Sulfur chemistry on the surface ice of Europa Jiazheng Li[1] and Cheng Li[1], [1]Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA (lijiazhe@umich.edu).

Introduction: The surface of Europa is bombarded by ions (primarily sulfur and oxygen ions) and energetic electrons with energy from keV to tens of MeV [1]. During the ion sputtering process, H_2O and H_2O products (H_2, O_2, etc.) are sputtered out of the surface ice and contributed to the tenuous atmosphere of Europa [2-9]. Ion and electron irradiation on ice can dissociate water molecules, which contributes to the release of gases from the ice and the chemical alteration of the ice [10-13]. Meanwhile, the sulfur ions from the magnetosphere bring sulfur to the surface of Europa, which leads to the formation of sulfur-containing species (e.g., SO_2, H_2SO_4) in the ice [14-17]. Experimental studies on the implantation of sulfur ions in water ice show that sulfuric acid and other sulfur-bearing species are generated in the ice [18-19]. Galileo Near-Infrared Mapping Spectrometer observations on the surface of Europa confirm the existence of sulfuric acid in the surface ice and show that sulfuric acid is likely to be found in the trailing hemisphere rather than the leading hemisphere due to the negligible sulfur ion flux at the leading hemisphere [20]. Studies also suggest that sulfuric acid hydrates, including monohydrate, tetrahydrate, hexahydrate, etc., could be abundant on the surface of Europa [21-23]. However, the sulfur chemistry on Europa and the pathways of the formation of the sulfur-containing species are still poorly understood. In order to fill these gaps, we use a comprehensive one-dimensional chemical-transport model to simulate the chemical process occurring in the surface ice of Europa. This model includes the irradiation on the ice and the implantation of sulfur and oxygen ions in the ice. It aims to resolve the formation and distribution of both sulfur-containing and non-sulfur-containing (e.g., O_2, H_2O_2) species.

Model setup: Our one-dimensional chemistry-transport model is developed based on the Caltech/JPL chemistry-transport model KINETICS. The governing equation of KINETICS is the continuity equation for each species *i*:

$$\frac{\partial n_i}{\partial t} + \frac{\partial \varphi_i}{\partial z} = P_i - L_i,$$

in which n_i is the number density, φ_i is the vertical flux, P_i is the production rate, and L_i is the loss rate at depth z and time t. P_i and L_i of each species i are determined by its related production and destruction reactions. The model finds a steady-state solution so that $\partial n_i/\partial t = 0$. In the model, we consider an ice shell of 50 cm. 50 cm is thick enough that the modelled density profiles are not influenced by the thickness of the ice shell. Two groups of chemical species are considered in the model: the non-sulfur-containing species and the sulfur-containing species. The non-sulfur-containing group includes H_2O, H, O, O_2, OH, H_2, O_3, HO_2, and H_2O_2. The sulfur-containing group includes S, S_2, S_3, S_4, SO, SO_2, SO_3, S_2O, HSO_3, $HOSO_3$ and H_2SO_4. In our model, we consider that the chemical alteration of the surface ice is driven by two components: the irradiation on ice and the implantation of the ions. The radiation flux at the surface of Europa is $\sim 8\times10^{10}$ keV/cm^2/s, which dissociates water molecules and produces radicals (H, O, OH) in the ice. As for the implantation of sulfur and oxygen ions, we consider a case for the center of Europa's trailing hemisphere. Since the sulfur and oxygen ions near the orbit of Europa are moving with Jupiter's rapidly rotating magnetosphere, most of the ions end up impacting the trailing hemisphere of Europa. In our model, we assume that once the ions go into the surface ice, they will quickly lose their charges and be neutralized to sulfur and oxygen atoms. Further chemical reactions are initiated by the radicals (H, OH and O) formed from the irradiation and the implanted S and O atoms. 53 chemical reactions are considered in our model. Meanwhile, the gas phase species (O, H, OH, O_2, H_2, O_3, SO) are allowed to quickly diffuse inside the ice and an extinction process with an extinction rate of 10^{-14} s^{-1} (corresponds to ~3 million years) is added to all solid phase species to mimic the resurfacing of the surface ice.

Simulation results: The density profiles of the compositions constructed by our model are shown in Figure 1. The non-sulfur-containing group and the sulfur-containing group are shown separately in Figures 1a and 1b. In the non-sulfur-containing group, H_2O_2 and O_2 are the most abundant species. O_2 is the dominant species above ~1 μm and below ~1cm, while H_2O_2 dominates in the middle part. The peak of H_2O_2 number density is $\sim 1.4\times10^{19}$ cm^{-3}. As for the sulfur-containing compositions, we see that H_2SO_4 is the dominant species in the ice. The number density of H_2SO_4 in the top 100 μm is $\sim 1.3\times10^{21}$ cm^{-3}, which corresponds to a mixing ratio of ~4.5 % compared to the number density of water molecules. Below 100 μm, the density of H_2SO_4 decreases with increasing depth. SO_2 and $HOSO_3$ are the next most concentrated sulfur-containing species other than H_2SO_4, whose densities are about 3 to 4 orders of magnitude lower than that of H_2SO_4.

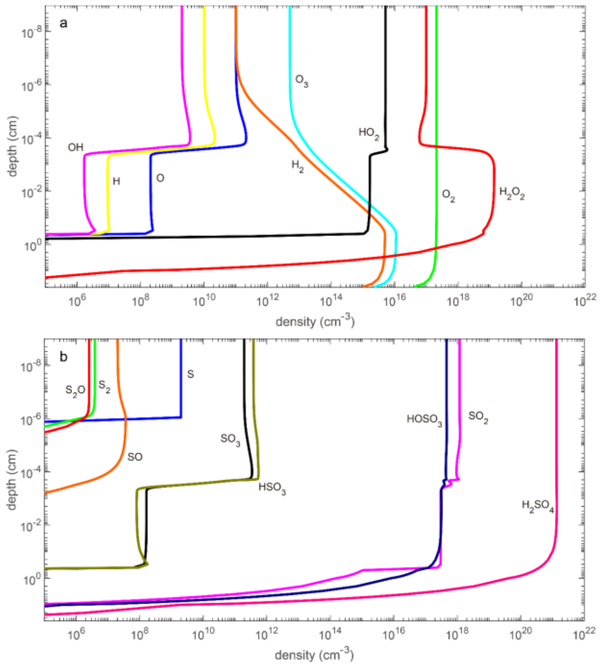

Figure 1. *Density profiles of the chemical species constructed in the model. (a) Non-sulfur-containing group. (b) Sulfur-containing group.*

The chemical pathway of forming H_2SO_4 from the implantation of sulfur ions is described as follows:

S atoms can quickly react with O_2 and produce SO:

$$S_2 + O \rightarrow SO + S.$$

SO is also generated from the reactions between S and HO_2, O_3, etc. The major SO loss mechanism is the reaction between SO and HO_2:

$$SO + HO_2 \rightarrow OH + SO_2,$$

which leads to the formation of SO_2. SO may also react with O or OH and generate SO_2. Reaction

$$HOSO_3 + OH \rightarrow H_2O + SO_2 + O_2$$

is the major source of SO_2 in the model, whose reactant $HOSO_3$ comes from the destruction reaction of H_2SO_4. The pathway from SO to SO_2 requires HO_2, O and OH. There are 3 major loss mechanisms of SO_2:

$$O + SO_2 \rightarrow SO_3$$

$$OH + SO_2 \rightarrow HSO_3$$

$$HO_2 + SO_2 \rightarrow OH + SO_3.$$

The pathway from SO_2 to SO_3 requires O or HO_2, and the pathway from HSO_3 to SO_3 requires O_2 via:

$$O_2 + HSO_3 \rightarrow HO_2 + SO_3,$$

SO_3 may also be generated from the reaction between $HOSO_3$ and O:

$$HOSO_3 + O \rightarrow HO_2 + SO_3$$

Nearly all SO_3 will then react with water molecules and generate sulfuric acid through Reaction 48. Based on our analysis, the chemical pathway of forming sulfuric acid in the surface ice is summarized in Figure 2.

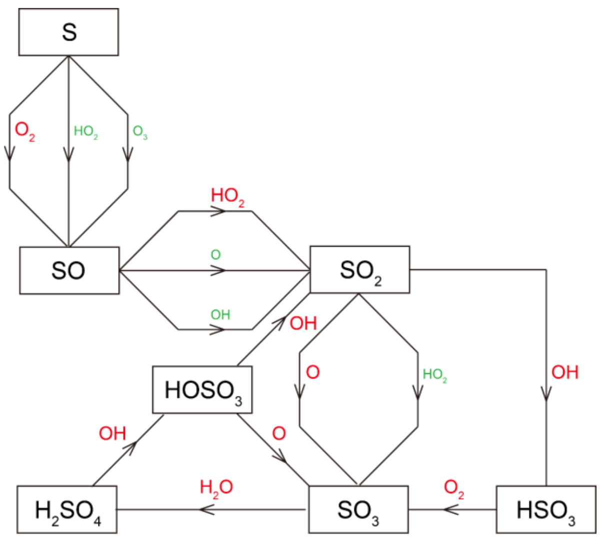

Figure 2. *Schematic diagram showing the chemical pathways to produce H_2SO_4. The compositions needed for the reactions are written next to the arrows, where the compositions in large red font represent the major reactions and the composition in small green font represent the minor reactions.*

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