

Photolysis and Radiolysis of Outer Solar System Ices (PROSSI) Workshop

INVITED ABSTRACTS Updated 25 Feb 2000

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Interstellar Medium :

Energetic and Thermal Processing of Interstellar Ices

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Silicate and carbonaceous particles produced in stellar outflows act as condensation nuclei when they pass through a dense molecular cloud. In cold dense environment such particles acquire icy grain mantles which are formed by efficient accretion of atoms and molecules from the interstellar gas. An active surface chemistry takes place on the grains that, in principle, provides many possible alternative routes to the formation of complex interstellar molecules. Regulatory mechanisms such as selective desorption, sublimation and grain explosion desorb material and return molecules back in the gas phase. The evolution of interstellar ices is determined by processes in the protostellar

environment, which can be quiescent or dominated by shocks. When molecular clouds evolve from an initial cold quiescent phase to warm, dense and active proto-stellar regions processes (such as ultraviolet irradiation, cosmic ray bombardment and temperature variations) may become important and alter the grain surface composition. Dust particles with icy mantles produced by these elementary processes are interspersed in dense interstellar gas with an abundance of around 10^{-12} per H atom. Despite their low abundance they act as important catalysts in the interstellar medium.

Icy grain mantles have been recently revisited with the Infrared Space Observatory (ISO). ISO allowed for the first time to observe the complete wavelength range between 2.5-200 μm , free of any telluric contamination. Several new molecules could be detected and accurate abundances of ice species could be determined. Astronomical observations indicate the existence of different types of ices in proto-stellar environments and toward field stars. Hydrogen-rich ices (polar ices), dominated by H_2O ice, are formed when H is abundant in the interstellar gas. Besides water ice they contain: CO , CO_2 , CH_4 , NH_3 , CH_3OH , and possibly traces of HCOOH and H_2CO . Apolar or hydrogen-poor ices are formed far away from the proto-star or in cold dense clumps and are composed of molecules with high volatility (evaporation temperatures of < 20 K) such as CO , O_2 , and N_2 . Thermally processed ice mantles, in which CO_2 ice is locked in intermolecular complexes with CH_3OH ice, have been discovered with the ISO satellite towards high-mass protostars.

The role of UV energetic processing of interstellar ices remains uncertain. The

UV radiation field of a young protostar is strongly attenuated within its close environment, and only cosmic rays can penetrate throughout the cloud, leading to an induced UV radiation field of only $\sim 10^3$ photons $\text{s}^{-1} \text{cm}^{-2}$. Laboratory experiments show that irradiation processes and thermal processing can indeed lead to the formation of radicals, complex molecules and even organic refractory material, but it is not clear if the experimental simulation accurately represent the conditions appropriate to the clumpy structure of molecular clouds. The formation of CO_2 in dense clouds in large quantities (namely 20% relative to water ice) remains a mystery. CO_2 may be formed by grain surface reactions, namely by oxidation of CO . Energetic processing (UV irradiation or cosmic rays) or gas phase production in shocks and subsequent accretion on grains are alternative formation routes. Recent ground-based observations indicate large amounts of CH_3OH in the line of sight toward some high massive protostars, but rather low CH_3OH ice abundances are observed toward low-mass protostars. CH_3OH may be either formed by grain surface reactions or by energetic processing. To study the formation and evolution of the key molecules CO_2 and CH_3OH in the laboratory may therefore help to reconstruct the temperature and irradiation conditions in protostellar environments. Recent ISO results show extensive ice segregation in the vicinity of protostars and evidence for acid-base reactions occurring on interstellar grain surfaces. This clearly indicates that thermal processing is a dominant factor in interstellar ice chemistry.

This review presents a schematic outline of energetic and thermal processes which lead to the chemical diversity of interstellar ices

and the formation of complex molecules in interstellar ice and gas.

Comets :

Heterogenous Cometary Composition – Evidence for Variable Processing in the Pre-planetary Nebula

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Cometary nuclei appear to contain the least processed material remaining from the era of planetary formation, and their compositions reflect their origin and history. The oxidation state of volatile carbon and the crystallinity of silicates both seem to differ among comets, suggestive of variable processing in the pre-planetary disk. The simplest members of the (CHO) homologous series of volatile carbon have been detected in recent comets: CO, CO₂, HCOOH, H₂CO, CH₃OH, and CH₄. A few higher order members (e.g. C₂H₆) have also been found. Methanol appears with abundances ranging from ~0.5% to 5% that of water and is sometimes more abundant than CO, thus the oxidation state of volatile carbon is variable in comets. CO is itself highly variable, and the ratio of ethane to CO (both hypervolatiles) also varies among comets. The organic ices are most easily modified and thus are most sensitive to origin-related processes, but most cometary carbon resides in refractory grains. Elemental compositions were measured for CHON grains in P/Halley but their chemical structures and abundances are unknown, hence the competing influences of kinetic, thermodynamic, and other factors affecting their end chemistry

remain obscure. When compared with information gleaned from the 500-plus organic species isolated from Murchison matrix, it is clear that the clues contained in cometary organics have barely been touched. A deep understanding will depend upon analysis of samples taken directly from the near surface layers of the nucleus, such as is planned on the ROSETTA mission, and on laboratory analysis of dust returned by the STARDUST mission. Our current understanding of cometary organics and their relation to interstellar and nebular processing will be discussed.

Planetary Surfaces :

Tbs

Interpreting Planetary Spectra :

Tbs

Ice Structures :

Ice Structures with a Focus on Ice Nanoparticles: Surface Structures, Adsorbate Interactions and H-Bond Chemistry

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After a review of the structures and relaxation processes of low pressure bulk ices (including clathrate hydrates) and their temperature dependencies¹, attention will be directed to the surface regions of the various forms of low pressure ice. The surface regions, that are so important in understanding the interaction of ice with its environment, are naturally most prominent in forms of ice that have a large surface to volume ratio; namely microporous amorphous ice and ice nanoparticles. For that reason, surface characteristics and H-bond chemistry of water ice nanoparticles and microporous amorphous ice, as revealed through FT-IR spectroscopy and computer simulations, will be examined in some detail.

To effectively categorize a *low pressure* form of water ice, several parameters must be stipulated: the degree and nature of any crystallinity/amorphicity (molecular-level structure), the surface-to-volume ratio of the ice (microscopic structure) and the population and molecular-level

environment of any non-water species. The crystallinity will be either hexagonal or cubic in form, with a cubic structure favored by low temperatures and/or the confinement of water in small spaces (i.e., small particles² or voids³). On a short term basis, an amorphous structure is expected to be dominant for ice formed below 130 K in the absence of epitaxy or a nucleating substrate⁴. However, both the molecular-level and microscopic structure of amorphous ice are strongly dependent on formation and/or environmental conditions^{5,6}. Amorphous ice (or amorphous solid water; ASW) can vary from microporous, with common water-molecule coordination numbers ranging from 2 - 5, to an annealed/compacted structure with nearly exclusively 4-coordinated water molecules and a local structure similar to that of crystalline ice. Ice nanoparticles can also be viewed as representing a separate form of ice as the unique surface and subsurface regions constitute a sizable fraction of the total ice present^{7,8}.

The non-water species present within an ice system may occur in one of four basic forms: as a guest species of a clathrate hydrate; as an adsorbate at the ice surface or on the walls of micropores; as the solute of an ASW solution; as aggregates in isolated domains/ concentrated pools within crystalline ice. Unless a hydrate is nucleated, only dilute amounts of individual non-water species are incorporated in a crystalline ice lattice as it forms.

Laboratory spectroscopic study of ice nanoparticles represents an especially versatile approach to observation of ice processes for a great range of ice structures and within a considerable range of environments; including the environments

of the Galilean moons⁹ and of accreted ice in interstellar space. By working with particles in the 2 nm to 100 nm diameter range over temperatures ranging from 40 to 140 K, one can deliberately select particles with interior structures ranging from amorphous to fully crystalline; and surface structures that vary from rough and energetic to smooth and relaxed. A particle form may thus be chosen that best represents one existing in nature; but the real advantage of nanoparticles in the laboratory resides in their high surface-to-volume ratio. This characteristic greatly facilitates the study of the spectra of the ice surface region^{7,8,10,11}, the surface interaction with physical or chemical adsorbates^{11,12} and the conversion of ice to hydrates through H-bond chemistry of the strongest adsorbates^{12,13}.

Observations/simulations of adsorbates on ice nanoparticles in the 40-140 K range have led to a categorization of a large number of molecules and a clearer appreciation of the conditions required for the conversion of ice to a new substance. Molecules have been categorized according to how they influence the three identifiable sections of an ice nanocrystal; the disordered surface, the strained subsurface and the crystalline core. "Weak" adsorbates, such as H₂, N₂, CO, ethane, ethylene, argon, O₂ and CF₄, adapt themselves to the ice surface structure, sometimes engaging in weak specific interactions but commonly occupying sites at which multiple weak interactions dominate¹⁴, such as the centers of water rings¹⁰. Such adsorbates cause minor shifts in the positions of the surface-water-molecule vibrational bands; but have no significant impact on the subsurface or core ice.

"Intermediate" adsorbates, such as SO₂, HCN, H₂S and acetylene, for which the

adsorbate-water bonding is comparable to the **weakest** surface H-bonds between water molecules, cause large shifts of the infrared bands of the ice and are capable of breaking the weakest and most strained H-bonds. (Many strained H-bonds exist as a result of the surface reconstruction that leads to the surface disorder⁸). **With the strained H-bonds replaced by bonds to the adsorbate, the surface reorders, causing much of the subsurface ice to relax to a form that appears spectroscopically as crystalline core ice.** It is this adsorbate induced relaxation, requiring a couple of hours at 125 K, that allows the most direct identification of the subsurface and its spectrum. This relaxation, the simulated structures and the comparison of experimental and simulated collective mode spectra for the adsorbate CF₄, are all evidence for disorder in the top bilayer of the ice nanocrystals.

At the temperatures of interest, the intermediate adsorbates cannot break the normal H-bonds of ice, do not penetrate beyond the ice surface, and do not nucleate a new phase. "Strong" adsorbates, such as NH₃, methanol, small ethers and strong acids, for which the adsorbate-water bonding is comparable in strength to water-water bonding, also reorder the ice surface and subsurface in the manner noted for intermediate adsorbates. However, strong adsorbates, at exposure levels beyond "surface saturation" are uniquely able to penetrate the ice and convert it to known hydrates¹². Since these processes involve the breaking and making of H-bonds by molecular agents, **each hydrate can be viewed as a product of "H-bond chemistry"**. A strikingly broad range of solid forms can be obtained as a product of this chemistry, including ionic hydrates of acids, clathrate hydrates of ethers, and

ammonia hydrates having molecular chain structures.

Arrays of ice nanocrystals are particularly useful in the study of the conversion of ice to the amorphous or crystalline hydrates of the strong adsorbates^{12,13,15}. Because of the unusual surface-to-volume ratio of the particles, the time scale for a complete conversion is greatly compressed relative to that for bulk matter, or even thin films; which facilitates kinetic and mechanistic studies by FT-IR spectroscopy, particularly at quite low temperatures. The several stages of strong adsorbate interaction with ice, from initial uptake, through monolayer saturation, nucleation of the new phase and, finally, complete conversion to a hydrate are readily monitored. This monitoring has made it particularly clear that the chemical activity of adsorbate molecules must surpass that of molecules tightly adsorbed in the first monolayer before nucleation of a new hydrate phase can occur¹⁵. This free energy barrier for nucleation of a new phase is a critical parameter of ice behavior in many environments. Here, particular attention will be given to the conversion of ice nanocrystals to the hemihydrate of ammonia.

Since ice nanoparticle structure can be deliberately varied from crystalline to amorphous, it is interesting to compare the surface properties to those of amorphous ice and, particularly, microporous amorphous ice, the other form of water ice with an inordinately large surface-to-volume ratio. The similarities and differences between these two forms of ice, with emphasis on the interaction with adsorbates, inclusion of adsorbates on warming and the formation of clathrate hydrates of molecules like small ethers, CO₂ and SO₂, will be noted. The physical

adsorption of the molecules H₂¹⁴ and CO on the surfaces of these two forms of ice will also be examined as particularly interesting cases.

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Structural Alterations :

The Role of Temperature and Structure in Radiation Induced Damage of Low-Temperature Amorphous and Crystalline Ice

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Low-temperature (< 150 K) water ice is a dominant constituent of many small bodies in the outer solar system. Since comets, interstellar grains and most outer solar system bodies do not have significant atmospheres, their icy surfaces are subjected to irradiation by ultraviolet photons, the solar wind, solar flare ions,

and galactic or extra-galactic cosmic rays.^{1,2} In addition, the icy surfaces of moons, such as those in the Jovian system, are transformed by the bombardment of energetic electrons and ions from the surrounding magnetosphere.³ For example, *i.*)the signature of O₂, O₃ and H₂O₂ have been reported in optical-reflectance measurements of Ganymede,⁴⁻⁷ *ii.*)excited atomic oxygen⁸ and hydrogen⁹ have been observed in Europa's tenuous atmosphere, and *iii.*)the Near Infrared Mapping Spectrometer aboard Galileo has recently yielded images of the Jovian moon surfaces which show features characteristic of icy and non-ice or damaged-ice regions.¹⁰ Interpretation of the high quality mission data and development of models to describe aging and processing of icy outer solar system bodies has stimulated the need for a detailed molecular level understanding of radiation-induced "damage" of pure and mixed ices. Though several extensive reviews and monographs on ice physics and chemistry have been published, many very fundamental questions concerning the static (physical) and dynamic (electronic) properties of pristine and irradiated low-temperature ice remain. A few examples discussed in this talk are:

i.)What is the electronic structure of low temperature ice and how does it change with temperature and phase?

Though few theoretical studies on the electronic structure of condensed-phase water have been carried out due to difficulties associated with treating the inherent proton disorder, several experimental investigations on ice electronic structure have been reported. These include, but are not limited to, high resolution electron energy loss spectroscopy¹¹, x-ray photoemission spectroscopy¹², and vacuum ultraviolet

absorption spectroscopy.¹³ The ground electronic configuration of the isolated water molecule can be written as: $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$. The $1a_1$ orbital is almost entirely of O $1s$ character (binding energy ~ 500 eV). The $1b_2$ and $2a_1$ orbitals are the primary constituents of the O-H bonds, while the $1b_1$ and $3a_1$ make up the oxygen lone pair orbitals.¹² The four lowest unoccupied molecular orbitals are the $4a_1$, $2b_2$, $2b_1$ and $5a_1$. The $4a_1$ and $5a_1$ are strongly antibonding - occupation of these states leads to O-H bond dissociation.

Experimentally it has been shown that the proton disorder effects the conduction band-width and leads to states in the band-gap, however, it does not change the electronic band structure significantly. In fact, there are only small differences in the electronic structure of the free gas-phase water molecule and condensed ice, with some broadening and minor shifting of the energy levels. The molecular orbitals retain much of their gas-phase character, so the peaks in the condensed-phase valence band density of states are usually labeled with the same spectroscopic notation. The conduction band of ice is very narrow, with the band minimum less than 1 eV below the vacuum level.¹¹ The Fermi level is estimated to be ~ 5 eV above the $1b_1$ band maximum.¹⁴ The unoccupied $4a_1$ orbital is in the band gap and has a localized (excitonic) character. In the solid state, these localized levels are better described as Frenkel excitons, in which the coulomb attraction localizes the electron-hole pair on the water molecule. The optical absorption spectra of ice shows a pronounced peak at ~ 8.3 eV, corresponding to a $1b_1 \rightarrow 4a_1$ transition, well below the photoelectric threshold of 10.5 eV.¹⁵ The $2a_1$ and $3a_1$ orbitals seem to be perturbed the most by hydrogen

bonding, broadening considerably in the solid state. Theoretical calculations of ice band structure show that these bands have the most dispersion, while the $1b_1$ and $1b_2$ bands are virtually dispersionless.¹⁶

Reduction of the band widths should occur if the hydrogen bonding is weakened, and thus, one would expect that electronic excitations involving bands with a_1 character would be the most sensitive to temperature and local potential changes. To demonstrate this, we have carried out the first temperature- and phase-dependent photoemission study of low temperature ice.¹⁷ Our results reveal a distinct narrowing of the $2a_1$ and $3a_1$ bands as well as a shift in binding energy position with increasing temperature. By changing the incident photon energy from 30 to 55 eV, the relative sensitivity of the bulk vs. surface was examined and the narrowing seems primarily associated with the surface molecules.

ii.) What is source of the temperature dependence observed in non-thermal (electronic) damage/reactive scattering in ice?

The primary electronic energy loss processes in ice are *i.)* ionization, *ii.)* direct impact excitation of (super)excited states and *iii.)* resonance scattering. Ionization initially creates free electrons and holes, which can either, trap or recombine to form excitons. There are many excited states of the water molecule which can lead to H^+ (D^+) emission. The primary proton desorption channels in ice have been assigned to the $3a_1^{-1} 1b_1^{-1} 4a_1^1$ excited state, which dissociates and produces "slow" (0-4 eV) protons, and the $1b_1^{-2} 4a_1^1$ excited state, which produces "fast" (4-7 eV) protons.¹⁸ *Hydrogen bonding apparently reduces the lifetime of the $3a_1^{-1} 2a_1^1$ state to the extent that it does not normally contribute to the desorption*

process. Our time-of-flight measurements¹⁸ indicate “H₂O²⁺” excited states are probably short-lived in the solid, and recapture an electron to form 2h1e states.

While there are many excited states of the water molecule which can lead to positive ion emission, only specific localized electron-molecule scattering resonances can lead to the production and desorption of negative ions. The H⁻ (D⁻) yield from ice as a function of incident electron energy exhibits resonant structure which has been assigned to the ²B₁, ²A₁ and ²B₂ dissociative electron attachment (DEA) resonances.^{19,20} These correspond to states having two 4a₁ electrons and a hole in the 1b₁, 3a₁, or 1b₂ orbitals, respectively. A negative ion resonance associated with a hole in the 2a₁ orbital is also observed near 22 eV and is tentatively assigned as the ²A₁ DEA resonance.¹⁹ The O-H (O-D) antibonding nature of the 4a₁ level makes these excited states highly dissociative.

Measurements of the total H⁺ (D⁺) and H⁻ (D⁻) yields and velocity distributions as a function of substrate temperature from 90 to 200 K shows that the ion yields change with surface temperature, film thickness, and phase.¹⁸⁻²⁰ The yields rise near 120 K on amorphous ice and near 135 K on crystalline ice. The amorphous-to-cubic phase transition near 155 K causes a drop in the total desorption yield. *The data collectively suggests that thermally activated reduction of surface hydrogen bonding increases the lifetimes of the excited states responsible for desorption, and that these lifetime effects are strongest for excited states involving a1 bands.* This is consistent with the a1 band narrowing observed in the temperature dependent photoemission studies.¹⁷

It is well known that the ion desorption accounts for a small fraction of the total mass loss during electron bombardment of materials and surfaces. In ice, this is partially due to hole hopping, efficient autoionization and electron-hole recombination. In the latter case, the lowest energy excitons formed as a result of recombination can localize at the surface or in the near surface zone and dissociate to produce atomic fragments such as H (¹S) O (³PJ, ¹D, etc.)^{21,22} and molecular products such as hydrogen²³ and OH. The fragments can react further to produce products such as peroxides and eventually molecular oxygen.²⁴ *Increasing the substrate temperatures from 88 K to 145 K also increases the yields of all the neutral electron-beam produced products.* This increased yield likely results from a combination of: *i.)* increased electron-ion recombination; *ii.)* exciton transport to the near surface region; and *iii.)* dissociation followed by inelastic scattering and desorption. The only channel which *decreases* with substrate temperature is the electron-stimulated desorption of molecular water. Thus, the primary mass-loss channel for electron-beam induced electronic excitation of low-temperature water ice is the production and desorption of molecular oxygen.

iii.) Does porosity and geometric structure of ice effect radiation damage cross sections?

Of the many known polymorphs of ice, only three are very stable under the ultrahigh vacuum and low temperature and pressure conditions typical of astrophysical environments; porous amorphous solid water (PASW), amorphous solid water (ASW), and crystalline ice (CI). Water deposited below 130 K forms ASW, with local bonding which may be similar to that of liquid water.²⁵ Below 100 K, PASW is

formed.²⁶ The porosity of PASW is dependent upon the deposition temperature and angles^{26,27} ASW is a metastable state of ice, and crystallizes rapidly near 155 K to form a CI film.²⁸⁻³⁰ If the growth substrate has a very good lattice match to crystalline ice, deposition above 140 K (or very slow deposition at lower temperatures) forms an oriented epitaxial crystalline ice film, which is thought to exhibit a reasonably well-ordered surface.³¹

The highly porous, low density form has the capacity to store and release inert gases and the release of gas near 150 K has been shown^{32,33} to be related to the amorphous-to-cubic phase transition. It has also been shown that ultraviolet radiation promotes the formation of H₂ in amorphous ice and converts crystalline ice to the amorphous form.³⁴ *Micropores may be rather important in this process since there is an increased probability of an encounter between two H-atoms within the pores³⁵ and the dissociation probability of surface water molecules is higher than those in the bulk.* Thus, the H₂ production probability may be enhanced within the pores. In addition, unimolecular decay channels, such as those discussed above, can produce hydrogen molecules *directly* at pore surfaces.

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Chemical Alterations :

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Polycyclic aromatic hydrocarbons (PAHs) are common in carbonaceous chondrites, and IDPs, and are probably the most abundant and widespread class of organic compounds in the universe. In dense molecular clouds where temperatures are low (<50 K) PAHs condense along with most gas-phase species into ices dominated by H₂O. Indeed, the presence of PAHs in interstellar ices have been demonstrated by recent astronomical observations and emission from PAHs were reported in comet P/Halley. Our previously reported laboratory studies of UV processing of

PAHs in H₂O showed that PAHs undergo reactions in interstellar ice grains which could be the source of certain hydrocarbons in carbonaceous chondrites and IDPs (Bernstein et al. 1999). At this workshop we will present the results of our more recent studies on the UV processing of aromatic molecules in ice under astrophysical conditions including: (i) regio-chemistry of these reactions which allow us to make specific predictions about what structures should be seen if this process is the source of polar aromatic hydrocarbons seen in meteorites and (ii) isotopic studies showing that such reactions may explain the deuterium enrichments in these meteoritic hydrocarbons. In addition, we briefly address possible implications of these compounds for the evolution of life since naphthaquinones are ubiquitous in living systems and perform a fundamental role in biochemistry.

M. P. Bernstein, S. A. Sandford, L. J. Allamandola, J. S. Gillette, S. J. Clemett, and R. N. Zare. "Ultraviolet Irradiation of Polycyclic Aromatic Hydrocarbons (PAHs) in Ices: Production of Alcohols, Quinones, and Ethers." *Science* **283**, 1135-1138 (1999), and references therein. See also the Perspectives piece by Pascale Ehrenfreund pp 1123-1124

Chemical Alterations: Radiolysis.

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Solar system objects such as planets, satellites, rings, and comets, are subjected to energetic processing by photons and ions. As a result, the chemical and physical properties of the materials composing these objects will change over

time. Predicting these changes requires, as with gas-phase chemistry, fundamental thermodynamic and kinetic data, yet unlike the gas-phase case, such data is almost totally lacking for low-temperature solids. Even worse, in many cases there is little knowledge of how relevant predictive data might be obtained for the icy materials of interest to planetary scientists.

In the absence of necessary thermodynamic and kinetic data, an alternative approach has been developed to study the radiolysis and photolysis of solar system ices. Laboratory ices, either pure or mixtures, are exposed to either ionizing radiation or vacuum-UV photons, and then probed by spectroscopic, diffraction, or mass spectrometric methods. Chemical reactions and physical properties can be studied in this manner, either in bulk or at the molecular level. It has been found that both irradiation and photolysis may destroy molecules, may synthesize new molecules, may cause changes of phase in pure materials, and may eject molecules from a frozen surface.

This laboratory approach has evolved over more than 20 years with much of the earliest work focusing on complex mixtures thought to represent either cometary or interstellar ices. Although the early experiments uncovered a rich solid-state photo- and radiation chemistry, they did not reveal details of reactions for particular solar system molecules, partly due to the multi-component nature of the samples. Since those first experiments, observers have made new detections of molecules, such as H_2O_2 , C_2H_6 , CH_3OH , and CO_2 , in and related to solar system ices, but no comprehensive picture of ice reaction chemistry has appeared. For the specific case of radiation-induced reactions, not even a qualitative general

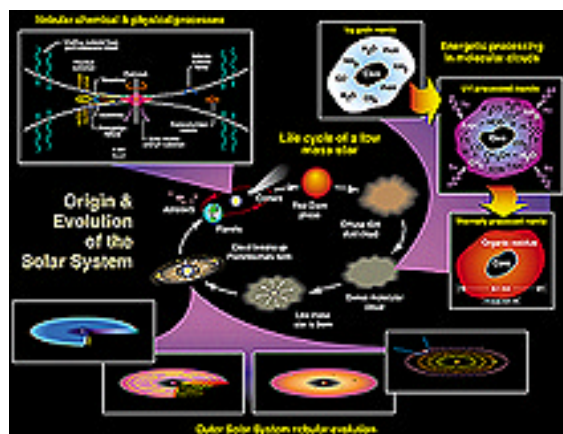
picture of ice reaction chemistry has emerged, so that the observations often are leading the laboratory work.

This presentation will focus on radiation chemical effects of relevance to solar system ices, starting with some of the earliest results and moving forward to the present. Interactions of high-energy radiation with molecules will be described and examples provided. Most examples will be drawn from laboratory experiments related to solar system ices composed of H_2O , CO , CO_2 , and common classes of organic molecules. The work in which I have participated at NASA/Goddard will form part of the review, but results from other research groups will be included. Time permitting, comparisons and contrasts between UV-photolysis and ion-irradiation experiments will be given. Finally, an attempt will be made at drawing a "big picture" of radiation chemistry in solar system ices, emphasizing changes which might be detected by observers. Guidelines for realistic ice reactions of small molecules will be suggested, drawn directly from laboratory experiments. Predictions of molecular evolution in complex ices will be made.

The Physical State of Ice :

Physical State Of Ices in the Outer Solar System. T. L. Roush, NASA Ames Research Center, Mail Stop 245-3, Moffett Field, CA 94035-1000, (troush@mail.arc.nasa.gov).

Introduction: The physical state of ices located in the outer solar system is a complex function of the composition of the original ices, their thermal histories, and the radiation environments they have encountered. Our ability to identify the ices currently present on objects in the outer solar system relies upon theoretical, observational, and laboratory efforts.



Theoretical Efforts: *Original Starting Materials -*

Figure 1. Schematic diagram of various stages of solar system origin and evolution. The central panel illustrates the life cycle of a typical low mass star; illustrating the connection between the interstellar molecular clouds within which the star condensed and the planetary systems formed by accretion within the protoplanetary disk surrounding the new star. The nuclear reactions in the star's core create chemical elements that are dispersed into the interstellar medium during the star's red giant phase which in turn become the raw material for new generations of stars and planetary systems.

The three panels in the upper right illustrate how initial icy materials can be energetically processed within dense molecular clouds; yielding more complex molecules. The four lower panels outline various stages in the evolution

of planetary bodies in the outer solar system. From left to right, they illustrate the evolution of gas and dust forming protoplanetary disks throughout the formation of planetesimals, the accretion of the cores of the major planets, and subsequent dissipation of remnant nebular material and ejection of remaining planetesimals into the Kuiper Belt and Oort Cloud. The panel in the upper left shows some of the various physical and chemical processes that acted within the protoplanetary disk during various stages in the formation of the planets.

The following summary draws heavily upon the discussion by Cottin et al. [1] and the references therein. The initial particles that condense in the atmosphere of cool giant stars, before being expelled to space by radiation pressure, appear to be silicates as inferred by a strong absorption feature near $9.7 \mu\text{m}$. In one evolutionary scenario [2], the particles are then cycled between diffuse ($T \sim 100\text{K}$) and molecular clouds ($T \sim 10\text{K}$) several times before becoming incorporated into the protosolar nebula (see Fig. 1). In the molecular cloud the H atom density is high enough to permit ices such as H_2O , N_2 , CO , CO_2 , NH_3 and CH_3OH to form and condense as mantles on the silicate grains (see Fig. 1). During this continued cyclic process the grains are subjected to irradiation by:

- Charged particles: galactic cosmic rays (GCR)
- UV: indirect (GCR induced) and direct (nearby stars)
- Thermal processes: cycling between cold dense clouds and warmer diffuse medium

These processes can lead to the formation of several generations of refractory mantles (see Fig. 1) associated with the energetic processing of the icy components. When the molecular cloud finally reaches a critical mass, it collapses and these grains become incorporated into the planets, satellites, and comets (see Fig. 1). Some relatively pristine aggregates

may be preserved in safe regions of the outer solar system. During and after accretion the processed materials are exposed to similar energetic processes, all of which can act to alter the original starting materials (see Fig. 2) by:

- Charged particles: GCR (outer regions) and energetic particles entrained in planetary magnetospheres
- UV: solar and nearby stars (outer region)
- Thermal processes: differentiation and heating by short-lived radioactivity (e.g. ^{26}Al)

Lewis [3] demonstrated the anticipated ubiquity of water ice as a major condensate in the outer solar system based upon models of condensation from an equilibrium solar nebula. Also important in this model was the retention of C and N in the form of methane clathrate ($\text{CH}_4 \cdot 6\text{H}_2\text{O}$) and ammonia hydrate ($\text{NH}_3 \cdot \text{H}_2\text{O}$). Later work showed that the equilibrium assumption in the solar nebula was incorrect [see 4] and that N_2 and CO were the dominant gaseous N and C compounds. Time dependent, nonequilibrium models for protoplanetary disks show highly nonequilibrium combination of CO_2 and NH_3 can form via ion-molecule chemistry driven by cosmic rays in the outer nebula [5].

Kargel [6] discusses the phase equilibria of a variety of volatile ice mixtures including ammonia-water, methane-nitrogen, and water-ammonia-methanol. The rheologies of these various mixtures are related to the morphological land forms observed on icy satellites in the outer solar system. The densities of resultant mixtures are used to discuss the differentiation that cryomagmas might experience.

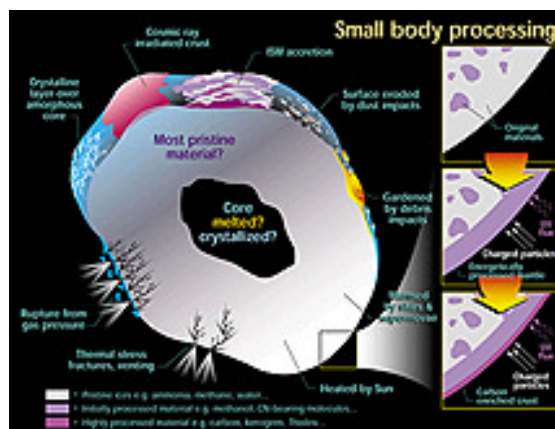


Figure 2. A variety of processes can continue to occur on small bodies such as planetesimals. These include heating events from internal (if enough radiogenic materials are present, e.g. ^{26}Al) and external (sun) sources, and irradiation processing of the surface due to UV and charged particles fluxes (right panel).

Modeling of Spectral Observations - Various models are used to represent the interaction of electromagnetic energy (solar flux) with materials in the outer solar system in order to interpret the telescopic observational data discussed in the following section. For solid particulate surfaces three basic mixtures occur. Areal, or "checkerboard", mixtures occur at macroscopic levels (~decimeters to kilometers), e.g. "rocks" or "outcrops", and imply that an incident photon interacts with more than one discrete region before exiting the surface. This type of mixing can be represented by a linear combination of the reflectances of each individual component contained within the instrumental field of view. Intimate, or "granular" mixtures, occur at the granular scale (micrometers to centimeters). The surface reflectance is a nonlinear function of the reflectances of each component because of multiple scattering in incident photon can encounter several grains before exiting the surface. Hapke [7] has developed an approximation to the intimate mixture case that allows the reflectance of these mixtures to be calculated from the optical properties of the individual components. The application of Hapke's approach to interpretation of satellite surface photometry is presented by Verbiscer and Helfenstein [8] and to compositional interpretation is presented by Cruikshank et al. [9]. Molecular

mixtures occur at atomic scales where one atom is substituted into the crystalline structure of a host material, for example CH_4 in N_2 . While effective medium theory address this issue in terms of the optical properties of the individual components it can not predict spectral properties that are introduced by distortion of the host crystal structure and any accompanying spectral changes.

Telescopic Observational Information:

Interstellar Composition - There is a vast, and growing, body of literature discussing the observational information regarding the composition of interstellar dust and ices. A relatively recent compilation of manuscripts is presented in [10]. Needless to say, there is ample evidence for silicates, various ices, and the by-products produced by the energetic processing of these ices.

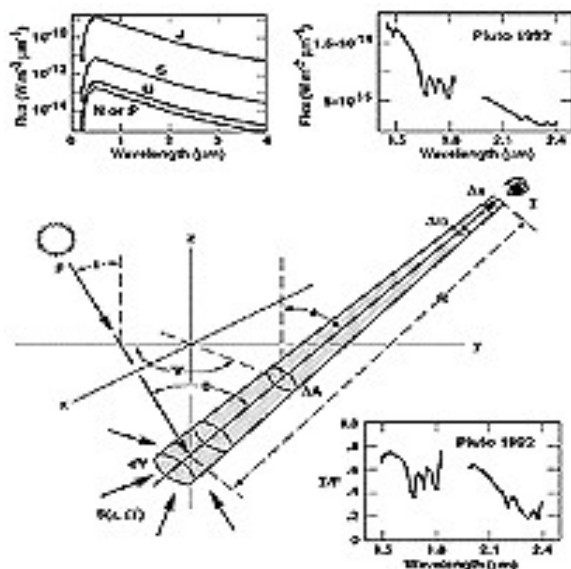


Figure 3. The central panel is a schematic representation of the viewing geometry associated with observations of surfaces from telescope and spacecraft. The upper left panel illustrates the incident solar energy distribution at Saturn (S) Uranus (U) and Neptune (N) or Pluto (P). The upper right panel illustrates the flux measured from Pluto. The lower right panel illustrates the ratio of the flux measured from Pluto to the incident solar flux.

Planetary Ices Observed/Identified - A schematic representation of the viewing geometry associated with space craft or

telescopic observations of solid surfaces is provided in Fig. 3. Also shown in Fig. 3 is the spectral distribution of the energy from the sun. For a given surface, the ratio of the reflected sunlight to that incident it provides a mechanism of determining what materials are present. A comparison of the planetary surface spectrum to the spectra of materials measured in the laboratory can provide a quick identification of the species present (see Fig. 4), but more detailed information, such as relative abundances of more than one species or grain sizes of surface constituents requires more detailed models. Recent summaries describe the ices observed on the satellites of Jupiter, Saturn, and Uranus [11-12], Triton, Pluto, and Charon [9] and recently reported identifications of additional ices on Triton [13-14], Pluto [15], and Charon [16] are summarized in Table 1. Also included in Table 1 are the identifications of icy materials on Centaur and Kuiper Belt objects [17-23]. Fink and Larsen [24] first discussed using spectral features of crystalline water ice to derive surface temperatures of icy objects. Grundy et al. [25] apply this technique to icy satellites in the outer solar system using a study of the temperature behavior of the crystalline water ice spectrum [26]. Fink and Sill [27] and Schmitt et al. [28] show that the visible and near-infrared spectra of amorphous and low-temperature crystalline water ice are distinctively different, as illustrated in Fig. 5. All the icy satellites appear to have crystalline water ice present on their surfaces, with the possible exception of Triton, where the presence of amorphous water ice is suggested, but not conclusive [13].

Laboratory Studies: Many studies germane to the investigation of the effects of photolysis and radiolysis of ices located in the interstellar medium and diffuse

clouds have been undertaken. Summaries are provided by [1] and [10]. These studies show the ready production of daughter materials from the initial starting ices. Several summaries discussing the effects of uv photolysis [29] and radiolysis [1,30-33] on ices germane to solid surfaces in the outer system are readily available. These generally focus upon the materials produced by the energetic processing. Some of these materials are beginning to be recognized on icy satellite surfaces [34-41]. A summary of recent efforts to determine the optical constants of a variety of unprocessed ices pertinent to planetary surfaces is provided by [26] and [28]. Energetic processing of gases and solids containing hydrocarbons have produced a variety of refractory organic residues [42-45] whose optical constants have been reported [44-45]. It is of interest to note that the optical properties of these organic residues have been used to infer their presence on the dark hemisphere of Iapetus [46] and 5145 Pholus [18]. In addition, the presence of water ice mixed with relatively light hydrocarbons has been suggested for Pholus [18]. It remains essential for future modeling efforts that optical constants of appropriate ices, their mixtures, and their irradiation products are available.

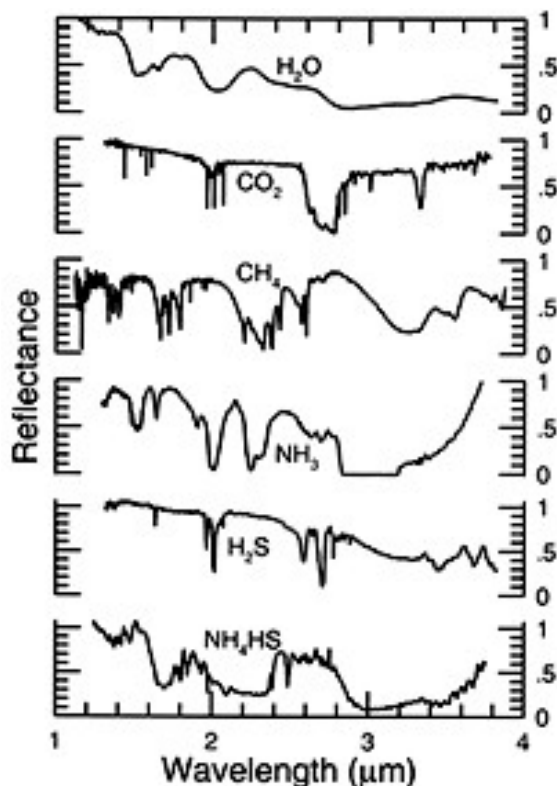


Figure 4. Measured Reflectance spectra of various volatile ices, adapted from Fink and Sill²⁷.

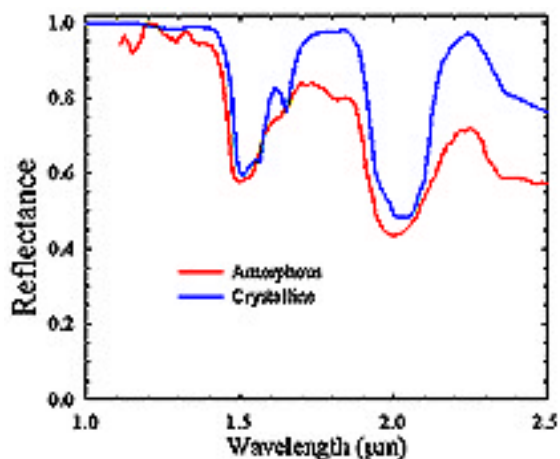


Figure 5. Calculated reflectance spectra of amorphous and crystalline water ice. Crystalline water ice has an additional distinctive reflectance minimum located near 1.65 μm that is lacking in amorphous water ice.

Summary: Water ice is ubiquitous throughout the outer solar system. The water ice appears to be dominated by a crystalline phase, even when found on bodies that whose surface temperature would suggest that the amorphous phase would be favored. Just within the past few years have we begun to recognize some of the by-products of irradiation on icy satellites in the outer solar system. No doubt that there remains much to be discovered.

Table 1. Ices Observed in the Outer Solar System

Jovian Satellites	Io: SO ₂ , SO ₃ , H ₂ S?, H ₂ O? Europa: H ₂ O, SO ₂ , CO ₂ ?, CH?, Salts, H ₂ O ₂ , H ₂ SO ₄ Ganymede: H ₂ O, O ₂ , O ₃ Callisto: H ₂ O
Saturnian Satellites	Mimas: H ₂ O Enceladus: H ₂ O Tethys: H ₂ O Dione: H ₂ O, C, HC, O ₃ Rhea: H ₂ O, HC?, O ₃ Hyperion: H ₂ O Iapetus: H ₂ O, C, HC, H ₂ S? Phoebe: H ₂ O Rings: H ₂ O
Uranian Satellites	Miranda: H ₂ O Ariel: H ₂ O, OH? Umbriel: H ₂ O Titania: H ₂ O, C, HC, OH? Oberon: H ₂ O, C, HC, OH?
Neptunian Satellites	Triton: N ₂ , CH ₄ , CO, CO ₂ , H ₂ O
Pluto	N ₂ , CH ₄ , CO, H ₂ O Charon: H ₂ O, NH ₃ , NH ₃ hydrate
Trans-Neptune Objects	H ₂ O, HC-ices (e.g. CH ₄ , CH ₃ OH), HC, silicates

References: [1] Cottin et al. (1999) *Planet. Sp. Sci.*, **47**, 1141 [2] Greenberg (1982) in *Comets*, L.L. Wilkening, Ed., U. Az. Press, 131 [3] Lewis (1972) *Icarus*, **16**, 241 [4] Prinn and Fegley (1989) in *Origin and Evolution of Planetary and Satellite Atmospheres*, S.K. Atreya et al., Eds., U. Az. Press, 78 [5] Aikawa et al. (1997) *Ap. J.*, **519**, 705 [6]

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Laboratory Measurements Applied to Missions :

The Role of Laboratory Measurements in Optimizing Cometary Mission Science

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Little is known about the composition and/or mineralogy of cometary nuclei, primarily because they are relatively small objects that are shrouded from detailed remote study by extensive and optically thick comae. Groundbased and spacebased observations of comae and tails, as well as studies of IDPs and the ISM, provide data that can be used to infer the presence of a number of materials on the nucleus itself [e.g., reviews in 1]. In addition, studies of some "transitional objects" like some asteroids, Centaurs, and KBOs provide insights on the probable compositions of cometary nuclei [e.g., 2-4]. But to date, only the Vega and Giott/Halley missions

have carried instruments capable of compositional determinations directly into the near-nucleus environment [e.g., 5]. This situation will change very soon, during what promises to be an exciting decade (and beyond) of cometary space missions (Table 1).

Laboratory investigations of potential cometary nucleus ices and minerals, particularly those that can be performed in an environment that closely simulates the nucleus (near vacuum, variable temperature, variable irradiation, etc.), have the potential to optimize the design and performance characteristics of instruments and investigations on the upcoming missions, as well as the interpretation of returned data. Specific examples will be described in this review talk, focusing on the compositional and mineralogic implications of reflectance spectroscopy, compositional and thermophysical implications of thermal IR observations, and compositional implications of mass spectroscopy and other chemical analyses of coma and nucleus materials.

Upcoming Cometary Space Missions.

Mission	Target(s)	Encounter Date(s)	Measurements
CONTOUR	Encke SW3 d'Arrest	2003 2006 2008	Multispectral images, near-IR spectra, dust analysis, mass spectroscopy
Stardust	Wild-3	2004	Imaging, dust analysis, sample return
Deep Impact	Tempel 1	2005	Multispectral images, spectra
Rosetta	Wirtanen	2011	Multispectral imaging, UV, IR, mm spectra, dust analysis, isotopes, mass spectra; APXS, microscopy, gas analysis
DS1	Wilson-Harrington? Borrelly?	?	Imaging? Spectroscopy?

References: [1] "Comets," (1982) L. Wilkening, ed., U. Arizona Press, Tucson. [2] Cruikshank, D.P. *et al.* (1998) *Icarus*, 135, 389-407. [3] Brown, R.H. *et al.* (1997) *Science*, 276, 937-939. [4] Bus, S.J. *et al.* (1991) *Science*, 251, 774-777. [5] Keller, H. U. (1990) in "Physics and Chemistry of Comets," W.F. Huebner, ed., pp. 13-68, Springer-Verlag.

Simulations :

LIMITATIONS OF LABORATORY SIMULATIONS

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Laboratory simulations of astrophysical ices are intended to measure their optical and physical properties as well as their physico-chemical evolutions. However in several cases, some practical limitations avoid to accurately reproduce the effective state of these ices and their evolutions. The results of the simulations may then not be totally relevant to the icy object studied and misleading identifications or improper interpretations of the physico-chemical state of the astrophysical ices may result.

One of the first problem encountered when trying to identify the molecular species that produce the bands observed in astronomical spectra is the availability of laboratory spectra of molecules in the relevant spectral range. For example, the UV range is especially poor in reliable data for most of the ices. But even in the most studied range, the mid-infrared, spectra of several molecular ices are available at only one or two temperatures.

A very important question to raise during ice identification or before starting a simulation of an astrophysical situation is the relevance of the physical state of the sample to that of the astrophysical ice in its environment. Both temperature and

composition during ice condensation as well as its thermal history mainly determine its physical state. The strong differences in the optical properties and physical behaviors between the amorphous and crystalline phases of a same ice are well known. However, with ice mixtures the thermodynamical state (i.e., in or out of thermodynamical equilibrium) not only determine the crystalline organization of the molecules, but also strongly influence the microscopic distribution of the different species within the ice structure and thus modify their various physical and chemical properties.

Four main types of ice sample formation techniques, with their respective advantages and limitations, are commonly used: 1) thin film obtained under "vacuum" by direct deposition from the gas phase on a cold substrate, 2) thick crystalline ice samples formed in a closed cell by crystallization from the liquid phase and 3) "frost" samples obtained by condensation under a controlled atmosphere, 4) powder samples prepared by crystal crushing. The first two are used when transmission spectroscopy is used to measure the optical properties of ices or as a tool to probe and monitor their composition during any physico-chemical processing. The last two are mainly devoted to reflectance spectroscopy.

Each techniques have different capabilities in reproducing the various states of ices and allow to measure different properties. In many cases their are complementary. For example, the maximum temperature of thin films is strongly limited by the sublimation temperature of the ice sample under vacuum. Even thin films of water ice cannot be syudied above about 180 K. Higher temperatures, up to well above the melting point, may be reached in closed

cells but, on the other hand, amorphous and metastable phases can only be produced by low temperature 'out-of-equilibrium' condensation. The complementary ranges of sample thicknesses offered by the two techniques also allow to measure the optical constants of absorption bands over a very wide range of intensities and thus over a wide spectral range.

Contamination of the samples by unwanted molecules is also one of the major limitations in many experiments. Different sources of contaminations (air, water, cell degassing, oil, ...), differing with the setup and the technique used, are known but not always well controlled. Depending on the level of contamination and on the contaminant(s), spurious spectroscopic effects or unwanted chemical reactions may occur. They are in most cases important issues in the interpretation of the results. Several techniques exist to limit these contamination effects or at least to estimate their contribution to the properties or the process studied.

In the case of the study of irradiation of ices by various types of energetic photons or particles, the total dose deliverable to a sample within laboratory time scales may be much smaller than that received by an icy surface over many years and up to the age of the solar system. On the other hand, the fluence necessary to reach a relevant total dose may be much higher than for solar system ices. This may lead to different chemical processes and pathways if, for examples, 'two particles' interactions occur or simply when the energy deposited by one particle has not been completely dissipated before the next interaction.

When studying the evolution of ices, the astrophysical time scale is generally much too large to be directly simulated in the laboratory. Thus accelerated evolutions need to be simulated. However, the physical and chemical time scales of the processes should be respected when varying a parameter that drive the evolution, otherwise out-of-equilibrium processes may occur that may be irrelevant to the ones occurring in the astrophysical context. For example, the evolution of an ice mixture during warmup may strongly depend on the relative values of the warming rate and the kinetic rate of the phase changes and/or the differential sublimations that may occur.

A number of other physical parameters of the real ice grains or surfaces, such as grain size and shape, surface porosity and roughness, etc, ... may be quite difficult to reproduce because of inherent limitations in pressure, temperature and time in laboratory simulations of the astrophysical environment.

One, or several of the limitations, or their effects, listed above may also explain the lack of reproducibility between apparently similar experiments performed in different laboratories, and even sometimes performed with the same setup in the same laboratory. A careful analysis of the experimental conditions generally allow to understand the origin of the differences in the results.

In this talk I will review the limitations of the different types of experiments currently performed on ices and illustrate the effects of several of them on the validity or relevance of the results to specific astrophysical problems.

Finally, I will give some general directions on what I consider to be the most important parameters to control when performing laboratory measurements

intended to be relevant to specific solar system ices issues.

--end PROSSI abstracts --