論文の内容の要旨

Laboratory experiments and telescope observations toward understanding physicochemical properties of Europa's surface materials

（エウロパ表面物質の物理化学特性の理解に向けた室内実験および望遠鏡観測）

氏名　　　　丹　秀也

Europa, one of the Jovian icy satellites, would have a liquid-water ocean beneath the icy crust. The interior ocean has been attracting attention due to its astrobiological potentials; however, the chemical composition and redox state of Europa's interior ocean are poorly constrained. Disrupted icy regions, called chaotic terrains, on the surface of Europa are suggested to be formed by movements of localized subsurface water reservoirs within the icy crust. Non-ice materials observed on Europa were interpreted as sulfate salts or sulfuric acids based on the data obtained by the Galileo spacecraft. Recent observations of Europa's surface by large ground-based telescopes suggested that a large abundance of Cl-bearing salts may be contained in chaotic terrains in order to explain relatively low reflectance and weak H_2O ice absorptions without any characteristic absorptions due to sulfate salts. Since these Cl-bearing salts are considered to originate from the subsurface water, their chemical composition would be the key to understand the ocean chemistry of Europa. Moreover, the abundance and grain size of the Cl-bearing salts would provide insights into geochemical and geological processes on Europa, including formation of chaotic terrains. However, the detailed compositions of Cl-bearing salts (e.g., NaCl, $MgCl_2 \cdot nH_2O$, $NaClO_4$, $NaClO_4 \cdot 2H_2O$, $Mg(ClO_3)_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$) are poorly constrained due to the limited observational data and laboratory-experimental investigations.

Here, we report the results of a combination of telescope observations, laboratory experiments, and model calculations, aiming to constrain the chemical composition of the Cl-bearing salts on Europa's surface. Based on the synthesis of our findings, we discuss the ocean chemistry, water-rock interactions on the seafloor, and astrobiological implications for Europa.

In Chapter 2, we first performed telescope observations for Europa's surface in wavelength of 1.0–1.8 μm, where hydrated salts (e.g., $MgCl_2 \cdot nH_2O$, $NaClO_4 \cdot 2H_2O$, $Mg(ClO_3)_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$) have characteristic absorptions. To investigate the presence of the Cl-bearing hydrated salts, the spatially-resolved reflectance spectra were obtained using the Subaru Telescope/IRCS and adaptive optics AO188 with high wavelength resolutions ($\delta\lambda \sim 2$ nm for 1.0–1.5 μm and $\delta\lambda \sim 0.9$ nm for 1.5–1.8 μm) and high signal to noise ratios (S/N ~ 300). The observational results show that reflectance spectra are smooth and featureless on Europa's surface. We found no remarkable absorption features at ~1.2 μm owing to the hydrated Cl-bearing salts. We estimate upper limit abundances of the hydrated salts as less than 10%. The estimated abundance is significantly lower than those of the Cl-bearing salts (~20−40%) required to explain Europa's low reflectance in the previous observations. This in turn suggests that the Cl-bearing salts on Europa are highly likely anhydrous salts, NaCl and/or $NaClO_4$.

In Chapter 3, we performed laboratory experiments to investigate formation of oxychlorides, such as $NaClO_4$, from chloride, such as NaCl, on Europa. Europa's surface is heavily irradiated by high-energy particles (e.g., electron) and solar UV light. Previous studies hypothesized that these irradiations could cause the oxidation of chlorides (e.g., NaCl and $MgCl_2 \cdot nH_2O$) into chlorates (e.g., $Mg(ClO_3)_2 \cdot 6H_2O$) or perchlorates (e.g., $NaClO_4$, $NaClO_4 \cdot 2H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$) through reactions with oxidative radicals and molecules formed by dissociation of H_2O ice. However, this oxidation process has not been investigated based on laboratory experiments. Using a newly-developed irradiation experimental system, the present study first investigated the formation of ClO_4 or ClO_3 through irradiations of ~10-keV electron or UV light onto mixtures of H_2O ice and chlorides. In addition, the irradiations of MeV electron onto mixtures of H_2O ice and chlorides were also performed using an electron-beam accelerator, ETIGO-III. The experimental results show no significant formations of ClO_4 and ClO_3 regardless of the experimental conditions (temperature, energy source, or presence of oxidants in ice). We estimated upper limits of conversion efficiency from NaCl to $NaClO_4$ in our experiments. Using the conversion efficiency, together with the flux of electrons or photons on Europa, upper limit abundances of $NaClO_4$ accumulated on the surface over Europa's surface age become less than ~2 mol% relative to H_2O ice. The estimated abundance suggests that

NaCl would be the major Cl-bearing salts on Europa.

In Chapter 4, we performed laboratory experiments to obtain the optical constants of irradiated NaCl. To constrain the grain size and abundance of NaCl on the surface of Europa, spectral model fitting of the observational data was performed using the optical constants. On Europa's surface, the color of NaCl is changed from standard NaCl crystal due to irradiations of high-energy particles. We obtain the optical constants of NaCl irradiated by 10-keV electron in near-infrared wavelengths using the measured transmission spectra. The results of spectral fitting show that the non-irradiated NaCl can poorly reproduce the observational spectra, calling for dark materials with a red slope in wavelength of 1.1–1.3 μm. We show that an addition of irradiated NaCl greatly improves the model fitting of the dark reflectance in the near-infrared wavelength because it has a red-slope in the near-infrared range due to color center absorptions in visible. In the best fits of our calculations, the abundance and grain size of irradiated NaCl on Europa are suggested to be 40−50% and > a few μm, respectively. The high abundances and large grain size of irradiated NaCl can be explained if chaotic terrains were formed by collapses of surface H_2O ice through freezing of subsurface brine reservoirs. Upon concentrations of dissolved species in freezing subsurface reservoirs, NaCl salt grains could precipitate and grow to large size. These slurry salt-containing brines could have erupted to the surface upon formation of chaotic terrains.

In General Conclusions, we discuss geochemical and geological implications for Europa's ocean chemistry and astrobiology. Based on our observations and spectral fitting, NaCl is suggested to be the major salts on Europa, rather than Mg-bearing salts. If the salt composition reflects the seawater composition, the $[Na^+]/[Mg^{2+}]$ ratio of seawater is suggested to be higher than ~10 based on our results. In order to achieve the Na-rich seawater, the water-to-rock (W/R) ratio of water-rock reactions on the seafloor needs to be less than ~15 based on our thermodynamic equilibrium calculations. The required low W/R ratios suggest that the abundance of seafloor rocks would have reacted with the seawater. This could have happened on Europa if seafloor rocks are relatively young and aqueous alterations proceeded effectively, or if the entire of seafloor rocks is aqueously altered at low temperatures throughout the history of Europa. In the former scenario, young seafloor rocks could have been generated by magma activity through rock melting due to intense heat within the rocky interior. Aqueous alterations of flesh rocks could provide reductants to the ocean, supporting a redox disequilibrium energy for possible chemoautotrophic life. Our experimental data, predictions, and suggestions on the surface materials on Europa, including chaotic terrains, will be used or may be testable in near-future observations using space telescopes, e.g., JwST, spacecrafts, e.g., Europa Clipper and JUICE, and landers, e.g., Europa Lander.