospheric photochemistry also removes oxygen, but fractionates the isotopic composition of the remaining gas in a mass-independent way. As a result atmospheric oxygen becomes anomalous (O-17 depleted) with respect to oxygen of the global atmosphere that would have been produced in the absence of stratospheric photochemistry. For estimating the magnitude of this anomaly, it is necessary to know the triple isotope fractionations of the relevant global processes. In the present research we carried out experiments in order to determine the ratio between the discriminations against O-17 and O-18 in dark respiration and in photorespiration. The obtained values are 0.518 and 0.506 respectively, and are different than in meteoric water fractionation (0.525). Assuming that the latter value applies to leaf-water (the substrate of all terrestrial photosynthesis), we estimate the magnitude of the anomaly as 258 permeg. This figure is significantly larger than 117 permeg estimated from stratospheric mass balance. Alternatively, by talking the 117 permeg value as representative of the anomaly, we calculate the ratio between the discriminations against O-17 and O-18 in leaf water as 0.511. Clearly, if we are to correctly estimate the atmospheric anomaly, careful determination of the triple isotope composition of global leaf-water is a prerequisite.

B61D-07 1045h

Tracing the Origin of the Oxygen-17 Anomaly of Tropospheric Oxygen

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It is now well established that many oxygen-bearing constituents of the Earth's atmosphere are characterized by mass-independent isotopic compositions. The isotopic anomaly of the most abundant of these constituents, molecular oxygen itself, has until recently been attributed solely to stratospheric O₂ influx, with the latter deriving its anomalous ¹⁷O depletion via reactions involving the formation and photolysis of stratospheric ozone. Accurate characterization of relatively small ¹⁷O anomalies, to a $\Delta^{17}\text{O}$ precision of a few tens per meg or better (where one per meg equates to 10^{-3} per mil), requires that the conventional reporting system of the three-isotope plot be revised to a truly linear (non-approximated) format that gives consistent slope values irrespective of the isotopic composition of the reference material or the range of attendant δ values. With this approach, a comparison of high precision measurements of the oxygen three-isotope fractionation line characteristic of terrestrial silicate rocks and waters (Miller, *Geochim. Cosmochim. Acta* 66, 1881-1889, 2002), on the one hand, and the line associated with aerobic respiration, (Luz et al., *Nature* 400, 547-550, 1999) on the other hand, reveals that the stratospheric O₂ influx contributes only about 56% of the total isotopic anomaly. Several conclusions may be inferred from these observations. Firstly, diverse geological processes and the abiotic hydrological cycle appear to produce a single 'bulk Earth' oxygen three-isotope fractionation line that is tightly constrained to a remarkable degree. This provides a robust and widely applicable reference datum from which ¹⁷O anomalies may be identified and quantified. Secondly, through rapid isotopic exchange with water, tropospheric CO₂ also fits on the same line. Thirdly, the slope is of notably greater magnitude than that associated with the isotopic fractionation of oxygen during aerobic respiration. With regard to the tropospheric O₂ component derived from stratospheric influx, it is generally accepted that its three-isotope composition is attributable to a sequence of reactions which transfers anomalous ¹⁷O enrichment from stratospheric ozone to coexisting CO₂, with concomitant depletion of ¹⁷O in the O₂ reservoir. The mechanism proceeds via photolysis of ozone to give O(¹D) and O₂, followed by reaction of the former with CO₂ to give a CO₃* complex which subsequently dissociates to CO₂ and O(³P). Hitherto, it has been assumed that this sequence transfers an existing isotopic anomaly without changing its magnitude. However, the recent finding that thermal decomposition of simple inorganic carbonates (under conditions which minimize the potential for back-reaction) itself generates anomalous ¹⁷O compositions in the decomposition products (Miller et al., *Proc. Natl. Acad. Sci. USA* 99, 10988-10993, 2002), suggests that dissociation of the CO₃* complex might modify the value of the inherited isotopic anomaly. In conjunction with recent measurements of the three-isotope composition of stratospheric CO₂ and coexisting ozone (Lämmerzahl et al., *Geophys. Res. Lett.* 29, 10.1029/2001GL014343, 2002), this possibility provides further potential clues towards elucidating the origin of that proportion ($\Delta^{17}\text{O} = 0.19$ per mil) of the isotopic anomaly in tropospheric O₂ which cannot be accounted for simply on the basis of the difference in fractionation line slope values between aerobic respiration and the bulk Earth (silicate and waters) oxygen reservoir.

B61D-08 1100h INVITED

Implications of $\Delta^{33}\text{S}$ for Evolution of Earth's Sulfur Cycle and Atmosphere

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The recent observation of large magnitude $\Delta^{33}\text{S}$ anomalies in parts of the rock record has changed the way that we view the sulfur cycle. On the basis of $\Delta^{33}\text{S}$ we can divide the sulfur cycle into three distinct phases - an Archean phase, an early Paleoproterozoic phase, and a modern phase. The occurrence of large magnitude $\Delta^{33}\text{S}$ anomalies in rocks of Archean age (>2.45 Ga) is attributed to deep UV photolysis of sulfur dioxide in an atmosphere that was largely anoxic with $\leq 10^{-5}$ PAL O₂. The presence of multiple exit channels for both oxidized and reduced atmospheric sulfur allowed efficient transfer of sulfur isotope anomalies to the Earth's surface reservoirs under these conditions (see Pavlov and Kasting, 2002). The absence of an active cycle of surface oxidation and bacterial (?) sulfate

reduction insured preservation of the anomalies in the rock record. During the early Paleoproterozoic (<2.45 Ga but > 2.1 Ga) the occurrence of isotopic anomalies with substantially smaller magnitudes points to an atmosphere with higher but probably still diminutive levels of oxygen. As suggested by variations in $\Delta^{33}\text{S}$ associated with rocks representing global glacial intervals, oxygen levels were probably fluctuating during this interval and reflect the preference of Earth's atmosphere for either a stable reduced or oxidized state. The absence of measurable anomalies in the rock record after 2.1 Ga points to an atmosphere that has been largely oxidized ($> 10^{-5}$ to 10^{-2} PAL O₂) since then. New $\Delta^{33}\text{S}$ data from a variety of terrestrial rock samples provide unique insights into the nature of Earth's early surface environment and allow well-constrained speculation about the evolution of Earth's sulfur cycle.

B61D-09 1115h INVITED

Measurements and Modeling of $\Delta^{17}\text{O}$ Variations in Atmospheric Nitrate

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The estimated doubling of HNO₃ production in the atmosphere in the next 50 years is important from both an ecological and an atmospheric chemistry perspective. The removal of NO⁻³atm (HNO₃ + aerosol nitrate) by dry and wet deposition can initiate serious environmental consequences including soil acidification, forest decline, the alteration of native plant diversity, and the promotion of eutrophication and toxic algae blooms in coastal waters. A reliable, quantitative, tracer of NO⁻³atm deposition, particularly in regions with multiple nitrate sources and heavy nitrogen cycling is still lacking. In the atmosphere, HNO₃ production is the primary sink for NO_x, which via direct and catalytic production of ozone regulates the oxidative capacity of the troposphere. The impact heterogeneous versus homogenous HNO₃ production exert on global O₃ and OH steady state concentrations has also been demonstrated in Global 3-D chemical models. Yet, the extent that anthropogenic activities have impacted heterogeneous and homogenous production, and how these pathways varied on ancient time scales is also unknown. Nitrate aerosols were collected in La Jolla, Ca. for a one-year period and their oxygen isotopic composition were analyzed ($\delta^{18}\text{O}$ and $\delta^{17}\text{O}$). A large $\Delta^{17}\text{O}$ ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.515 \delta^{18}\text{O}$) was observed and this isotopic signature exhibited a strong seasonal amplitude. The variability in $\Delta^{17}\text{O}$ is attributed to variability in HO_x and O₃ oxidation rates and the seasonal variation of homogenous versus heterogeneous nitric acid formation reactions. An isotopic model coupled to a photochemical box model reproduced the observed $\Delta^{17}\text{O}$ with good precision. Implications for the use of $\Delta^{17}\text{O}$ in nitrate as an investigative tool for NO_x related chemistry in both present day atmosphere and in ancient atmospheres is discussed. The magnitude of the $\Delta^{17}\text{O}$ signature also has implications as a tracer of atmospheric nitrogen deposition. Both the increased detection sensitivity, the ability to more accurately quantify nitrate deposition, and its insensitivity to post deposition fractionations (chemical, physical, biological) make $\Delta^{17}\text{O}$ measurements superior to current $\delta^{18}\text{O}$ methods for deposition studies.

B61D-10 1130h

Analysis of Atmospheric Nitrate Deposition in Lake Tahoe Using Multiple Oxygen Isotopes

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Lake Tahoe in the Sierra Nevada Mountain Range is world renowned for its depth and water clarity bringing 2.2 million visitors per year resulting in annual revenue of \$1.6 billion from tourism. In past decades the

lake has suffered from decreased water clarity (from 32 m plate depth to less than 20), which is believed to be largely the result of algae growth initiated by increased nutrient loading. Lake nutrients have also seen a shift from a nitrogen limited to a phosphorus limited system indicating a large increase in the flux of fixed nitrogen. Several sources of fixed nitrogen of have been suggested including surface runoff, septic tank seepage from ground water and deposition from the atmosphere. Bio-available nitrogen in the form of nitrate (NO₃⁻) is a main component of this system. Recent studies have estimated that approximately 50% of the nitrogen input into the lake is of atmospheric origin (Allison et al. 2000). However, the impact and magnitude of atmospheric deposition is still one of the least understood aspects of the relationship between air and water quality in the Basin (TRPA Threshold Assessment 2002).

The utility of stable isotopes as tracers of nitrate reservoirs has been shown in several studies (Bohlke et al. 1997, Kendall and McDonnell 1998, Durka et al. 1994). Stable nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotopes have been implemented in a dual isotope approach to characterize the various nitrate sources to an ecosystem. While $\delta^{18}\text{O}$ distinguishes between atmospheric and soil sources of nitrate, processes such as denitrification can enrich the residual nitrate in $\delta^{18}\text{O}$ leaving a misleading atmospheric signature. The benefit of $\delta^{15}\text{N}$ as a tracer for NO₃⁻ sources is the ability to differentiate natural soil, fertilizer, and animal or septic waste, which contain equivalent $\delta^{18}\text{O}$ values. The recent implementation of multiple oxygen isotopes to measure $\Delta^{17}\text{O}$ in nitrate has proven to be a more sensitive tracer of atmospheric deposition. The oxygen isotopes of atmospheric nitrate are mass-independently fractionated and contain $\Delta^{17}\text{O}$ values of 20 to 30 ‰, while all other sources are mass dependent ($\Delta^{17}\text{O} = 0$ ‰). Any subsequent fractionation of the atmospheric nitrate will leave the mass-independent signature unchanged making $\Delta^{17}\text{O}$ of nitrate a conservative tracer of atmospheric nitrate. Results from measurements of the oxygen isotope composition of nitrate in Lake Tahoe are used to resolve the atmospheric contribution.

B61D-11 1145h

Sulfur oxidation chemistry preserved in South Pole snow and ice: The origin of sulfur and oxygen mass-independent fractionations generated in plinian eruptions.

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Large explosive volcanic eruptions directly inject large amounts of SO₂ into the stratosphere. This gas is rapidly oxidized to sulfuric acid, which forms droplets that significantly enhance the stratospheric aerosol loading. This aerosol layer quickly disperses on a global scale and exerts an extra forcing on the earth's climate system. The volcanic explosions of El Chichon (1982, 17°N, 93°W) and Mount Pinatubo (1991, 15°N, 120°W) injected an estimated 7 and 15 Tg of SO₂ into the stratosphere. These two plinian eruptions were well-documented with modern instruments (ground-based, satellites, stratospheric balloons, etc) and the data revealed how these massive eruptions significantly disrupted the entire atmosphere.

The detailed analysis of oxygen and sulfur isotopic ratios ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, and $\delta^{36}\text{S}$) of sulfate is a unique tool to investigate the atmospheric chemical perturbation induced by large volcanic eruptions. Kinetics, evaporation/condensation, diffusion, gravity and thermodynamic isotopic fractionation processes produce a highly mass-dependent correlated arrays with $\delta^{17}\text{O} = 0.515 \delta^{18}\text{O}$ and $\delta^{33}\text{S} = 0.515 \delta^{34}\text{S}$. Isotopic ratios that deviate from this norm (called Mass-Independent Fractionation or MIF), and quantified by $\Delta^{17}\text{O}$ and $\Delta^{33}\text{S}$: $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.515 \delta^{18}\text{O}$, and $\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515 \delta^{34}\text{S}$ are the result of a select number of photochemical reactions. These isotopic anomalies can be used intelligently to probe a variety of atmospheric reaction mechanisms.

We have applied this new isotopic tool to volcanic horizons preserved in ice cores in order to gain new

insight into the stratospheric chemical perturbation induced by large volcanic eruptions. Three events with very different dynamics that are well preserved in South Poles snow and ice have been sampled. The total isotopic analysis of the volcanic sulfate ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$, $\delta^{34}\text{S}$, $\delta^{33}\text{S}$, and $\delta^{36}\text{S}$) of Mount Pinatubo (June 1991, 15Tg SO_2), Cerro Hudson (August 1991, 2 Tg SO_2) and the 1259 AD unknown event (320 Tg SO_2), along with the backgrounds surrounding these events have been carried out.

No $\Delta^{33}\text{S}$ was found for the background and Cerro Hudson sulfate samples, but they both show similar $\Delta^{17}\text{O}$ of 2.7 and 2.2 ‰, respectively. In contrast, both the Pinatubo and the 1259 AD produced sulfate with a $\Delta^{33}\text{S}$ (0.60 and -0.42 ‰, respectively). However and surprisingly, sulfate generated by the Pinatubo eruption have a much higher $\Delta^{17}\text{O}$ (4.7 ‰) relative to the 1259 AD, (0.8 ‰) despite the fact that both were well injected into the stratosphere. A tentative explanation on how similar eruptions can induce a sulfur MIF, and $\Delta^{17}\text{O}$ with such differing values will be given in the currently accepted isotope theoretical framework and the use of a photochemical model.

B62A MCC: 134 Saturday 1330h

Terran and Synthetic Environments: Where in the Solar System Can They Take Us? (joint with OS, P)

Presiding: J Baross, University of Washington; **M Meyer**, NASA Office of Space Science

B62A-01 1335h INVITED

Titan and the Origin of Life

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The known organic environments in the solar system other than the Earth and certain meteorites are in the outer solar system. Those of astrobiological interest or potential are Europa, Titan, and comets. Europa may contain organic compounds in a subcrustal liquid water environment, but this assumption will not be tested until after 2010. Titan is of interest because it is known to generate suites of hydrocarbons and nitriles in its stratosphere, which then fall to the surface and are protected from damaging particle and UV radiation by a thick atmosphere. Further chemistry, including in the presence of transient and localized areas of liquid water, may proceed on the surface in staccato fashion over geologic time. Titan, in summary, provides us with a planet-sized laboratory for testing the synthesis of organic compounds in a nearly neutral redox environment, over large spatial scales, both with and without liquid water. These natural chemical experiments could be ongoing today, and the products of such experiments in localized regions of elevated temperatures would be well preserved under the ambient 95 K temperatures and high atmospheric densities that shield the surface from destructive radiation. The Cassini-Huygens mission will make a complete inventory of the surface from a variety of remote sensing and in situ techniques, over the time period late 2004 through late 2008. In support of future exploration of Titan beyond Cassini-Huygens, the NASA Astrobiology Institute has initiated a Titan Focus Group, whose operation and initial results will be discussed.

URL: <http://www.nai.arc.nasa.gov/institute>

B62A-02 1350h INVITED

Alternative Life Styles for Extraterrestrial Chemists

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Life is no more (and no less) than a special type of organic chemistry, one that combines a frequently encountered property of organic molecules (the ability to undergo spontaneous chemical transformation) with an uncommon property (the ability to direct the synthesis of self-copies) in a way that allows new molecular features arising through spontaneous transformation to themselves be copied. Any chemical system having this combination will undergo natural selection, evolving in structure to replicate faster through more efficient use of molecular resources and energy. Axiomatically, life

cannot exist in an environment at thermodynamic equilibrium. If it were, by the second law of thermodynamics, no net chemical transformation would be possible. Beyond this constraint, it is difficult to define environmental conditions or chemical structures necessary for life. Water is certainly not required for a chemical system to copy itself; in the laboratory, non-aqueous environments appear to support this behavior better. Chemical transformations that might support energy and chemical metabolisms are known in environments as acidic as the aerosols in the atmosphere of Venus, or as basic as the atmosphere of Jupiter. Laboratory experiments with analogs of the nucleic acids, proteins, sugars, and lipids show that the particular molecular structures found in terrestrial life need not be universal, even those life in water near neutral pH. Indeed, while both water and biological macromolecules are commonly regarded as essential for terrestrial-like life, water destroys terrestrial biological macromolecules.

These chemical realities create a complex decision environment as NASA attempts to design instrumentation carried by missions, select places in the solar system to send them, and choose laboratory studies on Earth to provide their scientific support. This talk will review a hierarchy of chemical possibilities and constraints that start with the chemistry of terrestrial life, and takes steps towards weird life. We shall consider alternative amino acid building blocks for proteins, alternative building blocks for nucleic acids, alternative structural features of genetic and catalytic molecules, alternative nucleophile-electrophile pairs to support metabolism, non-polar reaction modes that might support metabolism, non-terrestrial pH (< 0, > 14) and solvent environments for life, extreme temperature ranges (especially sub zero Celsius) low temperature ranges, alternative thermodynamic design for metabolic pathways, alternative dimensionalities of genetic and catalytic molecules, and approaches for isolating life other than conventional cell structures. Each of these discussions will combine experimental and theoretical information. The first involves organic chemical synthesis that creates new forms of chemical matter to ask "What if?" and "Why not?" questions. The second draws on a century of literature in physical organic chemistry to formulate general constraints on the structure and transformation of organic matter to provide constraints on possible Darwinian chemistries in the galaxy.

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The Ultramafic-Hosted Lost City Hydrothermal Field: Clues in the Search for Life Elsewhere in the Solar System?

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The recent discovery of the peridotite-hosted Lost City Hydrothermal Field (LCHF) raises the possibility that such systems are prevalent not only on Earth, but that similar systems may have existed, or currently exist, elsewhere in the solar system. The LCHF, which rests atop the Atlantis massif at 30N on the Mid-Atlantic Ridge, is unlike any previously known hydrothermal field: 1) it is located on 1.5 my-old crust, nearly 15 km west of the spreading axis; 2) it hosts at least 30 active and inactive carbonate-brucite chimneys that tower up to 60 m above the seafloor; 3) the venting pinnacles appear to be the surface expression of warm (40-75°C), high pH (9-10) fluids emanating from fault zones that tap a region of active serpentinization in the underlying peridotites; and 5) hydrothermal flow is facilitated by exothermic serpentinization reactions at depth. The diffusely venting fluids support dense and diverse communities of mesophilic to hyperthermophilic organisms that may include sulfur-, methane- and hydrogen-oxidizers.

The Lost City Field may represent our closest analogue to hydrothermal systems operative during early Earth where ultramafic rocks were predominant. The reducing conditions associated with serpentinization of ultramafic material may be similar to those present in the Hadean ocean (4.5-3.9 Gyr) and it has been suggested that such high-pH systems were a requirement for the emergence of life on the seafloor. Model calculations based on thermodynamic considerations and experimental studies suggest that synthesis of numerous organic compounds is favored during mixing of warm, serpentinite-derived, high-pH, reducing fluids with cool, oxygenated seawater. Dissolved hydrogen, present in hydrothermal fluids due to reaction of olivine and other iron-bearing minerals with fluids, provides

the reduction potential and the thermodynamic drive for organic synthesis. Significant quantities of methane and hydrogen produced during serpentinization reactions form critical nutrients for microbial communities within submarine systems.

Many of the carbonate-veined serpentinites (ophicalcites) and breccias that underlie the LCHF are similar to those known from ancient ophiolites, including Archean (>3000 m.y. old) examples. These types of assemblages may represent a linkage to hydrothermal and possibly biological activity at the time of the oldest known life on Earth. The warm, organic- and volatile-enriched environment present within the porous interior of ancient hydrothermal deposits may have been extremely suitable habitats for the emergence of thermophilic or hyperthermophilic anaerobic organisms capable of utilizing methane and hydrogen.

The LCHF may provide new insights into the search for life elsewhere in the solar system. This hydrothermal field highlights the fact that volcanic heat is not a requirement for fluid flow, but that a large component of energy to drive flow may come directly from exothermic reactions as fluids interact with ultramafic material. It also shows that hydrothermal systems, and the life that they support, can exist far away from major spreading centers. Collectively, these observations indicate that water-bearing planets, chondritic in composition, that have experienced tectonic processes are potential sites for Lost City type systems and life.

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Direct Observations Of Microbial Activity At Extreme Pressures

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Microbial communities adapt to a wide range of pressures, temperatures, salinities, pH, and oxidation states. Although, significant attention has been focused on the effects of high and low temperature on physiology, there is some evidence that elevated pressure may also manifest interesting effects on cellular physiology, such as enzyme inactivation, cell-membrane breach, and suppression of protein interactions with various substrates. However, exactly how these factors affect intact cells is not well understood. In this study, we have adapted diamond anvil cells to explore the effects of high pressure on microbial life. We used the rate of microbial formate oxidation as a probe of metabolic viability. The utilization of formate by microorganisms is a fundamental metabolic process in anaerobic environments. We monitored in-situ microbial formate oxidation via molecular spectroscopy for *Shewanella oneidensis* strain MR1 and *Escherichia coli* strain MG1655 at high pressures (68 to 1060 MPa). At pressures of 1200 to 1600 MPa, living bacteria resided in fluid inclusions in ice-VI crystals and continued to be viable upon subsequent release to ambient pressures (0.1 MPa). Furthermore, direct microscopic observations indicate that these cells maintain their ability for cellular division upon decompression from such high pressures. Evidence of microbial viability and activity at these extreme pressures expands by an order of magnitude the range of conditions representing the habitable zone in the solar system. These results imply that pressure may not be a significant impediment to life. The maximum pressure explored in this work is equivalent to a depth of ~ 50 km below Earth's crust, or ~ 160 km in a hypothetical ocean. The pressures encountered at the depths of thick ice caps and deep crustal subsurface may not be a limiting factor for the existence of life. This suggests that deep (water/ice) layers of Europa, Callisto, or Ganymede, subduction zones on Earth, and the polar ice caps of Mars might provide viable settings for life unhindered by the high pressures.