Radiolytic influence on the surface composition of the Galilean satellites

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Radiolytic Processes on Europa

Europa is immersed in an intense high-energy radiation environment:
- the surface chemical composition is altered by radiolysis from energetic electron and ion bombardment
- Importance of radiolysis shown by presence of H₂O₂ and O₂ on Europa (1,2)
- Chemical lifetimes are short compared to geological time scales
- Ion implantation from the jovian plasma provides chemically reactive sulfur

The surface of Europa contains a hydrated compound
- producing distorted H₂O bands observed in Galileo NIMS spectra
- The hydrate was suggested to be radiolytically-produced hydrated sulfuric acid, H₂SO₄•₄H₂O (3)

In this work we discuss:
- our spectral fits using newly measured optical constants
- sulfur radiolytic reactions and new measurements
- The observed distribution of hydrate on Europa
- Compare observations with predicted concentrations from implantation and gardening
Previous fits (3) were based on diffuse reflectance measurements of pure sulfuric acid octahydrate and hemihexahydrate (their spectra are identical).

For comparison to Europa spectra, we recently measured the transmission of $\text{H}_2\text{SO}_4\cdot8\text{H}_2\text{O}$ to obtain the optical constants $n + ik$.

Spectral fits were obtained using radiative transfer theory for intimate granular mixtures and water ice (4).

Two example fits are shown. The top spectrum is for 82% (by volume) acid, with acid and ice grain sizes of 31 and 30 $\mu$m, respectively. The corresponding parameters for the bottom spectrum are 42%, 41 $\mu$m, and 104 $\mu$m.
SPECTRAL FITS - II

The fits to Europa spectra are encouraging, except at the short-wave band edges, where Europa’s absorption profile is sharper and shifted to shorter wavelengths (by ~ 0.01 to 0.02 \( \mu \text{m} \)).

These spectral differences are similar to changes observed in proton-irradiated and radioactive sulfates (5,6) due to radiolytic removal of loosely-bound \( \text{H}_2\text{O} \) (7) (similar shifts are seen in thermal dehydration) and production of defects that break symmetry and cause bands to broaden.

The Figure shows spectral alterations from proton irradiation equivalent to \(< 5 \text{ y on Europa} \) (5). Band shifts of 0.01 to 0.06 \( \mu \text{m} \) are found, as well as band shape changes. Similar shifts and shape changes are expected for \( \text{H}_2\text{SO}_4 \) and other hydrates on Europa.
The Radiolytic Sulfur Cycle – I

Radiolytic equilibrium produces a surface composition that is self-healing, with a dynamic equilibrium of production and loss.

The major chemical reservoirs in the radiolytic sulfur cycle are sulfur (S and Sₓ), sulfur dioxide, and hydrated sulfuric acid H₂SO₄·ₙH₂O, ₙ = 6.5, 8, (actually oxonium sulfate hydrate).

Production of sulfuric acid is principally:
1) S, Sₓ + H₂O → H₂SO₄·ₙH₂O
2) SO₂ + H₂O → H₂SO₄·ₙH₂O
And the acid is destroyed as
3) H₂SO₄·ₙH₂O → S, SO₂,...

Efficiencies of radiolytic reactions are often expressed as “G-values”, the number of molecules made (or destroyed) per 100-eV of absorbed energy. We summarize below current knowledge of these reactions and their efficiencies, and report new measurements.
THE RADIOLYTIC SULFUR CYCLE - II

S, S_x + H_2O \rightarrow H_2SO_4 \cdot nH_2O
Irradiated suspensions of sulfur in liquid water are known to rapidly produce sulfuric acid (8), but reactions in the frozen state were not determined. We measured the production of sulfuric acid for a 2% [S]/[H_2O] suspension at 77 K using electrons produced from Co^{60} \gamma-rays. We found \( G(H_2SO_4) = 0.01 \). Using the ionizing energy flux in the optical layer of Europa’s surface (9), the lifetime for S atom conversion to sulfuric acid is 30 years.

H_2SO_4 \cdot nH_2O \rightarrow S, SO_2, ...
Sulfates are decomposed by ionizing radiation, but they are among the more radiation resistant chemical compounds. The cations (H, Na, Mg, etc.) can be removed, and sulfate is dissociated to SO_3^−, followed by eventual formation of SO_2, S, and sulfide (e.g. H_2S)(11, 12). The sulfates are more stable when hydrated, and typically \( G \sim 0.005 \). The lifetime of hydrated sulfuric acid in Europa’s optical layer (and generally any hydrated sulfate) is \( \sim 1000 \text{ to } 2000 \text{ years} \). The primary radiolysis product is sulfur dioxide and oxygen, with S and H_2S each being \( \sim \frac{1}{4} \) of the SO_2 production (11).

SO_2 + H_2O \rightarrow H_2SO_4 \cdot nH_2O
Radiolysis of pure, frozen SO_2 produces mainly SO_3, with \( G = 5 \), along with sulfate and elemental sulfur (10). SO_3 reacts very rapidly with H_2O to form H_2SO_4, so the reaction lifetime in the optical surface layer is \( \sim 5 \text{ years} \). Radiolysis of SO_2/H_2O mixtures will be studied in 2001.
DISTRIBUTION OF HYDRATE ON EUROPA

The initial source of sulfur is hidden by ensuing radiolysis events, but the surface distribution of hydrated sulfuric acid may provide a clue to its origin. Source candidates include 1) ion implantation, 2) micrometeoroid infall, and 3) endogenic sources of sulfurous material [e. g. evaporite salts (13, 14) and sulfur dioxide (14)].

We used NIMS data and an emperical method (the ratio of radiances at 1.5 and 1.8 μm) to find the hydrate distribution. We verified the method using detailed radiative transfer fits.

Note the strong trailing side enhancement in the distribution map, suggestive of ion implantation.
The hydrate distribution is influenced by the source, the pattern of radiolysis, and sulfur removal processes such as gardening. Europa may be rotating asynchronously and this would modify exogenic influences.

The equatorial distribution of ion implantation (at right), for synchronous rotation, shows that a 1-cm thick deposit would be accumulated on the trailing side in $10^7$ years, and $\sim 1/10$ of that on the leading side.

Micrometeoroid infall would show the opposite asymmetry, with more accumulated on the leading hemisphere. This source is $<1\%$ of the sulfur ion implantation rate.

Since the observed amount of sulfur can be accumulated in just 30,000 years, some process must be removing surficial sulfur.
Gardening by micrometeoroid impacts will bury the accumulated sulfurous material. This process also increases the trailing/leading asymmetry, but asynchronous rotation will reduce the contrast. The Figure shows the measured equatorial distribution and predictions for synchronous and asynchronous rotation and three micrometeoroid impact asymmetry parameters, $\alpha = 0, \frac{1}{2}, (\frac{1}{2})^{1/2}$, ($\alpha$ is the ratio of the orbital velocity to the collision velocity and is expected to be $\sim 0.6$, Ref. 9).

The top panel shows the unlikely $\alpha = 0$ case (uniform gardening) to illustrate the averaging effect of asynchronous rotation. The trailing/leading ion implantation asymmetry is reduced to $\sim 1.5$. Impact gardening [through a factor $(1 + \alpha \cos\theta)^{2.2}$] (15) contributes additional asymmetry, and the two bottom panels represent plausible extremes. The middle panel ($\alpha = \frac{1}{2}$) shows consistency with asynchronous rotation with period $P \sim 2$ My, while the bottom panel is consistent with $P \sim 0.1$ My.