Europa's surface color suggests an ocean rich with sodium chloride

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Abstract The composition of Europa's surface may be representative of the subsurface ocean; however, considerable debate persists regarding the endogenous or exogenous nature of a hydrated sulfate feature on Europa. Direct evidence of oceanic salts on Europa's surface has been largely inconclusive. We show that the observed color within geologically young features on Europa's surface can be explained by sodium chloride delivered from the ocean below. We find that sodium chloride, when exposed to Europa surface conditions, accumulates electrons in F and M centers, yielding a yellow-brown discoloration comparable to Europa's surface. Irradiation of sodium chloride from Europa's ocean thus provides a simple and elegant solution to the color of the non-ice material observed on Europa. This evidence for endogenous salts suggests that Europa's ocean is interacting with a silicate seafloor, a critical consideration for assessing habitability.

1. Introduction

Jupiter's moon Europa likely harbors a salty subsurface liquid water ocean [*Kivelson et al.*, 2000; *Zimmer et al.*, 2000; *Hand and Chyba*, 2007]. Europa's heavily irradiated icy surface shows a distinct yellow-brown discoloration (Figure 1) that has long been attributed to sulfur chemistry, be it exogenous sulfur from Io or sulfur from Europa's ocean [*Geissler et al.*, 1998; *Carlson et al.*, 2009]. Recently, *Brown and Hand* [2013] identified a feature on Europa's trailing hemisphere that they attribute to magnesium sulfate. In their model, the magnesium is endogenous and the sulfur is exogenous (sourced from Io), and the sulfate forms as a result of radiolytic processing of Europa's surface.

Magnesium and sulfate, however, are only minor species in Earth's ocean; sodium chloride is the predominant salt in part because of its long residence time as Earth's ocean cycles with the seafloor [*Mottl and Wheat*, 1994; *Elderfield and Schultz*, 1996]. The magnesium concentration is largely derived from continental weathering, a process not expected on a world like Europa. While some geochemical models predict that Europa's initial chondritic composition should lead to a magnesium and sulfur-rich ocean [*Kargel et al.*, 2000; *Zolotov and Kargel*, 2009], water-rock cycling at the silicate seafloors would likely lead to a chloride-rich ocean [*Glein and Shock*, 2010].

Chloride salts, however, are spectrally inactive over the visible and much of the infrared, including spectral regions utilized by many spacecraft and telescopes. Thus, direct detection of this important endogenous component of subsurface oceans has not been possible with remote sensing.

We find, however, that radiation-induced color centers in alkali halides such as NaCl are created under conditions comparable to the surface environment of Europa. Europa's surface is irradiated by energetic electrons and ions within the Jovian magnetosphere. This radiation results in the trapping of electrons in halogen vacancies, yielding the so-called color centers, or F and M centers [*Seitz*, 1946; *Schneider and Bailey*, 1969]. In NaCl, these centers have strong absorptions at 450 nm and 720 nm, respectively, providing a highly diagnostic signature of otherwise transparent alkali halides [*Weerkamp et al.*, 1994; *Seinen et al.*, 1994]. Early work examined proton bombardment and conditions for volcanic material on Io [*Nelson and Nash*, 1979]; here we focus strictly on Europa and surface discoloration that may be indicative of subsurface ocean chemistry.

2. Method

Experiments were conducted to measure changes in NaCl as a function of exposure to the temperature, pressure, and radiation conditions relevant to Europa (Figure 1). Reagent grade NaCl was placed onto a diffuse aluminum target at the end of a cryostat coldfinger and loaded into an ultrahigh vacuum chamber.
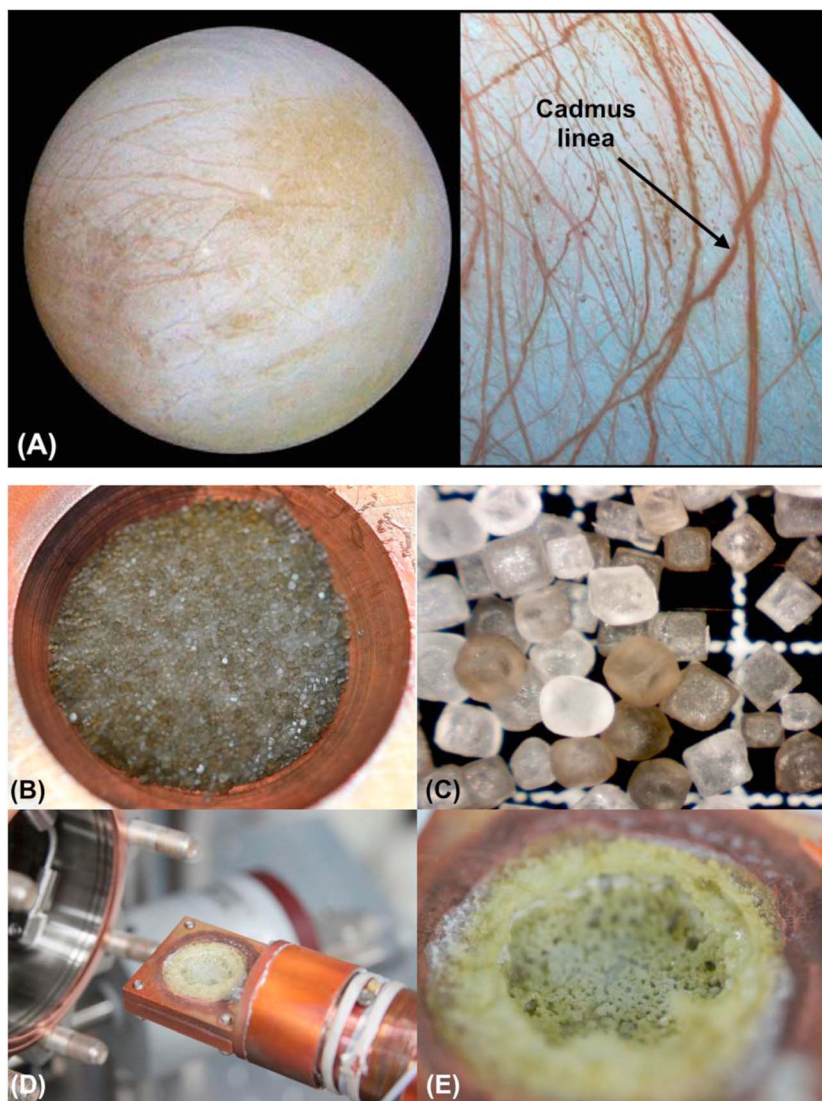
Figure 1. (a) Europa's surface shows a distinct discoloration along geological features that may bring material from the putative subsurface ocean to the surface. (left) The leading anti-Jovian hemisphere of Europa receives less exogenous sulfur than the trailing hemisphere and displays a yellow-brown color across much of the surface that may result from irradiation of alkali halides. (right) The color radiance of Cadmus linea shows a strong decrease in radiance with decreasing wavelength, which is likely due to irradiated sodium chloride (Figure 2). Credit: NASA/Jet Propulsion Laboratory-California Institute of Technology/Search for Extraterrestrial Intelligence Institute. (b) Pure NaCl grains after a 465 Grad dose showing coloration by F- and M-center accumulation. (c) Microscopic image of NaCl grains from Figure 1b; grid underneath grains show 1 mm squares. (d) NaCl evaporates upon removal from the vacuum chamber after receiving a dose of 494 Grad. (e) Detail of the evaporate shows the strong yellow discoloration from F and M centers. (Figures 1b–1e) Sodium chloride after irradiation under temperature (100 K), pressure ($<10^{-8}$ torr), and irradiation conditions (10 keV electrons) comparable to Europa.

The samples were then cooled to 100 K, and the chamber pumped down to $\sim 10^{-8}$ torr, achieving conditions comparable to the surface of Europa.

Three different experiments were conducted to examine a range of possible conditions for NaCl on the surfaces of Europa: 300 μm NaCl grains, 300 μm grains with water ice deposited on top, and an ultrapure H_2O solution saturated with NaCl. In the case of the last experiment, saturated water was loaded onto the cryostat target, the chamber was closed, and then the chamber was slowly pumped down to remove the water, leaving an evaporate deposit on the target.

In all cases, the samples were irradiated with 10 keV electrons with an average current of 1 μA. The penetration depth of a 10 keV electron into a pure NaCl crystal (2.16 g cm^{-3}) is calculated to be 1.2 μm [*Johnson*, 1990]. Total
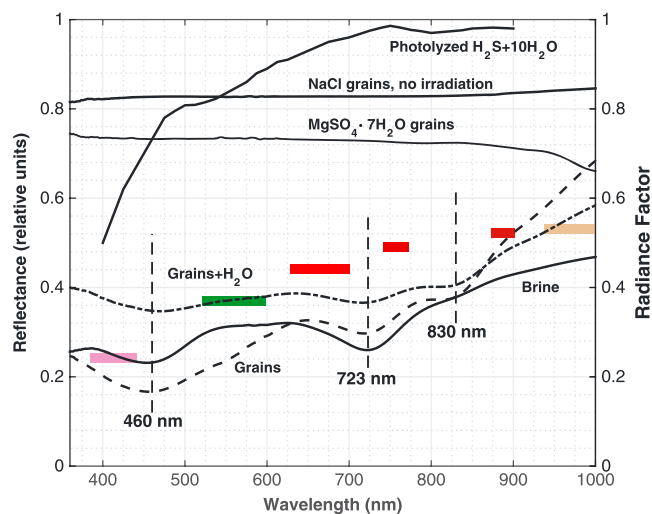
Figure 2. Spectra of 10 keV electron-irradiated NaCl showing the distinct absorption features at 460 nm and 720 nm for the F and M centers. For comparison, a spectrum of NaCl before irradiation is shown, as are the color filter radiance values (right axis) from the *Galileo* SSI observations of Cadmus linea [*Geissler et al.*, 1998]. Three irradiation experiments were performed to simulate a range of possible surface conditions on Europa: NaCl grains, NaCl grains with approximately 1 μm of water deposited on top, and an NaCl evaporate created by introducing a salt-saturated solution into the vacuum chamber and slowly removing the water. Also shown for comparison are spectra of cryogenic magnesium sulfate hydrate grains (~180 μm) and photolysed hydrogen sulfide (from *Carlson et al.* [1999]). These two materials are favored candidates for the non-ice material of Europa but are a poor match for the SSI data.

irradiation time and corresponding total deposited dose for each experiment were 20.9 h and 465 Grad for the pure grains, 45.3 h (26.3 before ice deposition) and 690 Grad (421 before ice deposition, 269 after) for the grains with water deposited on top, and 22.3 h and 494 Grad for the NaCl evaporite. These values correspond to 773 eV/16 amu for the pure NaCl grain experiment, 1150 eV/16 amu for the grains plus water, and 820 eV/16 amu for the NaCl evaporite. For comparison to Europa, 1 h of laboratory irradiation corresponds to approximately 800 h equivalent flux on Europa's surface. For an ~20 h experiment, our total laboratory dose into the salt corresponds to 10 to 100 years on Europa's surface [*Paranicas et al.*, 2009].

Samples were continuously monitored across the wavelength range from 0.4 μm to 14 μm, and mass spectrometry measurements were conducted from 1 to 130 amu for the duration. Here we present the 0.4–2.5 μm data as this is the primary region for detection of alkali halide color centers.

3. Results

Figures 2b–2e show NaCl grains and evaporate on the cryostat cold finger and under a microscope postirradiation. Irradiation and production of color centers turned the initially white salt grains to a yellow to brown color. Figure 2c shows ~300 μm grains in detail. The brown grains have accumulated F and M centers, whereas the white grains are from a deeper region of the sample and were largely shielded from the electrons.

Spectra corresponding to each case are shown in Figure 2, as is a spectrum of NaCl grains that have not been irradiated. The no irradiation case shows the typical featureless spectrum of NaCl in this wavelength region. Spectra of cryogenic magnesium sulfate hydrate grains (~180 μm) and photolysed hydrogen sulfide are also shown for comparison. These two materials are favored candidates for the non-ice material of Europa but are a poor match for the visible wavelength data from *Galileo*. Overlain on the spectra in Figure 2 are the measured radiances for the color filters on the *Galileo* solid-state imager (SSI) as reported by *Geissler et al.* [1998] for the fracture labeled Cadmus linea in Figure 1. In that work, it was shown that sulfur and ice mixtures are a poor match to the SSI data, and they offer organics in ice as a possible explanation. We find that irradiated sodium chloride provides a straightforward explanation for the SSI continuum across the visible wavelength range.

In all three irradiated cases, strong absorptions were measured for the F center at 460 nm and the M center at 720 nm. In both the pure grains and grains plus H_2O experiments, the small absorption near 580 nm is the plasma resonance band of colloidal aggregates of sodium [*Doyle*, 1958]. The feature at 830 nm is unidentified but could arise from potassium impurities. We note that in our examination of the visible and infrared data, we did not observe features expected for electron surface states [*Rajagopal et al.*, 1990; *Xia and Bloomfield*, 1993; *Honea et al.*, 1989]. Although excess electrons may have occupied surface states during our experiment, the specific features at 460 nm and 720 nm are diagnostic of electrons in color centers.

Pure NaCl grains show the strongest absorptions, consistent with energy deposition into NaCl alone and not into water molecules. The slightly subdued absorption features in the grains + H_2O experiment may be due to the deposited water shielding the salt crystal below, thus resulting in the creation of fewer color centers. Results for the brine experiment show deep and broad absorptions for both the F and M centers. This is significant because previous experiments have focused on larger crystals and F, M, and colloid centers are typically discussed in the context of electrons/anion-holes in the crystal lattice. One might expect that a brine evaporate yields less efficient color center production because the crystalline lattice is poorly organized in an evaporite sample. Our results demonstrate efficient F- and M-center production even in the evaporate phase. F- and M-center production in the evaporite is particularly important because the evaporate phase may be the closest analog to endogenous surface material on Europa. Significantly, in our evaporate experiment, the water was slowly removed from the salt solution, despite exposure to high vacuum. Our experiments thus differ significantly in process from earlier work on flash-frozen brines, in which solvated electrons may account for some of the observed spectroscopic features [*Orlando et al.*, 2005; *McCord et al.*, 2001]. Production of colloids does appear to be inhibited, as evidenced by the lack of a strong absorption at 580 nm in the evaporite.

Smakula's equation [*Smakula*, 1930], combined with the simplification for NaCl color centers detailed by *Seinen et al.* [1994], leads to $N = 1.18 \times 10^{16} k_m W_{1/2}$, where N is the number of centers per unit volume, k_m is the absorption coefficient in cm^{-1} at the band's center, and $W_{1/2}$ is the full width at half maximum of the band in eV. Converting to the reflectance configuration of our experiment leads to a concentration, C, of F or M centers of $C_{F,M} = A/(\beta l)$, where A is the integrated absorption of either the F or M band, $\beta = k_m W_{1/2}/N$, and l is the mean optical path length, which is found to be 3.2 mm in our experiment [*Carlson et al.*, 2009].

We find F- and M-center number densities of ~10^{19} cm^{-3} and ~10^{18} cm^{-3}, respectively, with the pure grains exhibiting the largest number of F centers (5.8×10^{19} cm^{-3}) and the brine exhibiting the largest number of M centers (6.5×10^{18}). These number densities are consistent with the observation that lower temperatures lead to a larger number of F and M centers and a lower number of colloids [*Seinen et al.*, 1994].

4. Conclusions

If the putative salty ocean of Europa delivers NaCl to the irradiated surface environment, the F- and M-center bands may offer the best chance for direct detection of endogenous salts. A reasonable assumption of a 1% band depth detection limit for the 460 nm F center corresponds to ~10^{17} F center per cubic centimeter in the case of a brine evaporite. For a linear mixture of water and irradiated NaCl (10^{19} to 10^{20} F center cm^{-3}, with the higher value taken as a saturation value) on the surface of Europa, the concentration detection limit is 1 to 10 parts per thousand. If we take surface layer concentrations as a proxy for oceanic salinities, this detection limit corresponds to brackish salinities on Earth and is considerably lower than Earth's oceanic concentration (35 parts per thousand).

Where salts found to be abundant on the surface, the F- and M-center bands of NaCl could be used to identify young, recently active areas if NaCl is the major component. Sites of fresh deposition, younger than 1 to 10 years, may show low color center concentrations, whereas older terrains, e.g., lag deposits, would show near-band saturation limits of ~10^{20} center/cm^{-3}.

The *Galileo* near-infrared spectrometer did not adequately cover the spectral range needed to observe these features on Europa, and the filters on the solid-state imaging camera [*Belton et al.*, 1992] were not specifically designed to detect color centers. The images of Europa's surface, however, clearly show a yellow-brown discoloration [*Geissler et al.*, 1998]. Although iogenic sulfur has long been implicated [*Carlson et al.*, 1999], our results indicate that irradiated NaCl from Europa's ocean is an alternative explanation for Europa's surface coloration that should be considered in the context of future observations. Interestingly, telescope observations [*McFadden et al.*, 1980; *Clark and McCord*, 1980] show possible absorptions at ~450 nm and ~720 nm, but since they are not spatially resolved spectra, it is impossible to distinguish sulfur absorptions at the shorter wavelengths from the color centers of irradiated salts. The features are in the right position but are not sufficiently broad or deep to warrant positive identification by comparison to our laboratory measurements. Additional ground and space-based spectroscopic measurements must be made.

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