Of the five key light stable isotope biomarkers, C, H, O, N and S, oxygen has received relatively limited application to the search for life and previous oxygen isotope studies of extraterrestrial materials have often focused on oxygen in carbonates and silicates. This is due, in part, to the limited study and development of other oxygen isotope ratio systems relevant to biological activity (e.g., phosphate, sulfate, nitrate) specifically for application to the search for extraterrestrial life. An overview of oxygen isotope biomarker systematics will be presented with emphasis on development of O isotope ratios of phosphate as a new biomarker in the search for life on Mars and Europa. Phosphate is central to life on Earth and has been widely recognized and applied as a biomarker molecule in the form of phosphate minerals, in studies of ancient life on Earth. The lack of multiple stable isotopes of P precludes direct stable isotope ratio studies of P, however, its occurrence as predominantly orthophosphate, PO_4, permits the use of oxygen isotope ratios of PO_4 to trace enzymatic reactions and biological cycling of P in natural environments. The unique chemical properties of PO_4 also make $\delta^{18}O$ values of inorganic environmental PO_4 (e.g., PO_4 in soils, rocks; dissolved PO_4) an ideal signature of the presence of both extant and extinct biological (enzymatic) activity as well as hydrothermal activity. Fundamental processes underlying the recording of biological signals in oxygen isotope ratios of environmental phosphate and development and application of $\delta^{18}O_P$ as a biomarker for Mars will be discussed, including characterization of $\delta^{18}O_P$ signatures of key Martian PO_4 source reservoirs by analysis of Martian meteorites, and consideration of the coevolution of $\delta^{18}O_P$ signatures with life on Mars and in terrestrial analogue systems.

P52B-06 1445h

Oxygen Isotope Composition of Silica in ALH84001: Implications for Water on Early Mars

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The oxygen isotopic compositions of silica and SiO2-rich glass have been measured in situ by ion microprobe in the Martian meteorite ALH84001. Two different textural occurrences, a large anhedral (40x60m) partially crystalline silica grain and a SiO2-rich glass-rich region of a granular band, have been studied. The large silica grain has been studied by electron microprobe [1] and micro-Raman spectroscopy [2] and is found to be compositionally similar to the fine-grained SiO2-rich regions in the granular band [1]. The SiO2-rich glass is finely intergrown with carbonate (of limited compositional range), chromite, feldspar and orthopyroxene. 18O/16O ratios were measured using the UCLA ims 1270 ion microprobe in multicollector mode using quartz mineral standards. Three analyses of the large silica grain in 2 analytical sessions gave a small range in oxygen isotopes (d18O=+24.41+/-0.80per mil to +25.3+/-2.6per mil; 2s); a similar range was measured for four regions of SiO2-rich glass in the granular band (d18O=+22.37+/-0.38per mil to +24.08+/-0.58 per mil; 2s). Our data show a limited range in d18O of silica which is in contrast to the large range found for ALH84001 carbonates (d18O: -10 to +28per mil [3-7]) and no evidence of low d18O values that would be indicative of magmatic or high-temperature silica [8]. Our results are heavier (by 2-4per mil) than a value published by [3] probably reflecting our more accurate correction for instrumental mass fractionation. The similar diffusivities for oxygen in calcite and quartz suggest that carbonate was deposited over a wide temperature range but that silica precipitated over a limited temperature interval. In the granular band, silica and carbonate appear to have been co-precipitated, potentially providing an opportunity to constrain the temperature and oxygen isotopic composition of the formation water for these two phases. The carbonate is too fine-grained for ion probe isotopic analysis, however the well-defined correlation of major-element and oxygen isotope compositions of ALH84001 carbonate [3-6] could be used to constrain its oxygen isotope composition. Electron microprobe analyses are in progress and will be reported at the meeting. These data should provide our best proxy for the oxygen isotope composition of water on early Mars. Implications for the search for life using the stable isotopes of oxygen will be discussed.

P52B-07 1500h

Biological Iron Isotopic Fractionations in Antarctic Endolithic Microbial Communities

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In the McMurdo Dry Valleys, cryptoendolithic microorganisms under sandstone surfaces secrete oxalic acid to leach iron oxides from the rock. A translucent surface rock layer is necessary to trsansmit sufficient sunlight to support photosynthetic primary production and long-term survival. Part of the mobilized iron is redeposited on the rock surface as a protective crust; the rest accumulates below the colonized zone. We report here that this weathering process results in redistribution of the iron isotopes, with the microbial zone being enriched in heavy isotopes relative to the rock crust and the accumulation zone. In a simulated laboratory experiment to understand the cause for this isotopic effect, hematite was incubated in 5 mM oxalic acid under light. Analysis of the initial dissolved iron showed that the dissolution in itself could not reproduce the isotopic shifts observed in the rock. Presumably, equilibrium isotopic fractionation between Fe(II) and Fe(III) species is the cause, as both are produced from oxalate-promoted dissolution of iron oxides. Subsequently, microorganisms would recycle oxalate for carbon nutrient and as a result destroy iron oxalate complexes. Without chelation, the ferric iron, which is isotopically heavier, would precipitate first and the ferrous iron later as they are transported downward through the circumneutral endolithic environment, effectively achieving a physical separation of the different isotopes. On Mars, if endolithic microorganisms had occurred and then became extinct as the planet dried and cooled, their iron isotopic biosignatures might be well preserved because subsequent reworking of iron would be unlikely without liquid water.

P52C MCC: 270 Friday 1530h

Space Weathering of Solid Surfaces in the Solar System and Elsewhere I

(joint with SA, SH, SM)

Presiding: **C A Hibbitts,** University of Washington**; J F Cooper,** Raytheon ITSS

P52C-01 1530h INVITED

Space Weathering on the Surfaces of Planets, Satellites and Asteroids

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The vapor deposition model of space weathering will be discussed. The changes in the optical properties of regoliths of silicate bodies without atmospheres, including spectral darkening, reddening and obscuration of absorption bands, are due to submicroscopic metallic iron. The iron particles are created during the deposition of vapor generated by both solar wind sputtering and meteorite impact vaporization. The history of the model will be briefly reviewed and evidence supporting it presented. It will be shown to be able to account quantitatively for changes in lunar optical properties, and to predict the alteration of spectra of ordinary chondrites to more closely resemble those of S-asteroids. Applied to Mercury, it implies that this body has a regolith in which FeO is low (2-6%), but not completely absent.

P52C-02 1545h INVITED

Space Weathering of Small Bodies

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Space weathering is defined as any process that wears away and alters surfaces, here confined to small bodies in the Solar System. Mechanisms which possibly alter asteroid and comet surfaces include solar wind bombardment, UV radiation, cosmic ray bombardment, micrometeorite bombardment. These processes are likely to contribute to surface processes differently. For example, solar wind bombardment would be more important on a body closer to the Sun compared to a comet where cosmic ray bombardment might be a more significant weathering mechanism. How can we measure the effects of space weathering? A big problem is that we don't know the nature of the surface before it was weathered. We are in a new era in the study of surface processes on small bodies brought about by the availability of spatially resolved, color and spectral measurements of asteroids from Galileo and NEAR. What processes are active on which bodies? What physics controls surface processes in different regions of the solar system? How do processes differ on different bodies of different physical and chemical properties? What combinations of observable parameters best address the nature of surface processes? Are there alternative explanations for the observed parameters that have been attributed to space weathering? Should we retain the term, space weathering? How can our understanding of space weathering on the Moon help us understand it on asteroids and comets? Finally, we have to leave behind some presuppositions, one being that there is evidence of space weathering based on the fact that the optical properties of S-type asteroids differs from those of ordinary chondrites.

URL: http://www.astro.umd.edu/∼mcfadden/swAGU.html

P52C-03 1600h

Space Environment Measurements for Icy Surfaces in the Solar System and Beyond

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There are dozens of icy satellites orbiting the giant planets and trillions of icy comets populating the Kuiper Belt and Oort Cloud. Such objects are likely to be common throughout other planetary systems, particularly those now known to have giant plants. Interactions of the local space environment with these bodies must be taken in account for proper interpretation of photometric and spectroscopic measurements related to surface composition. Most of these bodies either are known to have, or likely have, tenuous atmospheres of volatile gases produced by internal outgassing & surface sublimation, sputtering from charged particle and UV irradiation, and diffuse dust clouds produced from meteoritic impacts. Whether or not Pluto counts as a small icy planet or a big comet, its thin and variable atmosphere also allows direct surface exposure to the space environment. Even glacial ices on the surface of (e.g., Snowball) Earth may have been exposed to much of the interplanetary solar UV flux at early times when an effective ozone shield was absent, and the Mars atmosphere is thin enough today for direct irradiation of polar cap ices by high energy cosmic ray and solar flare ions. Planetary magnetic fields reduce exposure to interplanetary charged particles but add irradiation by magnetospheric plasma and energetic particles. At Europa the intense surface irradiation from the Jovian magnetosphere might play a role via radiolytic chemistry in possible evolution of life within the putative sub-surface ocean. Although an armada of spacecraft have been measuring for many years the parameters of the solar UV, plasma, energetic particle, and dust environments of rocky bodies, large and small, in the inner solar system near Earth's orbit around the Sun, only six spacecraft with varying capabilities (Pioneer 10/11, Voyager 1/2, Galileo Orbiter, Cassini Orbiter) have yet ventured into the domain of the icy bodies near and beyond the orbit of Jupiter. The first five have collectively provided extensive measurements on the high flux plasma and energetic particle radiation environments of the jovian and saturnian magnetospheres, and the sixth will arrive to begin a long orbital tour of the Saturn system in July 2004. For the Uranus and Neptune systems we have the Voyager 2 flyby data sets. Extensive interplanetary measurements beyond Jupiter's orbit have only been provided by the Pioneer and Voyager missions into the 30 - 60 AU region of observable Kuiper Belt Objects (KBO). Of particular note are the recent report of dust in the outer solar system from interstellar grain impacts on KBOs, which may be relevant to observed color diversity of these objects, and the likely emergence of the Voyager 1 spacecraft into the heliosheath region of the heliosphere within the next eleven-year solar cycle if not in the next few years. The solar wind termination shock now sought by Voyager 1 marks the inner boundary of the heliosheath where outward solar wind flow slows down. The heliopause at a few times that shock distance in AU is the outer contact boundary for entry into the local interstellar plasma and cosmic ray environment of the outer Kuiper Belt at about 100 -

1000 AU and the Oort Cloud extending out to 100,000 AU. Interestingly, an increasing number of Scattered Kuiper Belt Objects in highly eccentric solar orbits are being detected near their perihelia with aphelia ranging out to 1000 AU, and these objects cumulatively experience different effects of space weathering in multiple heliospheric regions. The planned New Horizons and Interstellar Probe missions will further extend environmental measurements into the varying environmental domains of Pluto and the KBOs.

P52C-04 1615h INVITED

Radiation Chemical Weathering of Water-Rich Surfaces

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Water ice is known to exist on nineteen different moons of the four giant planets, and also on Plutos moon, the rings of Saturn, trans-Neptunian objects, and comets. Other condensed volatiles have also been detected on many of these objects. These solar system ices exist in a variety of radiation environments that can include magnetospheric ions and cosmic rays. To study the radiation chemical weathering of water-rich ices, we record changes in the mid-IR spectra of low-temperature thin ice films during ion bombardment. We have completed a variety of MeV proton irradiation experiments on both pure H_2O and H_2O-dominated ices containing CO_2, CO, CH_4, and NH_3. This talk will focus on the radiation chemical processes that lead to the formation of H_2O_2 (a detected radiation product on Europa, (Carlson et al. 1999)) and carbonic acid, H_2CO_3 (a candidate whose IR spectrum is similar to observed features on Callisto, (Carlson, 2001)). We will identify other radiation products that are most likely to be observed from mixtures such as $H_2O + CH_4$, $H_2O + CO$, $H_2O + NH_3$. The role of CO_2 in the formation of O_2 will also be discussed.

This research is funded through NRA 344-33-01 and 344-02-57

Carlson et al. (1999) *Science*, **283**, 2062

Carlson (2001) private communication

P52C-05 1630h INVITED

Hubble Space Telescope Observations of Europa and Ganymede

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The first ultraviolet images of the surfaces of Europa and Ganymede were made with the Hubble Space Telescope in 1999 and 2000. Both satellites exhibit atmospheric emissions produced by the interaction of plasma electrons trapped in the Jovian magnetosphere with their very tenuous oxygen atmospheres. The Ganymede emissions are clearly auroral in nature, while the oxygen emission from Europa appears to be correlated more closely with visibly bright surface regions. Both satellites exhibit very low (∼ few percent) reflectivities at UV wavelengths (120-170 nm). At the wavelength of the strongest solar emission line in this wavelength range, HI Lyman-α (121.57 nm), Europa exhibits a surface reflectivity pattern that is anti-correlated in brightness with the visibly dark surface regions, and with the oxygen emission. At face value, the Europa observations imply either that the contaminant that darkens the surface at visible wavelengths has a lower reflectivity than the brighter visible regions (thought to be purer water ice), or that there is more hydrogen gas over the darker surface regions. Both explanations involve interaction of the trapped Jovian magnetospheric plasma with the surface of the satellite. The observations of Europa haev been challenging to explain, especially given the lack of UV reflectivity measurements for possible surface contaminants.

P52C-06 1645h INVITED

Radiolysis and Chemical Weathering on the Galilean Satellites

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The Galiliean satellites are bombarded by energetic particles that profoundly affect the surface composition. Reactive sulfur is implanted from the Iogenic plasma, and new chemical species are produced by radiolysis. Characteristic times for radiolytic destruction are very short compared to geological time scales, and the depth of direct radiolytic influence is about 1 mm, comparable to the depth of the optically observed layer.

Europa's radiolytic products include hydrogen peroxide and molecular oxygen, as well as a hydrated material that exhibits a strong trailing side enhancement. Carlson, Johnson, and Anderson (*Science* **286**, 97-99, 1999) identified the latter as hydrated sulfuric acid and proposed that it is part of Europa's radiolytic sulfur cycle, wherein elemental sulfur, sulfur dioxide, hydrogen sulfide, and sulfuric acid are in dynamic equilibrium between continuous production and destruction. A dark material that is spatially associated with hydrated sulfuric acid was suggested to be radiolytically produced sulfur allotropes. Sulfur dioxide was also found to be associated with the hydrate (Hendrix et al., Eurojove, 2002) and is present at levels consistent with the abundance of sulfuric acid and measured radiolysis rates (Carlson et al., *Icarus* **157**, 456-463, 2002). Ion implantation can provide the observed amount of total sulfur in just 30,000 years, suggesting that burial by impact gardening may be occurring. The variegated surface color may be due to diapiric heating of the surface, which sublimates water and preferentially concentrates lower vapor pressure sulfurous material. Any endogenic sources of sulfurous material would be rapidly assimilated into the radiolytic sulfur cycle.

Ganymede contains O_2 in its surface and atmosphere, likely produced from the radiolysis of H_2O. Both Ganymede and Callisto show CO_2 in their surfaces, and a corresponding CO_2 atmosphere has been found on Callisto. The trailing side enhancement of surficial CO_2 on Callisto suggests that charged particle impacts generate CO_2 and perhaps H_2CO_3 and C_2O_3.

P52C-07 1700h INVITED

Electron- and Vacuum Ultraviolet Photon-Induced Weathering of Outer Solar System Surfaces

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This talk will present an overview of the non-thermal processes involved in the electron- and vacuum ultraviolet (VUV) photon-induced transformation of outer solar system surfaces. An emphasis will be made on i.) Understanding the initial electronic states created during electron impact and VUV photon absorption, ii.) The subsequent energy partitioning and release of excited fragments, iii.) The reactive scattering of atomic and molecular fragments and iv.) The trapping of products. Experiments are carried out using ultrahigh vacuum surface science techniques to achieve the very low vacuum and low temperatures typical of the outer solar system. The use of tunable excitation sources, quadrupole and time-of-flight mass spectrometry and Fourier transform infrared spectroscopy allows the determination of product branching ratios and absolute cross sections as a function of energy. The specific systems discussed will be pure and mixed (CO2:H2O) low-temperature ices, frozen sulfuric acid hydrates and flash-frozen sodium and magnesium sulfate brines. The mixed ices are simple models of comets and icy grain surfaces, whereas the latter are reasonable surrogates for the non-ice material(s) present on Europa. The talk should clearly indicate the important role electronic transitions play in chemically altering surfaces present in regions within the solar system that contain magnetospheres.

P61A MCC: Hall D Saturday 0830h

Space Weathering of Solid Surfaces in the Solar System and Elsewhere II Posters *(joint with SA, SH, SM)*

Presiding: **R W Carlson,** Jet Propulsion Laboratory**; G H Jones,** Imperial College

P61A-0338 0830h POSTER

Interplanetary field enhancements - evidence of an interaction between the solar wind and interplanetary dust

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In 1980, 1983 and 1986 Pioneer Venus Orbiter detected sharply peaked magnetic disturbances lasting generally of the order of 15 minutes when Venus was downstream from the orbit of the asteroid 2201 Oljato. Events were much more frequent when Oljato was close to conjunction with Venus than when it was near aphelion. Similar events were seen at other ecliptic longitudes at 0.72 AU and at 1.0 AU by ISEE 3 and IMP 8, but none with such a tight grouping. Recently, such events have been found further from the Sun and well out of the ecliptic by the Ulysses spacecraft. Taking into account the radial expansion of the solar wind, these events agree in size, duration and occurrence rate with the early PVO, ISEE and IMP measurements. The Ulysses events too have been attributed to the interaction of the magnetized solar wind with interplanetay dust particles co-orbiting with their parent bodies. We compare the properties of the enhancements observed at quite different locations in the solar system, and discuss the possible processes that lead to their formation.

P61A-0339 0830h POSTER

The Optical Effects of Space Weathering Products on Silicate Surfaces

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The current paradigm for the optical alteration of soils due to space weathering processes involves the deposition of surface correlated nanophase iron ($npFe^0$), deposited both as a vapor from micrometeorite impacts and via solar wind sputtering. These alterations due to $npFe^0$ will effect all surfaces that contain iron-bearing minerals and are exposed to the harsh environment of space, i.e. the Moon, Mercury, asteroids. Space weathered materials containing $npFe^0$ have distinct optical properties. In addition to reducing the strength of spectral bands, space weathering adds a "characteristic continuum" to spectra that is generally darker and redder than the original material. The exact shape of this continuum, however, is dependent on both the amount and the size of the $npFe^0$ present. Miniscule amounts of $npFe^0$ (< 0.1wt%) cause the spectra to become sharply curved in the visible, while leaving the near-IR relatively unaffected. As $npFe^0$ accumulates (0.2-0.4 wt%), the continuum becomes less curved and significantly redder through the entire Vis-NIR range, eventually becoming nearly linear. These effects have been observed with natural lunar soils (Noble et al, MAPS 2001). With additional $npFe^0$ the spectra darken further, progressively losing redness until finally, with >1.0 wt% $npFe^0$, the spectrum becomes dark and featureless. The size of the $npFe^0$ is also important to the spectral properties. Small $npFe^0$ grains cause reddening, while larger grains only result in darkening. To better constrain the size where this reddening to darkening transition occurs, we have created synthetic analogs using silica gel impregnated with various amounts of $npFe^0$. Because these gels contain defined pore sizes, we can somewhat control the size of $npFe^0$ created, allowing comparison of samples with different $npFe^0$ sizes. Initial results suggest that the transition from reddening to darkening occurs between 15 and 25 nm.

P61A-0340 0830h POSTER

Ion-irradiation of materials spectrally similar to the non-ice surface of Callisto

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