KECK II OBSERVATIONS OF HEMISPHERICAL DIFFERENCES IN H₂O₂ ON EUROPA

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ABSTRACT

We present results from Keck II observations of Europa over four consecutive nights using the near-infrared spectrograph. Spectra were collected in the 3.14–4.0 μm range, enabling detection and monitoring of the 3.5 μm feature due to hydrogen peroxide. Galileo Near-Infrared Mapping Spectrometer results first revealed hydrogen peroxide on Europa in the anti-Jovian region of the leading hemisphere at a percent by number abundance of 0.13% ± 0.07% relative to water. We find comparable results for the two nights over which we observed the leading hemisphere. Significantly, we observed a small amount of hydrogen peroxide (~0.04%) during observations of Europa’s anti-Jovian and sub-Jovian hemispheres. Almost no hydrogen peroxide was detected during observations of just the trailing hemisphere. We conclude that the Galileo observations likely represent the maximum hydrogen peroxide concentration, the exception potentially being the cold water ice regions of the poles, which are not readily observable from the ground. Our mapping of the peroxide abundance across Europa requires revisions to previous estimates for Europa’s global surface abundance of oxidants and leads to a reduction in the total oxidant delivery expected for the subsurface ocean if an exchange of surface material with the ocean occurs.

Key words: astrochemistry – infrared: planetary systems – planets and satellites: composition – planets and satellites: surfaces

1. INTRODUCTION

The interaction of the Jovian magnetosphere with Europa results in radiolytic processing of the icy surface (Johnson 1990; Johnson & Quickenden 1997). Energetic electrons, ions, and protons dissociate water, yielding OH radicals, which then can recombine forming hydrogen peroxide and other oxidants (Cooper et al. 2003; Johnson et al. 2003; Bain & Gigüere 1955). Importantly, Europa is synchronously locked to Jupiter (Europa rotates on its axis once per 86 hr orbit around Jupiter), and thus Europa’s hemispheres maintain the same orientation with respect to Jupiter and the radiation environment of the magnetosphere. Over 75% of the incident radiation is from electrons (Cooper et al. 2001) and, due to their small gyroradii and the fast rotation of Jupiter (10 hr) relative to Europa’s orbital period, the trailing hemisphere of Europa receives the majority of the radiation. Furthermore, low-energy sulfur ions in the plasma torus are preferentially deposited on the trailing hemisphere. This relationship is made evident by the trailing hemisphere “bulls-eye” feature of dark material (Paranicas et al. 2001), most likely a radiolytically processed sulfur compound such as hydrated sulfuric acid (Carlson et al. 1999b) and endogenous magnesium ions that have been radiolytically processed to magnesium sulfate (Brown & Hand 2013).

Galileo Near-Infrared Mapping Spectrometer (NIMS) observations of Europa first detected hydrogen peroxide in the anti-Jovian region of the leading hemisphere at a percent by number abundance of 0.13% ± 0.07% relative to water (Carlson et al. 1999a). As shown by Loeffler et al. (2006), the equilibrium peroxide concentration for ion-irradiated 80 K and 120 K ice is 0.14% and 0.1% by number, respectively. Though peroxide has been reported for other regions of Europa, those observations were noisy and poorly quantified (Hansen & McCord 2008).

Here, we present new results for measurement of the peroxide abundance across all four major hemispheres of Europa (leading, trailing, sub-Jovian, and anti-Jovian) using ground-based spectroscopy.

2. OBSERVATIONS

Observations of Europa were obtained over four consecutive nights from 2011 September 17–20 using NIRSPEC, the facility near-infrared spectrograph (McLean et al. 1998), on the Keck telescope. We covered a wavelength range from 3.14 to 4.00 μm in the low-resolution mode with R ~ 2000, which is still a factor of ~20 better than the NIMS instrument. We used the 0.76 wide slit, such that for a given observation most of the observable hemisphere of Europa was within the slit. At the time of our observations the 3120 km diameter of Europa subtended 1″/28, or approximately 2300 km. While observers of the Galilean satellites often use other Galilean satellites for telluric and solar flux correction, as they are bright and adjacent, we chose instead to avoid the possibility of spectral contamination and used HD 9986, a V = 6.67 G5V star that was 13° away from Europa at the time of observations. Observations on the target and calibrators were obtained in an ABBA pattern, with a single pointing for Europa consisting of 60 2 s co-adds and for the calibrator star 10 1 s co-adds. A journal of the observations is shown in Table 1.

The initial data reductions were performed using standard routines that subtract adjacent pairs of images, correct for the curvature in the spatial and spectral dimensions, fit and subtract residual line emission, and optimally extract the remaining spectrum. From the initial extracted spectra, it was clear that the data were affected by variable water vapor absorption and by a line-shape difference between the resolved target and the point source stellar calibrator. To correct for these effects, we first created a grid of model telluric spectra using the online ATRAN (Lord 1992) tool for SOFIA’s spanning a range of airmasses and water vapor overburdens, convolved to the resolution of the NIRSPEC data. We divided each stellar spectrum by the model spectra, finding the parameters that minimized the residuals and determined the effects of slight changes in the water vapor burden and airmass for the stellar spectra. We then performed a

http://atran.sofia.usra.edu/cgi-bin/atran/atran.cgi
The resulting spectra are generally excellent, but with clear data, so wavelength calibration is performed by matching the sources. Few atmospheric emission lines are visible in the raw data, so spectral broadening of the target, the precise wavelength to the broad \(3\) \(\mu\)m water feature so as to enable removal of the continuum. The peroxide band was integrated to get the total number of \(H_2O_2\) molecules, which when divided by the average hemisphere temperature of \(100\) K (Spencer et al. 1999).

The reflectance data for each night was normalized to the maximum reflectance value for the bright, leading hemisphere on the night of September 18, which showed good agreement with previous albedo measurements for Europa’s surface (Calvin et al. 1995; Grundy et al. 2007; Carlson et al. 2009).

The surface abundance of hydrogen peroxide, expressed as its percent by number abundance relative to water, was determined by converting reflectance values, \(R\), to absorbance, \(A = -\ln (R/R_{\text{Baseline}})\), where the baseline reflectance used was the maximum reflectance value for the night of September 18, which was the spectrum representing the purest ice. We then used a second degree least-squares polynomial fit to the broad \(3\) \(\mu\)m water feature so as to enable removal of the continuum. The peroxide band was integrated to get the total band area from \(3.4\) to \(3.6\) \(\mu\)m (2760–2950 cm\(^{-1}\)). As part of the polynomial fit we calculated the one standard deviation values above and below the fit and then integrated the corresponding band areas to get \(1\sigma\) values for the total absorbance.

To generate peroxide concentrations for each night of observations we used the temperature-dependent band strength values from Loeffler et al. (2006), and selected \(A_{100K} = (5.0 \pm 0.5) \times 10^{-17} \text{cm molecule}^{-1}\) as a reasonable value for the average hemisphere temperature of \(100\) K (Spencer et al. 1999). Dividing the integrated band strength by the \(A\)-value yields the total number of \(H_2O_2\) molecules, which when divided by the number of water molecules for the optical depth yields the concentration relative to water. Following Hodgins et al. (1993) and Carlson et al. (1999a) we use a \(50 \mu\)m grain size and optical depth, and an ice density of \(3 \times 10^{22}\) molecules cm\(^{-2}\). Figure 1 shows the averaged spectrum for each night, and shows the polynomial fit and \(1\sigma\) bounds. The band with the continuum subtracted is shown with the Galileo NIMS data overlain (x marks).

The leading hemisphere of Europa, as determined by observations with a central Europa longitude ranging from \(52^\circ\) to \(62^\circ\), has a \(0.113 \pm 0.032\) (0.074–0.161) percent by number abundance relative to water, where the range in parenthesis includes the uncertainty in the \(A\)-value. This range is in close agreement with the NIMS observations, which had an uncertainty of \(\pm 0.07\). For added comparison we analyzed the Galileo NIMS data using the more recent band strengths (Loeffler et al. 2006) and found that the NIMS data lead to a percent by number abundance of \(0.118\%\) peroxide relative to water. This value is slightly less than the \(0.13\%\) value reported by Carlson et al. (1999a), but well within the published error bars for that observation, and is in very close agreement with our observations.

The trailing hemisphere of Europa, which is dominated by a darker non-ice material, was found to have a peroxide abundance close to or equal to zero. These observations had a central Europa longitude ranging from \(256^\circ\) to \(264^\circ\) and thus were centered on the apex of the trailing hemisphere. As the spectrum shows, there is only a slight rise above the continuum at \(3.5\) \(\mu\)m. The measured concentration range is \(0.0\) to a maximum of \(0.038\) (or \(0.043\) for \(A_{100K} = 4.5 \times 10^{-15} \text{cm molecule}^{-1}\), using the low-end value for the error limits on \(A_{100K}\)) percent by number abundance, with our best-fit value being \(0.018\) for a \(100\) K surface.

Observations that included the sub-Jovian (Jupiter facing) and anti-Jovian hemispheres of Europa show peroxide concentrations of approximately one-third that of the leading hemisphere, though as shown in Table 1 the longitude ranges for these observations do partially overlap with the leading and trailing hemispheres. The September 19 observations centered on a longitude of \(158^\circ–161^\circ\), covering the leading to anti-Jovian hemispheres, and indicate a concentration of \(0.045 \pm 0.019\) (0.023–0.072) percent by number abundance. The September 17 observations that centered on a longitude ranging from \(315^\circ\) to \(316^\circ\), and thus covered the trailing to sub-Jovian hemispheres, yield a concentration of \(0.042 \pm 0.041\) (0.0–0.092) at \(100\) K.

### Table 1

| Date (UT) | Target | Time Start/End | Airmass Start/End | Longitude Start/End | Exp. Time (s) |
|-----------|--------|----------------|------------------|---------------------|--------------|
| 2011 Sep 17 | Europa: sub-Jupiter HD 9866 | 12:45/12:54 | 1.01/1.01 | 315/316 | 840 |
| 2011 Sep 18 | Europa: leading HD 9866 | 11:40 | 1.02 | 40 |
| 2011 Sep 19 | Europa: anti-Jupiter HD 9866 | 11:25 | 1.02 | 158/161 | 1440 |
| 2011 Sep 20 | Europa: trailing HD 9866 | 11:48 | 1.04 | 256/264 | 5760 |

4. DISCUSSION

Our results show a non-uniform distribution of hydrogen peroxide across the surface of Europa. Three key factors likely control the production and abundance of peroxide on Europa’s surface: (1) the availability of water molecules; (2) radiation (UV, electrons, and ions all yield peroxide; Johnson & Quicken den 1997; Johnson et al. 2003); and (3) temperature (Moore & Hudson 2000; Loeffler et al. 2006; Hand & Carlson 2011). Though the trailing hemisphere of Europa has a higher radiation flux, it is also dominated by a strong non-ice component that limits the production and steady-state abundance of hydrogen peroxide. Our results, coupled with water ice abundance maps (Grundy et al. 2007; Carlson et al. 2009; Brown & Hand 2013), clearly show that peroxide abundance maps most directly to the availability of water, which is the precursor molecule that provides the OH radical upon dissociation by irradiation (Cooper et al. 2003). Though water molecules may present as part of the hydrated sulfate that dominates the trailing hemisphere (Carlson et al. 2009), peroxide does not appear to be a dominant product of the sulfate radiolysis.

Ice temperature significantly modulates peroxide production and stability, as the trapping of OH and electrons in the ice matrix (Quicken den et al. 1991) decreases in efficiency over the \(\sim 70–130\) K temperature range of Europa’s surface (Spencer et al. 1999), leading to reduced concentrations at higher temperature (Hand & Carlson 2011). However, variation...
in band absorption from 80 K to 120 K yields a \(~10\%\) change in concentration (Loeffler et al. 2006) and thus cannot explain the difference in concentration across hemispheres. Interestingly, comparison with Loeffler & Baragiola (2005) indicates that the state of peroxide on Europa is that of dispersed \(\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}\) trimers. In warmer regions and on, e.g., Ganymede and Callisto—where peroxide has not been observed—the expected state of peroxide is that of the precipitated and crystallized dihydrate. Our ground-based observations agree with these lab-based measurements for the state of peroxide on Europa.

Given that condensed \(\text{O}_2\) has been reported as a component in the surface ice of Europa without longitudinal variation (Spencer & Calvin 2002), and that \(\text{H}_2\text{O}_2\) is a useful precursor molecule in pathways to \(\text{O}_2\) production (Cooper et al. 2003), the differences in peroxide concentrations may provide some bearing on the origin of Europa’s oxygen distribution and production pathways. Teolis et al. (2005) note that destruction of hydrogen peroxide alone cannot explain the observed oxygen abundance and thus other pathways are important to consider. We suggest that perhaps Spencer & Calvin (2002) did observe longitudinal variations in \(\text{O}_2\) that could be associated with \(\text{H}_2\text{O}_2\) as a precursor, but given the limited measurements and the sensitivity of the 5770 Å band, they did not have sufficient evidence for such a conclusion. Indeed, close inspection of their Figure 2 reveals that the oxygen absorption on the leading hemisphere is deeper and broader than that of the trailing hemisphere, with a band depth difference of \(~10\%–25\%\). Our measurements showing variations in \(\text{H}_2\text{O}_2\) across Europa’s surface provide a compelling rationale for a more detailed investigation of Europa’s \(\text{O}_2\) abundance and distribution.

Nevertheless, the Spencer & Calvin (2002) observations do show significant \(\text{O}_2\) on the trailing hemisphere. In light of our results, we propose that \(\text{O}_2\) may be a more stable radiation product (as is clearly the case in Earth’s atmosphere) and thus the low levels of peroxide on the trailing hemisphere do not prohibit a measurable steady-state abundance of oxygen on the trailing hemisphere. The high abundance of sulfur on the trailing hemisphere may also serve to scavenge OH radicals to form \(\text{H}_2\text{SO}_4\), and \(\text{SO}_2\) may be an alternative precursor to \(\text{O}_2\).
Additionally, oxygen can easily migrate across the surface of Europa as it transitions from solid to gas phase with Europa’s diurnal temperature cycles (Hall et al. 1995; Cassidy et al. 2007). The leading hemisphere may be the dominant source of O\(_2\) production in the ice, but warming releases that oxygen to the exosphere, where it then migrates and recondenses depending on the diurnal thermal pulse. This scenario is further aided by the fact that UV photolysis is enhanced during the day, and photolysis of peroxide yields OH and possibly alternative pathways for O\(_2\) formation (Grunewald et al. 1986; Johnson et al. 2003).

Finally, we note that the radiolytic production of surface oxidants has long been of interest in the context of Europa’s subsurface ocean chemistry (Gaidos et al. 1999; Chyba 2000; Chyba & Hand 2001). If Europa’s oxidant-laden surface ice mixes with the ocean water then radiolysis could be a key mechanism for maintaining a chemically-rich and potentially habitable ocean (Chyba 2000; Hand et al. 2009). Previous estimates all assumed a globally uniform layer of peroxide within the ice layer and calculated delivery rates based the NIMS concentration of 0.13% relative to water.

Our new results indicate that only the most ice-rich regions of Europa reach the concentrations measured by NIMS. The trailing hemisphere concentration is nearly an order of magnitude lower than the leading hemisphere and the sub-Jovian and anti-Jovian hemispheres are down by a factor of \(\sim 3\) relative to the leading hemisphere. As a result, the average global surface abundance of peroxide in the surface ice of Europa may be better represented by the sub-Jovian and anti-Jovian hemisphere concentrations of \(\sim 0.044\%\). This reduces the low-end estimate of Chyba & Hand (2001) from \(\sim 10^9\) moles per year peroxide delivered to the ocean to \(\sim 10^8\) moles per year delivered. Compared to models for seafloor production of reductants, such as methane and hydrogen sulfide, which yield \(\sim 3 \times 10^9\) moles per year delivered to the ocean, it appears that our new results for peroxide on Europa could lead to an ocean limited by oxidant availability. This conclusion also depends strongly on the global geographic distribution of O\(_2\), which may have concentrations significantly larger than peroxide (Hand et al. 2007).

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