**SPACE WEATHERING OF HYDROHALITE BY KEV ELECTRONS: COLOR CENTERS.** C. A. Hibbitts, K. Stockstill-Cahill, E. Lloyd, Johns Hopkins Applied Physics Laboratory, 11101 Johns Hopkins Rd., Laurel Md., 20723; karl.hibbitts@jhuapl.edu

**Introduction:** Sodium chloride (NaCl) has been identified on the surface of Eurpoa through the observation of an absorption band centered near 460nm in spectra obtained by Earth-based telescopes [e.g. 1] that correlate with color centers observed in laboratory measurements of irradiated NaCl at similar temperatures [e.g. 2,3]. These color centers are at ~ 460 nm (F-center defect) and 720 nm (M-center defect). The shorter wavelength band is caused by optically active electrons that replace Cl- after those anions have been dislodged from their positions in their crystal lattice. The M-center is a cluster of F-centers. Only the 460nm feature is observed on Europa. The lack of an M-center band is consistent with a shallow F-center band, ie. with a low density of F-centers. This identification has been confirmed by UV observations of Europa [4] and laboratory measurements [5].

Given that the hydrated version of NaCl, hydrohalite ($NaCl*2H_2O$) is the preferred physical state of NaCl on the surface of Europa, assuming equilibrium crystallization from a subsurface ocean saturated with NaCl, we have explored the nature of color centers in hydrohalite at relevant temperatures and appropriate electron energies and fluences. Future work is planned to explore the formation of color centers in flash-frozen saturated brines, and more dilute brines of similar concentrations as expected in the Europan oceans. Hydrohalite is an endmember example, even if formed under conditions not widely expected on Europa.

**Procedure**: Hydrohalite was made from a 23% concentration solution by weight of NaCl and water. The solution was cooled it to -20C and hydrohalite precipitated out over the course of 8 to 16 hours. It was filtered through a Buchner funnel and filter paper. The salt was collected and stored at below -20 following the procedure outlined in [6]. Pellets were made using a hydraulic press. The dye and anvil were cooled in liquid nitrogen, about 100mg of hydrohalite was placed in the die, and pressed into a pellet at 20000 PSI for about 30sec. We found lower pressure did not result in coherent pellets.

The pellet was then placed in a holder also precooled with liquid nitrogen, which was then inserted into a cryostat in a UHV chamber equipped with an e-gun and various spectrometers (see details in [7]). The hydrohalite pellet was irradiated using a Kimball Physics Model EGF-6104 electron gun, with Vis-IR spectra obtained in 15 min increments. The pellet was maintained at 120K and initially irradiated with 1keV

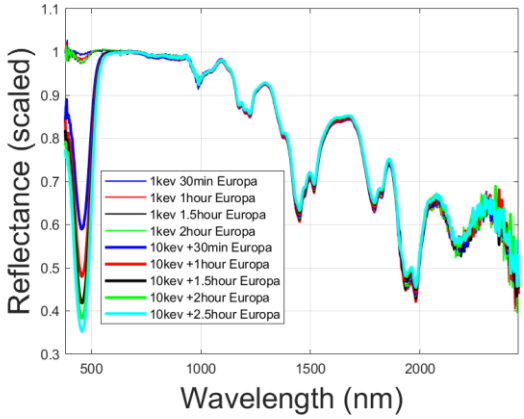


Figure 1. The F-center band and unaffected IR portion of the spectra of hydrohalite when exposed to 1 and 10keV irradiation at 80namps. Thin lines: 1keV. Thick lines: 10 keV.

electrons at 80 namps, which equates to a fluence ~ 166 x that of Europa, assuming a particle fluence at Europa of 3e9 electrons/cm2/sec (Figure 5, of [8]). Beam energy was confirmed using a Faraday cup placed directly above the sample and in plane with the sample. We expect the measurement of beam current accuracy to be better than 10%, limited by drift over time, even though we periodically checked and adjusted the electron beam. The pellet was subsequently irradiated with 10keV eletrons, with fluence maintained at 80 namps. Spectra from 380 nm to 2400 nm was obtained,

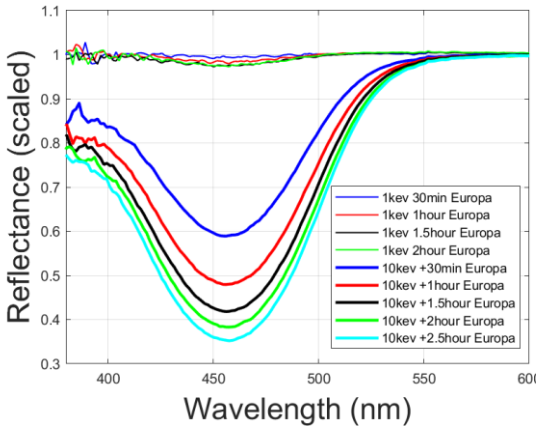


Figure 2. The F-center band and unaffected IR portion of the spectra of hydrohalite when exposed to 1 and 10keV irradiation at 80namps. Thin lines: 1keV. Thick lines: 10 keV.

while pausing the radiation, using an SVC spectrometer and quartz-halogen light source. It is likely the illumination warms the sample, and with a thermocouple that measures the temperature of the sample holder adjacent to the illuminated pellet, the warming would go unrecorded [e.g. 9]. However, the pellet has high thermal conductivity, at least compared to a powder used by [9]. While the temperature of a cryogenic loose power, under vacuum, can be raised by several 10s of degrees higher than the temperature reported by a thermocouple mounted on a flange adjacent to the sample, the pellet should be less prone to heating.

**Results**: The infrared spectra of the pellet before and after irradiation (Figures 1 and 2) are consistent with hydrohalite [10]. The infrared bands were unaffected by the irradiation. We irradiated the pellet to almost saturation and to a band depth that exceeds 60% of the continuum, beyond the point at which M-centers would have been expected to form in NaCl (Figures 1 and 2). The F-center band is at 457 nm, slightly longer than the 451 nm reported for anhydrous NaCl at 120 K by [11]. The lack of the formation of M-centers may be due to water molecules inhibiting the formation of defect clusters, ie. intervening water molecules may prevent defect clustering upon F-band saturation in the NaCl-$H_2O$ complex. Optical saturation of F-centers occurred relatively quickly in the sample when irradiated with 1keV electrons compared to irradiation with 10 keV electrons, which never reached saturation. This may be a result of the shallower penetration depth of 1keV electrons compared to 10 keV electrons. It is also consistent with an optical depth of visible light at least as great as the penetration depth of the 10 keV electrons in order for the increased number of deeper defects to have an effect on the spectra, which according to [2] is on the order of a micron. Also, the saturation of the 1keV induced F-center band is seen to decrease slightly over time even with continued radiation (Figure 3). This decrease in band depth of the color center may be due to athermal photobleaching [5] or may be due to thermal bleaching. Thermal bleaching of similar magnitude is reported by [11]. It is worth noting that the spectral features of hydrohalite in the infrared are inconsistent with the observed spectra of Europa [e.g. 12] suggesting that if present, those absorption features are relaxed through another process, possibly ion bombardment. Alternatively, it is possible that hydrohalite, if it initially formed on Europa, may be desiccated more easily than $MgSO_4$ to evolve into anhydrous NaCl due to the lower affinity of water for NaCl compared to $MgSO_4$. The F-center band position at 457 nm is also longer than is observed for the feature on Europa, suggestive that if hydrohalite is a precursor molecule to anhydrous NaCl, it is no longer present at great abundance.

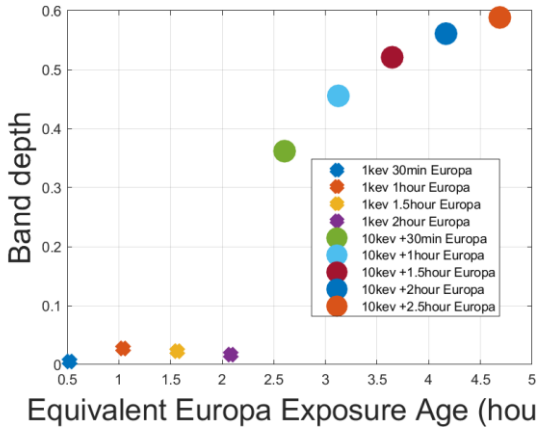


Figure 3. The F-center band from 1 keV electrons quickly saturates but doesn't reach saturation for 10 keV electron bombardment, which are more representative of Europa.

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**References:** [1] Trumbo, S.K., Brown, M.E., Hand, K.P., (2019) Science Adv., 5; eaaw7123. [2] Hand, K.P. and Carlson, R.W., (2015), Gephys. Res. Lett., 42, 3174-3178. [3] Poston, M.J., Carlson, R.W., Hand, K.P. (2017). J. Geophys. Res: Planets, 122, 2644-2654. [4] Trumbo, S.K. et al.(2022), Astro-Phys (pre-print); [5] Brown, M.E., Denman, W.T.P., Trumbo, S.K. (2019), Astro-phys, in-press. [6] Bakkenes, H. W.; Albertus, J.; Meijer, M.; Schokker, D.; Steensma, M. Sodium Chloride Production Process. 8888867 B2, 2014; [7] Hibbitts, C.A., Stockstill-Cahill, K., Wing, B., Paranicas, C. (2019) Icarus, 326, 37-47. [8] Paranicas, C. et al., (2009), in Europa, ed by Pappalardo et al., Ariz. Press; [9] Hinrichs, J.L. and Lucey, P.G. (2002), Icarus, 155, 169-180. [10] Light, B.L., Carns, R.C., Warren, S.G. (2016), L. Geophys. Res: Oceans, 121, 4966-4979. [11] Denman, W.T.P., Trumbo, S.K., Brown, M.E. (2022), Astro-phys, (in-press). [12] McCord, T.B. et al (1998), Science, 280, 1242-1245.