Radiolytic Gas-Driven Cryovolcanism in the Outer Solar System

John F. Cooper¹, Paul D. Cooper², Edward C. Sittler³, Steven J. Stümer⁴,⁵, Abigail M. Rymer⁶, and Matthew E. Hill⁶

¹Heliospheric Physics Laboratory, Code 672, NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD, 20771 USA
²Department of Chemistry and Biochemistry, MS 3E2, George Mason University, 4400 University Drive, Fairfax, VA, 22030 USA
³Geospace Physics Laboratory, Code 673, NASA Goddard Space Flight Center, Greenbelt, MD, 20771 USA
⁴CRESST and Astroparticle Physics Laboratory, Code 661, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA
⁵Universities Space Research Association, 10211 Wicopin Circle, Suite 500, Columbia, MD 21044, USA
⁶Applied Physics Laboratory, Johns Hopkins Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723-6005, USA

Submitted to Journal of Geophysical Research - Planets, August 6, 2007
Abstract

Water ices in surface crusts of Europa, Enceladus, Saturn’s main rings, and Kuiper Belt Objects can become heavily oxidized from radiolytic chemical alteration of near-surface water ice by space environment irradiation. Oxidant accumulations and gas production are manifested in part through observed H₂O₂ on Europa, tentatively also on Enceladus, and found elsewhere in gaseous or condensed phases at moons and rings of Jupiter and Saturn. On subsequent chemical contact in sub-surface environments with significant concentrations of primordially abundant reductants such as NH₃ and CH₄, oxidants of radiolytic origin can react exothermically to power gas-driven cryovolcanism. The gas-piston effect enormously amplifies the mass flow output in the case of gas formation at basal thermal margins of incompressible fluid reservoirs. Surface irradiation, H₂O₂ production, NH₃ oxidation, and resultant heat, gas, and gas-driven mass flow rates are computed in the fluid reservoir case for selected bodies. At Enceladus the oxidant power inputs are comparable to limits on non-thermal kinetic power for the south polar plumes. Total heat output and plume gas abundance may be accounted for at Enceladus if plume activity is cyclic in high and low “Old Faithful” phases, so that oxidants can accumulate during low activity phases. Interior upwelling of primordially abundant NH₃ and CH₄ hydrates is assumed to resupply the reductant fuels. Much lower irradiation fluxes on Kuiper Belt Objects require correspondingly larger times for accumulation of oxidants to produce comparable resurfacing, but brightness and surface composition of some objects suggest that such activity may be ongoing.
Introduction

Explosive volcanism on Earth originates from gas-driven (mostly H$_2$O vapor and CO$_2$) ejection at high temperature of an incompressible fluid from a subsurface magma reservoir to the planetary surface. High temperatures and plume gas output from volcanic hot spots at Io suggest a similar propulsive process. Comet outgassing from solar heating on approach to the Sun is well known, presumably involving release of trapped gases from cometary ices. Outgassing of N$_2$ has previously been detected [Soderblom et al., 1990] by Voyager 2 at Triton, the largest moon of Neptune, and appears to be similarly driven by solar heating [Brown et al., 1990; Kirk et al., 1990], but the presence of subsurface fluids is unknown. Charon now shows potential surface evidence in ammonia hydrates for cryovolcanic flows from the subsurface [Cook et al., 2007]. Absence of any ongoing surface change on Europa [Phillips et al., 2000] suggests lack in the surface-accessible ice crust environment of cryovolcanic energy sources. A thick ice crust would likely preclude direct access to Europa’s surface of dissolved gases from a putative subsurface ocean indicated by surface geologic features and induced magnetic fields [Pappalardo et al., 1999].

Dramatically visible ice plume activity at Enceladus [Porco et al., 2006] now provides unique opportunities for investigation with repeated observations during the continuing Cassini mission at Saturn. The measured presence of H$_2$O, CH$_4$, simple hydrocarbons, and a yet-unresolved mixture of CO and N$_2$ [Waite et al., 2006] in the plume gas may indicate cryovolcanism involving the liquid water reservoir inferred by Porco et al. [2006]. However, a comet-like process involving only heat-driven release of trapped gases from ice clathrates has also been suggested [Kieffer et al., 2007]. Although NH$_3$ is not highly abundant in either the plume gas [Waite et al., 2006] or in the surface ice [Brown et al., 2006], high temperature chemistry at the deep core-mantle boundary has been proposed by Matson et al. [2006] as the gas and hydrocarbon source.
Here we propose an alternative process for production of volatile gases that could drive cryovolcanism on Enceladus and other icy bodies with irradiated near-surface water ices. This process arises from interaction of continuously produced radiolytic oxidants and primordial chemistry. First, the unique aspect of this model is that chemical energy for oxidation arises in the outer ice crusts of planetary bodies from the continuous irradiation of near-surface water ice by energetic charged particles from the magnetospheric, heliospheric, and local interstellar space environments. Second, chemical energy and cryovolcanic driver gases are released by oxidation of primordially abundant reduced “fuel” compounds including ammonia, methane, and other hydrocarbons that originally accreted with water ice to form the underlying low density ice mantles of these bodies. Gravitational tides, internal tectonic activity, and radioisotope decay provide internal heating to increase rates of oxidant-fuel chemical reactions in cryogenic ice environments. The high exothermic energy yields of these reactions can potentially make the reactions self-sustaining. The subsurface liquid reservoir advocated for Enceladus by Porco et al. [2006] would provide an ideal high thermal gradient environment around the ice-liquid margins of the reservoir to sustain such reactions. Since reaction rates would increase with temperature in the 80 – 273 K range expected at the margins of a high-temperature water reservoir, exothermic heat production would raise local temperatures at reaction sites, and the reactants may concentrate in these locations, explosive results might be expected as observed.

The primary oxidant, O$_2$, in Earth’s atmosphere comes from biological photosynthesis, but surface oxidants on icy surfaces in the outer solar system are naturally produced in exposed water ice by radiolysis from irradiation by energetic charged particles and solar ultraviolet photons. Europa, Ganymede, and Saturn’s rings all have atmospheric environments of molecular oxygen presumably arising from particle or photon irradiation [Hall et al., 1995, 1998; Johnson et al., 2006], while all three icy Galilean moons have condensed phase O$_2$ in the surface ice [Spencer et al., 1995; Spencer and Calvin, 2002]. Ozone is a sensitive proxy for atmospheric oxygen and is detected at Ganymede [Noll et al., 1996], as well as at the Saturn moons Dione and Rhea [Noll et al., 1997]. Presence of oxidants may be indirectly
indicated by detection of atmospheric CO₂ as a potential oxidation product at Callisto [Carlson, 1999] and of surface CO₂ at Europa [Mccord et al., 1998b], Ganymede [Hibbitts et al., 2003], and Callisto [Hibbitts et al., 2000, 2002]. Further Callisto spectral observations and associated models [Strobel et al., 2002; Liang et al., 2005] suggest that atmospheric O₂, CO₂, and CO may be even more abundant on Callisto than the CO₂ first reported by Carlson [1999]. Cassini spectral mapping measurements [Buratti et al., 2005] show CO₂ in the ice-rich surface environment of the small outer moon Iapetus at Saturn. The present paper explores the possibility that N₂ and CO₂ in the Enceladus plume gas [Waite et al., 2005] might arise as oxidation products of radiolytic processes.

The radiolytic oxidant of highest known yield, hydrogen peroxide (H₂O₂), is produced in low-temperature laboratory measurements [Johnson et al., 2004; Moore and Hudson, 2000; Gomis et al., 2004a, 2004b; Loeffler et al., 2006a] at yields of G = 0.1 – 0.4 H₂O₂ molecules per 100 eV of ionisation energy deposited by incident primary charged particles. The measured yield depends on existing abundances of other oxidants and is highest in the presence of O₂ and CO₂ within the irradiated ice. Although present experimental yields for direct production of O₂ are highly uncertain [Johnson et al., 2004] by orders of magnitude at G = 10⁻⁴ to 10⁻¹, even slow accumulation over millions of years in volume ice could saturate the ice crusts of irradiated icy moons and ring bodies, while also boosting the H₂O₂ yield and cumulative concentrations. Sublimation of directly irradiated water ice can also concentrate the H₂O₂ product [Loeffler et al., 2006a], potentially producing explosive [Andrews, 1990] heating and oxidation transients upon exothermic dissociation of the concentrated peroxide.

Hydrogen peroxide has been detected at the maximally high source rates on Europa’s heavily irradiated surface with surface concentrations ~ 0.1% relative to water ice [Carlson et al., 1999] and is possibly present as a UV-absorbing component in surface ices of Ganymede and Callisto [Hendrix et al., 1999a, 1999b]. There are preliminary reports of detection via near-infrared absorption on Enceladus [Newman et al., 2006, 2007]. The relatively short lifetimes (four days at Jupiter, twenty days at Saturn) for H₂O₂ dissociation by solar
ultraviolet photons make surface detection difficult at sensible depths up to a few hundred
micrometers. Products of more penetrating irradiation at millimeter to meter depths [Cooper
et al., 2001] beyond the UV penetration range ~0.15 μm [Carlson et al., 1999] would,
however, continue to accumulate. Furthermore, burial of radiation products by water frost
deposition from cryovolcanic emissions may be faster than the production rate. Burial by
meteoritic impact gardening may also protect radiolytic products from photolytic destruction
as suggested earlier for Europa [Cooper et al., 2001].

Low abundances of gaseous CH₄ in the atmospheres of Earth, and of Mars [Formisano et
al., 2004; Mumma et al., 2004], illustrate that oxidants and reductants cannot long co-exist in
chemically reactive environments where continuous sources must replenish the observed gas.
The presence of abundant frozen CH₄ on Pluto, Eris, and other Kuiper Belt Objects
[Cruikshank et al., 1997; Brown et al., 2005], and of atmospheric CH₄ on Titan [Niemann et
al., 2005], indicates that oxidized water ices are not presently in direct chemical contact with
the sensible surfaces and atmospheres of these bodies. However, the CH₄ surface layers on
icy bodies, and the dominant CH₄ hydrocarbon in Titan’s atmosphere, could be ejecta from
past and even ongoing cryovolcanism, as arising from occasional interactions of otherwise
segregated oxidant and reductant concentrations in the near-surface environment.

Fluid environments are thought to be essential for evolution of life but also enable the
dramatic effects of gas-driven volcanism by the combined gas-piston interaction of
subsurface fluids and gases. Liquid water oceans at tens to hundreds of kilometres in depth
may account for induced magnetic field measurements at the icy Galilean moons of Jupiter
[Kivelson et al., 2004], and a south polar water reservoir may account in part for the plume
activity at Enceladus. Other internal heat sources, e.g. radioisotope decay, may account for
modern presence of fluids even in cases of weak tidal heating, as at Callisto [McKinnon,
2006; McKinnon and Barr, 2006]. If so, even the icy dwarf planets of the Kuiper Belt, many
much larger than Enceladus, might have subsurface reservoirs of the requisite incompressible
fluids at eutectic temperatures, e.g. 173 K for H$_2$O-NH$_3$ mixtures, to enable active cryovolcanism.

In this paper we quantitatively model radiolytic gas-driven cryovolcanism for illustrative cases of Enceladus and elsewhere in terms of the proposed sequence of radiolytic chemical processes from surface irradiation and oxidant production, to exothermic H$_2$O$_2$ dissociation and fuel oxidation, and finally to gas production giving rise to plume emissions. Underlying assumptions in the model are vertical mobility of radiolytic products and underlying fuel compounds in the south polar ice crust, trace abundances of metal catalysts to trigger H$_2$O$_2$ dissociation even at low temperatures, an unlimited supply of fuel compounds presumably brought up by rheological flows from deep primordial reservoirs, and a subsurface H$_2$O fluid reservoir that underlies the polar cap. The fluid reservoir provides a steep thermal gradient around its warm ice margins to accelerate exothermic chemical reactions, becomes pressurized with gaseous oxidation products, and provides the bulk of plume mass flow through gas-driven propulsion of the incompressible fluid. Using representative flux spectra for electron or proton irradiation in selected orbital environments of the outer solar system, we compute the radiolytic model parameters for icy bodies in these environments under the above common assumptions to show the full potential range of cryovolcanism that could be driven by radiolytic gases in diverse outer planet environments from Europa and Enceladus to the Kuiper Belt and the Oort Cloud. In the final discussion we then characterize the strengths and weaknesses of this model with respect to those of other models previously published and widely reported for Enceladus.

Enceladus

The water ice [Porco et al., 2006], neutral gas [Waite et al., 2006], and dust [Spahn et al., 2006] plumes of Enceladus provide the second known example of active cryovolcanism and are also produced, like on Triton, in an icy surface heavily irradiated by energetic particles, mostly electrons, in the orbital environment of a planetary magnetosphere. We suggest that
the plume activity at Enceladus could at least partly arise from sporadic interactions of radiolytic oxidants and primordially abundant reductants brought into direct chemical contact within the near-surface (tens of meters to kilometers) environment by internal rheologic processes. Volatile gas products of such reactions, and the primary drivers for cryovolcanic activity, could include CO₂ and CO, commonly found in outgassing from comets, from CH₄ oxidation, and N₂ from NH₃ oxidation. Plume neutral gas measurements by the Cassini Ion Neutral Mass Spectrometer (INMS) instrument [Waite et al., 2006] do not distinguish N₂ from CO, but if N₂ output is significant as now indicated by recent modelling of data from the Cassini Plasma Spectrometer [Smith et al., 2007], active cryovolcanism and associated outgassing on Enceladus today could be a model for early formation of gravitationally bound N₂ atmospheres on more massive icy bodies such as Titan [Owen, 2000; Niemann et al., 2005].

Laboratory data [Loeffler et al., 2006b] indicate that NH₃ in thin films of water ice reacts strongly with radiolytic products of direct energetic particle irradiation to form N₂ gas, but near-infrared surface measurements [Brown et al., 2006] at Enceladus find no evidence for NH₃ above trace abundances less than one percent relative to H₂O. This low surface abundance is consistent with a similar upper limit 0.5 % reported from neutral plume gas measurements by the Cassini Ion Neutral Mass Spectrometer [Waite et al., 2006]. Any NH₃ brought to the surface of Enceladus by rheological transport, or as redeposited to the surface with plume ejecta, is then destroyed rapidly by direct irradiation processes. Absence of NH₃ and other reduced compounds above trace levels also means that oxidants can accumulate near the surface without immediate losses to oxidation of these compounds. This circumstance motivates our stratigraphic model (Figure 1) in which oxidant layers are transported downward from the surface to interact with layers of reduced compounds similarly transported upward from deep primordial reservoirs.

Chemical energy introduced by radiolytic oxidant production at icy surfaces provides an energy source for cryovolcanic activity and could be particularly effective in warm ice and
liquid near-surface environments suggested [Porco et al., 2006; Spencer et al., 2006] for
Enceladus. The young geologic age from crater counts in the south polar region [Porco et al.,
2006], and a current model for polar reorientation by diapirism [Nimmo and Pappalardo,
2006], could indicate ongoing material exchange between the irradiated surface, the
subsurface source layers for the visible plumes, and the deeper interior. Despite assumptions
in other Enceladus plume models to the contrary [Matson et al., 2006], this vertical transport
cycle apparently does not extend to the moon’s ice mantle boundary with the hot rocky core,
since no Europa-like [McCord et al., 1998a, 1998b] mineral salt species from rocky material
are detected at the surface. Lack of Europa-like non-ice material extrusion or ejection to the
surface, relative to water ice deposition [Verbiscer et al., 2007], is likely why Enceladus
maintains its high visual albedo. Similar considerations may apply to internal transport within
bright Kuiper Belt Objects, perhaps with darker objects being so due to lesser internal
differentiation during primordial formation as compared to the brighter objects.

Sublimation of the H\(_2\)O ice matrix in the warm [Spencer et al., 2006] (145 K) south polar
region could produce high H\(_2\)O\(_2\) concentrations [Loeffler et al., 2006a] which could migrate
to the subsurface environment in warm ice flows. High solubility of H\(_2\)O\(_2\) in liquid H\(_2\)O
would greatly increase downward and lateral transport rates in near-surface melt water or
brine flows and within subsurface water reservoirs. Highly exothermic molecular reactions of
the oxidants could occur in liquid phase with a near-surface reservoir of dissolved reductants
(e.g., NH\(_3\)) in solution with H\(_2\)O, or in solid-state phase with hydrate forms of reductants as
illustrated in Figure 1. Mixtures of H\(_2\)O and H\(_2\)O\(_2\) have lower freezing temperatures than
pure H\(_2\)O and may be energetically favored in early and present cryospheric environments of
Earth [Liang et al., 2006], Mars [Schulze-Makuch and Houtkooper, 2006; Houtkooper and
Schulze-Makuch, 2006], Europa [Chyba and Hand, 2001], and elsewhere for biological
evolution.

The illustration in Figure 1 shows a variety of oxidant and reductant species, but for this
report we focus on sequences starting with the catalytic dissociation of H\(_2\)O\(_2\) to O\(_2\) in the
presence of a thermal gradient on the ice margin of a subsurface fluid reservoir and of a metal catalyst X. Exothermic reaction sequences can be ignited in H₂O-NH₃ or H₂O-CH₄ mixtures by the hot O₂ from H₂O₂ dissociation. The principal reaction equations and associated exothermic heat outputs are as follows:

\[ \text{H}_2\text{O}_2 + X \rightarrow \text{O}_2 \quad \Delta H_r = 98.2 \text{ kJ/mol (1.02 eV/H}_2\text{O}_2) \]
\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} \quad \Delta H_r = 1359 \text{ kJ/mol (14.1 eV/NH}_3) \]
\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_r = 890 \text{ kJ/mol (9.2 eV/CH}_4) \]

The activation energy needed to initiate these reactions can be provided in-situ by the initial H₂O₂ dissociation or by catalytic reactions of radicals such as OH or HO₂. The subsequent oxidation of NH₃ and CH₄ respectively forms N₂, CO, or CO₂ gases as drivers for cryovolcanic activity. The H₂O₂ dissociation can be catalysed even in low temperature environments by trace abundances of dissolved transition metal ions (e.g., Ti, V, Fe, Ni, Cu, Zn, Mo). Silver or platinum catalysis of H₂O₂ monopropellent at concentrations of 70 – 98% in water is used to produce hot (>873 K) steam mixtures of the H₂O and O₂ combustion products in rocket propulsion systems [Andrews, 1990]. OH and HO₂ radicals are catalytically produced in the Fenton’s Reagent-like transition metal decomposition of H₂O₂. Iron in the form of FeSO₄ salt is the typical catalyst for Fenton’s Reagent reactions and the metal is universally abundant as a potential catalytic agent for Enceladus. Since we are mainly concerned with visible cryovolcanic activity in the near-surface environments of icy bodies, these low-temperature catalytic reactions may be more directly linked to such activity than high-temperature [Matson et al., 2007] (500 – 800 K) reactions, e.g. for endothermic NH₃ dissociation (2NH₃ → N₂ + 3H₂), in the deep interior of Enceladus and other icy moons.

Ammonia has not yet been identified at Enceladus from initial Cassini Ion Neutral Mass Spectrometer (INMS) measurements of the neutral plume gas [Waite et al., 2006], but nitrogen as an atomic or molecular ion is certainly present in the magnetospheric plasma of Saturn at the orbit of Enceladus [Smith et al., 2005; Sittler et al., 2005; Sittler et al., 2006]. Cassini Plasma Spectrometer (CAPS) measurements for radial distributions of nitrogen ions are consistent [Smith et al., 2007] with a molecular nitrogen source at Enceladus. Apparent
low abundance <1% of NH₃ in the neutral gas does not rule out presence of ammonia in other forms such as the ammonium ion NH₄⁺, highly abundant at neutral pH in H₂O–NH₃ fluid mixtures and indistinguishable from H₂O⁺ at the same mass/charge in plasma ion data. Alternatively, H₂O₂ oxidation of NH₃ may be rapid in the fluid state and consistent with absence of these species in the plume gas. As depicted in Figure 1, the primary reaction sites contributing to plume gas production might occur at lower but more sustainable rates in hydrate [Kieffer et al., 2006] phases within warm ice in boundary regions surrounding a central liquid reservoir with the main non-H₂O components being gaseous products of oxidation from these regions.

The advantage of gas-driven fluid flow models for cryovolcanism is that modest molar production rates for gas can lead to much larger mass ejection rates for incompressible fluids. The measured [Waite et al., 2006] volatile gas abundances relative to H₂O at Enceladus correspond to a gas-rich subsurface source environment at a total pressure ~ 10² bars. Bubbles of hot, 10³ K, gas emerging at this pressure into, and rising within, a water reservoir would expand until pressure and temperature equalize with respect to the ambient hydrostatic environment. At the one-bar level, nearly equivalent to one kilometer depth in pure 273 K water at surface gravitational acceleration g ~ 0.1 m s⁻², the mass flow ratio of displaced water and N₂ gas is 800:1 as used for the plume flow rates in Table 1. This ratio proportionately increases for declining hydrostatic pressure toward the surface until water depths less than ten meters [Porco et al., 2006] at which sublimation vapour pressure exceeds hydrostatic pressure. Thus a liquid near-surface environment has an advantage in our model of high mass ejection for plume fluid relative to gas production.

Enceladus offers the best available test for cryovolcanic models, since in-situ flyby measurements are available from the ongoing Cassini mission with more planned in the future. At minimum flow speeds of 240 m s⁻¹ for gravitational escape, the measured or inferred quantities are H₂O mass loss rates: 3 – 90 kg s⁻¹ from direct neutral gas measurements [Waite et al., 2006], 150 – 350 kg s⁻¹ from far ultraviolet absorption [Hansen...
et al., 2006], and up to 100 kg s\(^{-1}\) from plasma flow deflection by pickup ion mass loading

[Tokar et al., 2006]. Averaged over the south polar cap region of area 72,220 km\(^2\) southward of 55\(^\circ\)S, these limits respectively correspond to kinetic power, delivered to the subsurface reservoir fluid in our model by oxidation product gases, of 0.001 – 0.04, 0.06 – 0.14, and 0.04 mW m\(^{-2}\). Neutral gas data [Waite et al., 2006] also suggest a narrow density spike of mass flow \(-0.015\) kg s\(^{-1}\) near Cassini closest approach. Overall gas data allow a large range of spatial and temporal variability in the flow.

As discussed in the next section, the energy fluxes delivered to the south polar region of Enceladus by magnetospheric electron and cosmic ray proton irradiation, and the heat fluxes arising from oxidative reactions, overlap the plume flow power requirements. However, the model gas production rates from radiolytic oxidation are near, or well below, measured lower limits on plume emissions for the product gases and suggest that relatively high abundances of gas have already accumulated in a liquid fluid reservoir after depletion of dissolved NH\(_3\). That is, the current radiolytic oxidant input could maintain the kinetic power of the plume flows but presently be uncorrelated to the cumulative non-H\(_2\)O gas composition of the fluid. This suggests a gas-driven cryovolcanic system that is presently in high output phase but that will eventually decline in output as the reservoir gas pressure is released until more gas accumulates as we expect from oxidation of reductant fuels. Since the inflowing chemical energy from radiolysis is continuous, and the potential fuel reservoir from the moon interior is large, there could be many cycles of high and low activity in the familiar pattern of the Old Faithful geyser at Yellowstone National Park on Earth.

Another measured quantity from Cassini measurements is the \(\sim 80\) mW m\(^{-2}\) average surface power of the total 5.8 GW thermal emission from the south polar cap [Spencer et al., 2006] of Enceladus below 55\(^\circ\)S. If this emission level were continuous, our estimates on steady-state radiolytic inputs, as discussed in the next section, would be far too low to account for it. However, even the globally averaged (area = 798,650 km\(^2\)) tidal and radiogenic internal heating [Porco et al., 2006], each being about 0.5 GW (0.6 mW m\(^{-2}\)) and
comparable to the incident energy flux (Table 1) at the global surface from magnetospheric
electrons, fall far short as well. The peak temperature of the measured thermal emission at
145 K [Spencer et al., 2006] is far too low [e.g., Matson et al., 2007] to ignite the oxidation
sequences producing CO$_2$ and N$_2$ from hydrocarbons and ammonia, so any direct link
between the heat, water plume, and gas emissions remains highly speculative. Since heat may
be retained for long intervals within a body of sufficiently low thermal conductivity [Kargel,
2006], the current thermal emission could be from an earlier transient pulse of high internal
heating. Conceivably this heat pulse might have created or expanded the putative liquid
reservoir. The enhanced thermal environment would not directly create cryovolcanic gases
but would do so indirectly through acceleration of catalytic reactions such as we discuss for
the radiolytic model.

Radiolytic oxidant accumulation in the ice crust over tens of thousands of years or longer
could account for transient heat emission and plume activity even at current levels, e.g. if
large clumps of peroxide-saturated ice had recently come into contact with concentrations of
ammonia or other fuels as illustrated in Figure 1. The relatively distinct layers of oxidants and
frost depicted in this figure would break up into clumpier concentrations during downward
rheological transport and could aggregate into distributions of many smaller clumps and some
large clumps over time. Lower freezing temperature of H$_2$O$_2$-enriched ice could produce
more concentrated pockets of H$_2$O$_2$ over successive local melting and freezing cycles in the
vicinity of the liquid reservoir. Relatively explosive activity may explain the large increase of
February 2004 in neutral oxygen density observed via ultraviolet emissions [Esposito et al.,
2005] as Cassini approached the Saturn system. The inferred doubling of E-ring mass by
5x10$^8$ kg and subsequent dissipation to previous mass level over a two-month period is
equivalent to Enceladus outgassing at 100 kg/s over this same period.

Energy Input and Gas Production
The Cassini Orbiter has now flown several times across the jovicentric orbit of Enceladus, but measurements of the energetic particle flux environment at the orbit of this moon are also available from the past Pioneer 11 and Voyager 2 Saturn flybys. Representative flux spectra for the magnetospheric radiation environment of Enceladus and other icy moons of Saturn have been incorporated from the Pioneer and Voyager data into the SATRAD model [Garrett et al., 2005] developed by NASA’s Jet Propulsion Laboratory. The electron flux spectra from SATRAD are plotted in Figure 2 for the local magnetospheric environments of Mimas, Enceladus, Tethys, Dione, and Rhea. The respective integrated energy fluxes above 10 keV for these moons are 2.5, 0.7, 0.5, 0.4, and 0.3 mW/m², so Enceladus’s radiation environment is of intermediate intensity in the Saturn magnetosphere.

In comparison, the energy flux at Europa in the Jupiter magnetosphere is forty times higher [Cooper et al., 2001] even than at Mimas, and yet there is no evidence thus far for ongoing cryovolcanism or any other surface activity there [Phillips et al., 2000]. High radiation energy flux at icy moon surfaces is evidently not sufficient to produce visible plume activity. The present cryovolcanic model further requires radiolytic product access from the irradiated surface to subsurface deposits of reductant fuels such as ammonia and methane. Cassini magnetometer data on ion cyclotron waves suggest a weaker ion source at Dione by a factor of 300 as compared to Enceladus [Leisner et al., 2007]. In the context of the radiolytic model this difference is either due to correspondingly lower abundance of reductants in the upper ice crust of Dione, or to absence of a liquid subsurface reservoir in the event that reductant abundances are similar to those of Enceladus.

For Enceladus the SATRAD spectrum, shown again in Figure 3, provides a useful median sample of the moon’s radiation environment even over the twenty-eight years since the Pioneer 11 flyby in 1979. Figure 3 additionally shows current low and high limits for flux distributions of electrons at Enceladus. A collection of other measured MIMI spectra is also included from several other traversals of the moon’s orbit around Jupiter. These assorted measurements are mostly well bounded by the upper and lower limit spectra.
Integrated input energy, H$_2$O$_2$ production, oxidative heat, and N$_2$ gas fluxes from these distributions are listed in Table 1 for catalyzed exothermic dissociation of H$_2$O$_2$ to O$_2$ and subsequent exothermic oxidation of NH$_3$ to H$_2$O and N$_2$ gas. For these estimates we use the maximum measured radiolytic yield, G = 0.4, a reasonable upper limit from laboratory data [Moore and Hudson, 2000] for an ice crust potentially saturated with CO$_2$ and O$_2$ products of radiolytic chemistry. The plume flow rates in Table 1 are computed for N$_2$ gas displacement of H$_2$O fluid at the 1-bar pressure (1-km fluid depth) level.

The lower limits on incident energy flux come from the Cassini’s Enceladus I flyby, and fluxes were substantially higher a quarter century ago during the Pioneer and Voyager flybys. Subsequent Cassini data show variable fluxes up to the SATRAD level. As a primary source of neutral gas for the Saturn magnetosphere, high plume output may suppress, via energy loss through atomic ionisation, the low-energy seed population of energetic electrons in the magnetosphere. Depletion of low energy plasma electrons in the inner magnetosphere was earlier found by Voyager as a direct indicator of electron energy loss in the E-ring and associated neutral gas environment [Sittler et al., 1981]. The electron fluxes in Figure 3 are measured away from the moon and are representative of globally averaged irradiation at the surface but would vary there with longitude and latitude location. Magnetospheric magnetic fields [Dougherty et al., 2006] and plasma flow [Tokar et al., 2006] appear significantly perturbed around Enceladus, so energy flux at the surface may concentrate at higher values, e.g. by a factor of two, in the polar regions with reduced values at the equator. Enhancement of more dense or amorphous H$_2$O$_2$ ice in the tiger stripes region [Newman et al., 2006] is consistent with polar focusing of the magnetospheric particle fluxes.

Comparative incident flux distributions are also shown in Figure 3, along with corresponding energy flux values in Table 1, for electrons at Europa [Cooper et al., 2001] and for cosmic ray proton irradiation of Saturn’s main rings [Johnson et al., 2006] and of other icy objects [Cooper et al., 2003; Cooper et al., 2006] in the outer heliosphere (40 AU, heliosheath) and local interstellar medium. Cosmic ray interactions with Saturn’s ring
material partly accounts for the observed oxygen atmosphere of these rings through total oxidant production. The dominant oxidant energy source in the rings is presently thought to be solar ultraviolet irradiation [Johnson et al., 2006], and, based on earlier work for Europa [Cooper et al., 2001], we estimate ~ 0.014 mWm⁻² as the contribution of this radiation component at the south polar cap (south of 55°S) of Enceladus. Extrapolation of the cosmic ray energy flux through Saturn’s planetary magnetic field to Enceladus gives an approximate surface contribution there well below the contribution limits from magnetospheric electrons but extending more deeply into the surface. Total UV and cosmic ray energy flux contributions at the Enceladus polar cap are then of order 0.02 – 0.03 mWm⁻², one to two orders of magnitude below the magnetospheric electron input.

The depth profiles of time scales for accumulation of radiolytic dosages computationally sufficient to convert 90% of all irradiated H₂O ice molecules to H₂O₂ at G = 0.4 are shown in Figure 4 for the electron and proton flux spectra in Figure 3. Within the visibly sensible layer, less than 1 mm in depth for inferred ice grain sizes of order 10² μm [Brown et al., 2006], the time scales are 10⁵ years for Enceladus, 10³ years for Europa, and 10⁸ – 4x10⁹ years for the outer heliosphere and beyond. Complete conversion to H₂O₂ in the visible layer can therefore occur on moon and minor planet icy bodies, photolytic destruction and other losses being ignored, over time scales from those of terrestrial ice ages and glacial flow times to the solar system age.

On Enceladus the 10⁷-year turnover of the meter-thick icy regolith layer, as approximated from a Europa model [Cooper et al., 2001] of impact gardening, produces a peroxide fraction to water ice of nearly 10% in this layer. Paucity of large impact craters in the south polar region [Porco et al., 2006] indicates continual resurfacing to kilometers in depth. Over the solar system age, up to ~50 m of water ice at G = 0.4 is then converted to H₂O₂ on Enceladus as compared to ~5 km within Europa’s surface and to 20 cm for Kuiper Belt Objects and Saturn’s rings. These values suggest that the upper ice crusts of both Enceladus and Europa, and much of the sensible and deeper impact regolith layers on KBOs, could be saturated with
\( \text{H}_2\text{O}_2 \) and other oxidants. Since the condensed thickness of Pluto’s ~10-microbar \( \text{N}_2 \) atmosphere [Elliot et al., 2003] is equivalent in mass to ~0.1 cm of \( \text{H}_2\text{O}_2 \), the much thicker radiolytic accumulation of \( \text{H}_2\text{O}_2 \) there may have a significant chemical impact on the atmospheric evolution of Pluto. Higher surface thicknesses ~ 10 cm to 100 m for \( \text{N}_2 \) ice on Triton [Cruikshank et al., 1984], the other site of directly observed cryovolcanic activity, could easily arise from radiolytic chemistry, since that moon orbits Neptune within a hot plasma magnetospheric environment. Neptunian energetic electrons and protons provide \( 10^9 \) W energy input to Triton auroral excitation [Krimigis et al., 1990] as compared to our upper limit of \( 1.5 \times 10^8 \) W from Saturnian electrons at the south polar cap of Enceladus. Greater distance from the Sun at Triton would further increase relative importance of the local radiolytic energy source as compared to previously discussed solar energy sources for the Triton \( \text{N}_2 \) geysers.

Finally, limits on \( \text{N}_2 \) gas mass flux up to 0.08 kg s\(^{-1}\) from \( \text{H}_2\text{O}_2 \) dissociation to \( \text{O}_2 \) and \( \text{NH}_3 \) oxidation are given in Table 1 for all cases. Incompressible fluid displacement factors \( 10^3 \) or greater from the \( \text{N}_2 \) mass flux at fluid depths less than 1 km, the one-bar pressure level, are then sufficient to produce observed total plume mass flows \( 10^1 \) – \( 10^2 \) kg s\(^{-1}\). However, the Cassini INMS [Waite et al., 2006] measured upper limits ~0.2 – 6 kg s\(^{-1}\) for the measured number ratio \( \text{N}_2: \text{H}_2\text{O} \) of 0.04:1.0 of Enceladus plume gas are well above even the upper limit of steady-state production from the radiolytic model.

Since the energy and heat fluxes in Table 1 are comparable to limits on the plume kinetic power, the disparity in gas fluxes suggests a lack of direct coupling between radiolytic gas injection and plume gas ejection. Together with low measured limits from INMS on abundance of \( \text{NH}_3 \) in the plume gas, this disparity may indicate that the plume gas is originating from a gas-saturated subsurface environment in which local abundances of \( \text{NH}_3 \) near the liquid reservoir have recently been depleted by cumulative oxidation. Apparent lack of \( \text{H}_2\text{O}_2 \) in the plume gas, if we assume for the moment that INMS has any significant sensitivity to such reactive species, similarly argues that \( \text{H}_2\text{O}_2 \) and \( \text{NH}_3 \) react mainly in the
boundary regions surrounding the putative liquid reservoir and that only the gaseous oxidation products persist in that reservoir. Future improvements in laboratory calibration of INMS with respect to reactive oxidants may change this assessment. Unless the plumes are unique to the present epoch, the depleted NH$_3$, also including that part lost at the surface by direct irradiation [Loeffler et al., 2006b], must eventually be resupplied by upward transport of NH$_3$-rich ice from the deep interior.

Discussion

The radiolytic model depends on the near-surface production of oxidants that should be present near the surface of icy bodies of the outer solar system, wherever water ice is irradiated by energetic particles and ultraviolet photons from the magnetospheric, heliospheric, or interstellar space environments of these bodies. Chemical energy accumulates in these oxidants over a vast range of time scales in different magnetospheric, and heliospheric, locations. This energy can be released when the oxidants come into contact with reductant fuels such as NH$_3$ and CH$_4$ in the presence either of high temperatures or catalytic materials Hydrogen peroxide is produced by ice radiolysis and photolysis in low-temperature environments and has the advantage of exothermic, potentially explosive, dissociation to O$_2$ in the presence of iron and other commonly abundant metal catalysts. No laboratory measurements are yet available on metal-catalyzed dissociation rates at the observed temperatures of 80 – 145 K on Enceladus but these rates would rapidly increase in the warmer ice surrounding a liquid water reservoir. This initial exothermic reaction could then initiate oxidation of reductants to produce volatile gases driving cryovolcanic activity. Trace hydrocarbon species, such as the INMS-detected [Waite et al., 2006] acetylene and propane at Enceladus, could be produced in the high temperature sequences initiated by H$_2$O$_2$ dissociation. These species may take part in further reactions, potentially with explosive results, as found by Benit and Roessler [1993] for proton-irradiated acetylene frost at 77 K, even at the low end of the Enceladus temperature range.
Visible manifestations of cryovolcanism include emissions of ice grains, neutral gas, pickup ions, and dust, but the generally bright reflective surfaces of other icy bodies, as in the Kuiper Belt, are also highly suggestive of sustained cryovolcanism. New observations of ammonia hydrate on the surface of Charon in the Pluto system [Cook et al., 2007] suggest that cryovolcanism is active there. In the Saturn magnetospheric environment the Enceladus ice grain output sustains the E-ring population which then globally bombards and brightens [Verbiscer et al., 2007] the surfaces of Enceladus and other moons. Cyclic activity at Enceladus could produce stratigraphic layers (Figure 1) of high oxidant accumulation during low activity intervals and of high albedo water frost from direct plume output and surface bombardment by E-ring grains during high activity phases. Currently high plume and thermal emission suggests that Enceladus is now in its most active phase, and that any non-ice materials, including abundant oxidants expected from continuous magnetospheric irradiation, are now mostly buried from view by water ice frost from plume ejecta.

Enceladus outgassing into Saturn’s magnetosphere, and resultant electron energy loss in E-ring dust and neutral gas, should lead to anti-correlation of plume output with the fluxes of energetic and lower-energy suprathermal electrons near and beyond the orbit of Enceladus. The large decrease in low energy (< 0.5 MeV) electron and energetic (> 0.5 MeV) ion fluxes inward from the orbit of Rhea (8.75 Rs) to that of Enceladus (3.75 Rs) was first discovered by Pioneer 11 measurements [McDonald et al., 1980; Simpson et al., 1980; Trainer et al., 1980; Van Allen et al., 1980]. The subsequent Voyager measurements found dropouts in suprathermal (0.03 – 6 keV) electron [Sittler et al., 1981], ring current ion [Connerney et al., 1981; Acuña et al., 1981], and energetic (> 500 keV) ion [Krimigis et al., 1981, 1983; and as reinterpreted by Paranicas et al., 2004] fluxes.

These inward flux decreases are now clearly attributable to Enceladus neutral gas and E-ring ice grain interactions a quarter century after the first suggestion of a potential E-ring interaction by Thomsen and Van Allen [1979] in a report published just after the Pioneer 11 flyby. In comparison, the Pioneer and Voyager energetic electron fluxes increased with no
evident E-ring interaction toward Saturn, until cutoff by the main rings, from source regions in the Enceladus–Rhea region and beyond. Generally reduced fluxes of energetic electrons near the orbit of Enceladus, as recently measured by the Cassini MIMI instrument (Figure 3), suggest that the currently high plume output may be attenuating the supply of low-energy electrons feeding via magnetospheric acceleration processes into the energetic electron population. If so, the current rate of surface oxidant production is now low but will again increase if plume output subsides and the low-energy electron source of the energetic electrons at Enceladus is no longer attenuated in diffusing inward through the E-ring region.

Negative feedback of Enceladus plume activity to the electron source could produce cyclic high phases of “Old Faithful” activity initiated after long periods of high oxidant accumulation rates during low activity phases. Cyclic plume activity elsewhere may be confined to planetary magnetospheric environments in which the cryovolcanic emissions are large enough to attenuate source fluxes of energetic particles producing the surface oxidants. In heliospheric environments the activity may be more episodic and driven by subsurface circulation of reductant fuels to the oxidant-saturated near-surface water ice environment. In all cases, interactions of clumps of highly concentrated oxidants and reductants, as in Figure 1 for Enceladus, could produce transiently high plume activity and heat output after slow accumulations over much longer time intervals, e.g. thousands of years for Enceladus as compared to the quarter-century of our present Voyager-Cassini measurements for the E-ring and now for Enceladus. In comparison, long term storage of heat, e.g. due to low thermal conductivity in the ice mantle [Kargel, 2006], can be theorized for alternative theories invoking episodic tidal heating, but we have yet no independent evidence for such episodes in the surface features and chemical composition of Enceladus.

Enceladus has the highest density, 1.6 g/cc, of all major Saturn satellites excluding Titan, but the sensible surface does not show composition consistent with continuing chemical contact to the requisite rocky core [Porco et al., 2006] underlying the outer ice mantle at this density. There is no evidence from near-infrared imaging spectroscopy [Brown et al., 2006]
for surface presence of Europa-like [McCord et al., 1998a, 1998b] sulfate hydrates or other
non-ice species that might directly convect through warm ice crust layers to the surface or
become manifested through the plume outflow. We suggest that this poses a significant
problem for the widely publicized theory of Matson et al. [2007] that the plumes are a
manifestation of high temperature (> 500 K) ammonia chemistry and resultant gas production
deep in the moon interior at the core-mantle boundary. A deep source is also difficult to
connect to plume variability strongly suggested by the large transient increase [Esposito et
al., 2005] in magnetospheric neutral gas during Feb. 2004. Such transients are more likely to
arise from plume source dynamics closer to the surface.

We acknowledge the suggestions of Kargel [2006] and Kieffer et al. [2006] that gas
clathrate decomposition in the presence of thermal gradients could contribute to Enceladus
cryovolcanism, but production of the enclathrated gases then remains to be explained. If
formed during original accretion and differentiation of Enceladus, these gases would have
long since escaped, since this moon is too small to retain an atmosphere like that of Titan
[Owen, 2000]. Sequestration of the ammonia in rocky ammonium minerals was suggested as
one alternative [Kargel, 2006], but lack of surface compositional expression for continuous
ice mantle circulation from the rock core boundary provides no current support for this
alternative. The radiolytic model instead postulates that primordial ammonia, methane, and
other hydrocarbon sources of cryovolcanic gases are abundant within the ice mantle, e.g. in
the form of hydrates, and that gas production occurs in the warm ice basal margins of a near-
surface liquid reservoir on contact with oxidants from the irradiated surface.

Even at the relatively high temperature of pure liquid water, the spontaneous dissociation
of H₂O₂ to O₂ must be catalysed in the radiolytic model by non-ice contaminants, e.g.
universally abundant Fe, originating either from the rocky mineral composition of the deep
interior or from meteoritic bombardment. The absences of detectable minerals on the surface
and of O₂ in the atmospheric environment argue that this dissociation cannot occur very near
the surface, and that radiolytic H₂O₂ can continuously accumulate and concentrate in the
near-surface ice environment. If the near-surface environment undergoes cyclic melting and freezing phases, the non-ice materials will accumulate as brines at lower depths below the melt layers. These contaminants will similarly have low abundances within a liquid subsurface reservoir and likely contribute only at trace levels to composition of cryovolcanic plumes. For the present model we assume that sufficient trace abundances of Fe and other metals are mixed with continuously upwelling fuels, e.g. hydrates of NH₃ and CH₄, to trigger H₂O₂ dissociation at the basal thermal margins of the fluid reservoir as depicted in Figure 1, and that these metals do not limit the accumulation of H₂O₂ above the reservoir. This vertical gradient in catalyst density allows the requisite inverse gradient in oxidant accumulation to occur and sets the stage for the exothermic reactions leading to gas production and fluid ejection to form cryovolcanic plumes. Initial vertical segregation of oxidants and fuels may be essential to the explosive form of cryovolcanism potentially accounting for the spectacular plumes of Enceladus.

Saturn kilometric radiation (SKR) provides a new diagnostic for limits on magnetospheric mass loading by ions originating from Enceladus plume gas and ice grains. During the 1980 – 1981 flybys the two Voyager spacecraft discovered these radio emissions with a periodicity of 10 hours 39 min 24 ± 7 s, then thought to arise from intrinsic rotation of Saturn [Desch and Kaiser, 1981]. Later Ulysses radio observations from 1994 to 1997 showed changes in SKR periodicity up to 1% relative to the Voyager observations. Initial Cassini measurements determined a more precise value of 10 hours 45 min 45±36 s [Gurnett et al., 2005] for an increase of 6.35 minutes (1%) since 1980 - 1981. Slippage of the coupled magnetosphere-ionosphere system with respect to planetary rotation, due to magnetospheric plasma loading by Enceladus outgassing and subsequent ionisation of plume neutrals, is proposed [Gurnett et al., 2007] to account for the radio SKR period. A theory of rotationally-driven plasma convection [Goldreich and Farmer, 2006] estimates the mass loading for the 1% SKR period variation at 10 kg/s radial mass outflow from Enceladus and the E-ring. Although zonal
variations of Saturn's atmospheric rotation speeds presently preclude independent measurement of intrinsic planetary rotation, differential changes in SKR period could be monitored as a linear measure of Enceladus plume output. Stability of this period within 1% does imply relative stability over the last quarter century but does not limit longer term stability. Continued monitoring of SKR periodicity, as compared to Enceladus plume activity and magnetospheric particle fluxes, is needed to further quantify Enceladus two-way coupling to the magnetosphere.

The current plume flow limits of 3 - 350 kg/s for Enceladus project over the solar system age to the cumulative loss of 0.4 – 46 % from the moon’s total mass. For spherical symmetry a flow rate of 70 kg/s extrapolates to complete loss of the nine percent of total moon mass southward of 55°S. Enormous redistribution of mass would have globally occurred within the deep interior if the plumes had been continuously active at such rates. A far lower limit on cumulative mass loss of 0.03%, corresponding to 0.2 kg/s in flow rate, comes from the observed ~ 0.5-km depression of the south polar cap region [Porco et al., 2006], although much of the plume mass has likely returned to the surface. Thus the average flow rate may have been even much lower even than 3 kg/s, and there could have been long intervals for accumulation of stored radiolytic energy to fully account for all aspects of current plume flow and polar cap heat emission. The present epoch of high activity, manifested in the E-ring during the Voyager era of 1980 – 1981, and now seen directly by Cassini, may be a short-lived and periodic event over the history of Enceladus. An apt analogy may be Old Faithful with variable output eruptions over a few minutes at intervals of about ninety minutes. It is therefore now advisable to calibrate remote long-term indicators of plume activity, potentially including SKR emission that be monitored from Earth, to the ongoing Cassini measurements within the Saturn system.

Oxidant chemistry induced by cosmic ray irradiation could drive resurfacing on the large bright Kuiper Belt Objects such as Eris and more generally account for the diversity of surface brightness and color [Jewitt and Luu, 2001; Doressoundiram et al., 2002] among the
icy dwarf planets of the outer solar system. Water ice mantles should be common on KBOs and deep water-ice absorptions are directly seen on some objects such as the 2003 EL₆¹ collisional family [Brown et al., 2007; Barkume et al., 2006] and Charon [Brown and Calvin, 2000]. Although N₂ and CH₄ ices are dominant on larger bodies such as Pluto [Brown and Calvin, 2000] and Eris [Brown et al., 2005], surface layers of these volatile molecules would not be retained on smaller objects [Brown and Calvin, 2000] and, if present, would have to be renewed by outgassing from the subsurface, e.g. by cryovolcanism. Oxidant production from cosmic ray irradiation of visible surface or near-surface water ice must therefore be accounted for as one chemical energy source for potential cryovolcanic activity of these objects. The respective Voyager 2 and Cassini flyby observations have given the first close looks at active cryovolcanism on Triton and Enceladus. New Horizons is our next opportunity to search for such activity at Pluto and Charon during the April 12, 2015 flyby of this icy dwarf planet system.

Finally, the suggested vertical segregation of near-surface radiolytic oxidants and deeper-lying reductant fuels on irradiated icy bodies potentially provides chemical energy resources for future exploration and habitation of the outer solar system and beyond. Since heliocentric orbits of many of these bodies, such as Centaurs, are dynamically unstable, oxidant and fuel mining can be envisaged on icy objects having more recently entered the inner solar system after billions of years of radiolytic processing in the Kuiper Belt or Oort Cloud regions. If there is ever the need to divert such an object from impact with the Earth, this potentially accessible chemical redox energy accumulated within the body could become a critical resource. In these respects, if the radiolytic model proves to be correct, Enceladus may be viewed not only as an object of intense scientific interest but also as a natural model for astroengineering. Sagan [1994] suggested utilization of icy bodies as spaceships to other stars, and Enceladus may be a spectacularly visible model for fulfilment of this vision.
References


Johnson, R. E., R. W. Carlson, J. F. Cooper, C. Paranicas, M. H. Moore, and M. C. Wong (2004), Radiation effects on the surfaces of the Galilean satellites, In Jupiter - The Planet,


Acknowledgements. This work was supported in part by the Cassini Plasma Spectrometer (CAPS) Project and the Space Physics Data Facility at Goddard Space Flight Center.
Table 1. Radiolytic Cryovolcanism Model Parameters for Enceladus

<table>
<thead>
<tr>
<th>Body - Model</th>
<th>Particle Energy Flux mWm⁻²</th>
<th>H₂O₂ Number Flux (cm²-s⁻¹)</th>
<th>Chemical Heat Flux mWm⁻²</th>
<th>N₂ Source Flow kg s⁻¹</th>
<th>Plume Flow kg s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europa – e</td>
<td>100</td>
<td>1.7x10¹¹</td>
<td>5.4</td>
<td>3.8</td>
<td>3000</td>
</tr>
<tr>
<td>Enc – high e</td>
<td>2.1</td>
<td>3.6x10⁹</td>
<td>0.11</td>
<td>0.08</td>
<td>64</td>
</tr>
<tr>
<td>Enc – mid e</td>
<td>0.7</td>
<td>1.2x10⁹</td>
<td>0.039</td>
<td>0.027</td>
<td>22</td>
</tr>
<tr>
<td>Enc – low e</td>
<td>0.1</td>
<td>1.7x10⁸</td>
<td>0.0054</td>
<td>0.0038</td>
<td>3.0</td>
</tr>
<tr>
<td>Enc – CRP</td>
<td>0.002</td>
<td>3.4x10⁶</td>
<td>0.00011</td>
<td>7.7x10⁻⁵</td>
<td>0.062</td>
</tr>
<tr>
<td>Rings – CRP</td>
<td>0.0005</td>
<td>8.5x10⁵</td>
<td>2.7x10⁻⁵</td>
<td>1.9x10⁻⁵</td>
<td>0.015</td>
</tr>
<tr>
<td>40AU SolMin - CRP</td>
<td>0.003</td>
<td>5.2x10⁶</td>
<td>0.00016</td>
<td>0.00012</td>
<td>0.096</td>
</tr>
<tr>
<td>HS – CRP</td>
<td>0.0035</td>
<td>6.0x10⁶</td>
<td>0.00019</td>
<td>0.00013</td>
<td>0.10</td>
</tr>
<tr>
<td>LISM – CRP</td>
<td>0.0083</td>
<td>1.4x10⁷</td>
<td>0.00044</td>
<td>0.00032</td>
<td>0.26</td>
</tr>
</tbody>
</table>

*Computed at maximum radiolytic yield \( G = 0.4 \) for \( \text{H}_2\text{O}_2 \).

Abbreviations: Enc – X – e (high, middle, and low electron flux models for Enceladus), CRP (cosmic ray proton), Ring (Saturn’s main rings), SolMin (solar minimum), HS (heliosheath), LISM (local interstellar medium).
Figure Captions

Figure 1. Illustration of radiolytic gas-driven cryovolcanism for potential subsurface liquid water reservoir near the surface of Enceladus. A continuous rain of energetic electrons (yellow arrows) drives radiolysis and saturates the upper ice surface with oxidants (blue), mostly $\text{H}_2\text{O}_2$ but with mix of other species. Transient plume activity ejects ice grains falling back to the surface (white ballistic curves) and depositing multiple layers of water frost (white) interspersed with oxidant concentrations accumulating during lower plume activity. Ice upwelling continuously supplies fresh “fuels” (red), e.g. hydrates of $\text{CH}_4$ and $\text{NH}_4$, from the deep interior. Exposure to increasing temperature within the ice margins of the fluid reservoir initiates sequences of exothermic reactions from $\text{H}_2\text{O}_2$ dissociation to fuel oxidation, resultant gas production, and fluid reservoir heating. Percolation of expanding hot gas bubbles from the margins into the incompressible water fluid becomes the driving force for upward movement (white arrows) of gas-saturated fluid to form the plumes. Interactions of lower (left side) or higher (right side) concentrations of oxidants and fuels produce correspondingly less or more gas.

Figure 2. Representative differential flux spectra of Saturn magnetospheric electrons at the equatorial jovian-centric orbits of the icy moons Mimas, Enceladus, Tethys, Dione, and Rhea as determined from the SATRAD model [Garrett et al., 2005].

Figure 3. Differential flux spectra of energetic electrons (red curves) at Enceladus and Europa, respectively from the planetary magnetospheres of Saturn and Jupiter, and of cosmic ray protons (black curves) irradiating icy bodies within and beyond the heliosphere. The thickest solid Enceladus curve is from the SATRAD model. The two medium-thickness Enceladus curves are respectively upper and lower limits from Voyager and Cassini/MIMI electron data. The upper limit comes from Voyager measurements compiled by Maurice et al. [1996], and the lower limit is from Cassini electron flux measurements by the Magnetospheric Imaging Instrument (MIMI) experiment [Krüuger et al., 2004] near the
Jupiter-fixed longitude of this moon during the 9 March 2005 flyby. The limiting flux curves for Enceladus are extrapolated into the SATRAD curve at higher energies. The thinnest red curves are MIMI measurements for other selected periods of Enceladus orbit crossings: Julian days 48, 195, and 266 of 2005. A small peak at 0.03 MeV in the spectrum from day 48 is from a transient injection event. The Europa flux spectrum [Cooper et al., 2001] is a composite of Galileo Orbiter data below 1 MeV from the Energetic Particle Detector [Williams et al., 1992] and Pioneer-Voyager model data [Divine and Garrett, 1983] at higher energies up to 40 MeV. The Enceladus and Europa model spectra are extrapolated for surface interaction modelling as power laws to 1000 MeV from the lower energy measurements. Proton flux spectra are also shown as derived for cosmic ray protons (four dashed curves) in the outer supersonic heliosphere within the classical Kuiper Belt near 40 AU and in the outer heliospheric boundary regions [Cooper et al., 2006] of the heliosheath and the local interstellar medium. The two 40-AU spectra are respectively for minimum [Cooper et al., 2003] and maximum solar activity, the latter data being provided from previously unpublished Voyager data of co-author M. E. Hill.

Figure 4. Surface depth profiles in H₂O ice for time in years to accumulate chemically significant dosages of 60 gigarad (~ 110 eV per irradiated H₂O molecule) from total magnetospheric electron irradiation of Enceladus and Europa as compared to trans-neptunian objects. The two thin solid curves show the partial contributions of higher energy electrons at 1–10 MeV and 10–100 MeV to the Enceladus total irradiation at 10 keV to 1000 MeV, as compared to the total irradiation profile for Europa (dot-dot-dash curve). Comparative profiles (dashed curves) are also shown for cosmic ray proton irradiation of objects near 40 AU near solar minimum [Cooper et al., 2003] and on highly eccentric orbits [Cooper et al., 2006] passing through the heliosheath and into the local interstellar medium. Dosage time profiles are computed for isotropically incident fluxes onto flat surfaces from the flux spectra in Figure 3. The GEANT radiation transport code (http://wwwasd.web.cern.ch/wwwasd/geant/), as implemented in our earlier work [Sturmer et al., 2003; Cooper et al., 2006], is used here for complete interactions of primary electrons, protons, and secondary
interaction products at energies above 10 keV from the flux spectra in Figure 3. Due to limitations on spatial step resolution in GEANT, the proton profiles have been extended to lower energies with stopping range and differential energy loss data of the Stopping and Range of Ions in Matter (SRIM) model [Ziegler et al., 1985] (http://www.srim.org/) also used in the earlier work [Cooper et al., 2001].
Figure 1. Illustration of radiolytic gas-driven cryovolcanism for potential subsurface liquid water reservoir near the surface of Enceladus. A continuous rain of energetic electrons (yellow arrows) drives radiolysis and saturates the upper ice surface with oxidants (blue), mostly $\text{H}_2\text{O}_2$ but with mix of other species. Transient plume activity ejects ice grains falling back to the surface (white ballistic curves) and depositing multiple layers of water frost (white) interspersed with oxidant concentrations accumulating during lower plume activity. Ice upwelling continuously supplies fresh “fuels” (red), e.g. hydrates of $\text{CH}_4$ and $\text{NH}_4$, from the deep interior. Exposure to increasing temperature within the ice margins of the fluid reservoir initiates sequences of exothermic reactions from $\text{H}_2\text{O}_2$ dissociation to fuel oxidation, resultant gas production, and fluid reservoir heating. Percolation of expanding hot gas bubbles from the margins into the incompressible water fluid becomes the driving force for upward movement (white arrows) of gas-saturated fluid to form the plumes. Interactions of lower (left side) or higher (right side) concentrations of oxidants and fuels produce correspondingly less or more gas.
Figure 2. Representative differential flux spectra of Saturn magnetospheric electrons at the equatorial jovicentric orbits of the icy moons Mimas, Enceladus, Tethys, Dione, and Rhea as taken directly from the SATRAD model [Garrett et al., 2005].
Figure 3. Differential flux spectra of energetic electrons (red curves) at Enceladus and Europa, respectively from the planetary magnetospheres of Saturn and Jupiter, and of cosmic ray protons (black curves) irradiating icy bodies within and beyond the heliosphere. The thickest solid Enceladus curve is from the SATRAD model. The two medium-thickness Enceladus curves are respectively upper and lower limits from Voyager and Cassini/MIMI electron data. The upper limit comes from Voyager measurements compiled by Maurice et al. [1996], and the lower limit is from Cassini electron flux measurements by the Magnetospheric Imaging Instrument (MIMI) experiment [Krimigis et al., 2004] near the Jupiter-fixed longitude of this moon during the 9 March 2005 flyby. The limiting flux curves for Enceladus are extrapolated into the SATRAD curve at higher energies. The thinnest red curves are MIMI measurements for other selected periods of Enceladus orbit crossings: Julian days 48, 195, and 266 of 2005. A small peak at 0.03 MeV in the spectrum from day 48 is from a transient injection event. The Europa flux spectrum [Cooper et al., 2001] is a composite of Galileo Orbiter data below 1 MeV from the Energetic Particle Detector.
ingeries up to 40 MeV. The Enceladus and Europa model spectra are extrapolated for surface
interaction modelling as power laws to 1000 MeV from the lower energy measurements.
Proton flux spectra are also shown as derived for cosmic ray protons (four dashed curves) in
the outer supersonic heliosphere within the classical Kuiper Belt near 40 AU and in the outer
heliospheric boundary regions [Cooper et al., 2006] of the heliosheath and the local
interstellar medium. The two 40-AU spectra are respectively for minimum [Cooper et al.,
2003] and maximum solar activity, the latter data being provided from previously
unpublished Voyager data of co-author M. E. Hill.
Figure 4. Surface depth profiles in H_2O ice for time in years to accumulate chemically significant dosages of 60 gigarad (~110 eV per irradiated H_2O molecule) from total magnetospheric electron irradiation of Enceladus and Europa as compared to trans-neptunian objects. The two thin solid curves show the partial contributions of higher energy electrons at 1–10 MeV and 10–100 MeV to the Enceladus total irradiation at 10 keV to 1000 MeV, as compared to the total irradiation profile for Europa (dot-dot-dash curve). Comparative profiles (dashed curves) are also shown for cosmic ray proton irradiation of objects near 40 AU near solar minimum [Cooper et al., 2003] and on highly eccentric orbits [Cooper et al., 2006] passing through the heliosheath and into the local interstellar medium. Dosage time profiles are computed for isotropically incident fluxes onto flat surfaces from the flux spectra in Figure 3. The GEANT radiation transport code (http://wwwasd.web.cern.ch/wwwasd/geant/), as implemented in our earlier work [Sturner et al., 2003; Cooper et al.,]
is used here for complete interactions of primary electrons, protons, and secondary interaction products at energies above 10 keV from the flux spectra in Figure 3. Due to limitations on spatial step resolution in GEANT, the proton profiles have been extended to lower energies with stopping range and differential energy loss data of the Stopping and Range of Ions in Matter (SRIM) model [Ziegler et al., 1985] (http://www.srim.org/) also used in the earlier work [Cooper et al., 2001].