

THE FORMATION AND NATURE OF EARLY OCEANS ON ICY SATELLITES: GEOCHEMICAL CONSTRAINTS. M. Yu. Zolotov¹, M. V. Mironenko³, C. R. Glein¹, and E. L. Shock^{1,2}, ¹School of Earth and Space Exploration, ²Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, ³Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, E-mail: zolotov@asu.edu.

Introduction: The incorporation of abundant water ice and rocky materials containing radioactive elements on non-planetary bodies in the outer solar system could have led to the formation of water oceans. Early oceans could have existed on the Galilean satellites of Jupiter, certain satellites of Saturn and Uranus, Triton, and multiple trans-Neptunian objects. Water-rock interactions on these bodies would have resulted in the dissolution of solids, precipitation of secondary phases, and formation and escape of gases. These processes would have affected oceanic compositions, which could be reflected by the present-day compositions of surfaces, atmospheres, and geysers on ice-rock bodies. Here, we discuss the geochemistry of ocean-forming processes using insights from aqueously altered chondrites, observations of icy satellites, and physical-chemical modeling of rock-water-gas interactions (see Appendix).

Insights from aqueous processes in asteroids: Despite the different sizes of asteroids (i.e., parent bodies of chondrites) and icy satellites, the early stages of their evolution could have been similar. Some asteroids (e.g., Ceres [1]) could represent the silicate cores of earlier water-covered bodies. Fortunately, the formation and evolution of aqueous solutions on asteroids can be revealed by studying the mineralogy and isotopic composition of chondrites [2,3], and can be quantified using physical and chemical models [e.g., 4-7].

Asteroids accreted a mixture of reduced and anhydrous solids (e.g., Fe-Ni metal, Mg-silicates, Ca-Al-oxides, FeS, presolar grains), amorphous and organic materials, and water ice. The decay of short-lived radionuclides (e.g., ²⁶Al) melted ice [4], and the chemistry of aqueous solutions was controlled by the dissolution of primary minerals, precipitation of secondary minerals, inorganic-organic reactions, and production and escape of gases. As alteration progressed, water was consumed by hydration and oxidation reactions. The oxidation of Fe, Ni, S, P, C, and Si led to the formation of ferrous and ferric minerals (e.g., magnetite), Ni-rich alloys and sulfides, pyrrhotite, phosphates, carbonates, sulfates, and oxygenated organic compounds. H₂ was produced by oxidation reactions, and the oxidation of Fe-rich metal was a major source of H₂. The separation and escape of H₂ as well as elevated temperatures (*T*) favored oxidation. The formation of sulfates occurred in water-rich, porous bodies, such as the parent bodies of CI/CM chondrites, where the production and escape of H₂ was highly efficient. Impermeable rocks and ice sealants would have restricted H₂ escape, which would have inhibited oxidation and caused reduction in H₂-rich localities. Although restricted fluid convection in small bodies (< ~80 km [8]) led to isochemical alteration, the closing of pores during the formation of hydrated minerals could have squeezed fluids toward the surface of asteroids. Despite the transfer of water toward the surface, low gravity and limited water content prevented the formation of oceans on typical (i.e., small) asteroids. Aqueous alteration on asteroids ceased after ~10-15 My [3].

Initial composition of icy satellites: Satellites of giant planets may have formed from a mixture of water ice and rocky materials that slowly accumulated from the surrounding solar accretion disk [9,10]. In contrast to asteroids, these rocky materials would not have been processed in the accretion disk and would have consisted of dust particles (< ~1 μm in diameter) without chondrules. The bulk composition of the building blocks of icy satellites was most likely solar. The accretion of solids as dust implies that minerals would not have been aqueously altered prior to accretion. Thus, icy satellites might have accreted similar materials as asteroids did (i.e., reduced and anhydrous solids), together with amorphous and organic compounds, and possibly NH₃. The initial composition of icy satellites probably graded between that of asteroids and comets with increasing heliocentric distance.

Chemistry of ocean-forming processes: Compared to water-bearing asteroids, aqueous processes on icy satellites were characterized by higher water/rock ratios and migration of fluids and rocks in stronger gravity fields. In addition, the higher volume/surface area ratio of icy satellites and generation of tidal heat in some cases supported the prolonged existence of oceans on some bodies (e.g., Galilean satellites, Titan, Triton).

The melting of water ice led to the outward migration of liquid water and its accumulation in peripheral parts of icy satellites. The chemistry of primordial oceans was a result of low-*T* (~0°C) aqueous alteration, often in the presence of partially melted ice. The composition of ocean-forming fluids and early oceans was controlled by the kinetics and thermodynamics [11] of water-rock interactions in the uppermost layers of rocky cores. The dissolution and oxidation of primary minerals and precipitation of secondary minerals (e.g., Mg-Fe-phyllsilicates, magnetite, phosphates) produced very reduced (H₂-rich) and alkaline (pH > 11) primordial oceans. Our models [e.g., 11] indicate that early oceans were dilute NaCl solutions depleted in Mg and sulfide species. Sulfates would not have formed in the reduced oceans.

Geochemical modeling reveals that the exsolution of H₂-rich gas from aqueous solutions occurred in low-pressure (*P*) peripheral zones of the bodies. The accumulation of H₂-rich gas beneath ice shells eventually led to its escape owing to impact/tectonic disruptions of ice and diffusion through ice. Despite H₂ escape, aqueous systems would not have re-equilibrated under more oxidizing conditions because redox reactions would have been kinetically inhibited at low *T* [11]. Our calculations indicate that oxidation was faster in H₂-poor systems (e.g., Fe⁰ → Fe₃O₄), and H₂ removal was necessary to insure Fe-rich metal oxidation even at relatively low *P* (e.g., ~1-2 kbar below Europa's ocean [12]). After Fe-rich metal was exhausted, the rate of H₂ production decreased, and the depth of gas separation decreased as well. Further H₂ escape and oxidation were limited by the permeability of ice shells.

On large bodies (e.g., Ganymede, Titan, Triton), thick ice shells suppressed H₂ separation at high *P*, retarded H₂ diffusion, and caused extremely reducing conditions in oceans (i.e., high activities of dissolved H₂). In addition, strong gravity slowed H₂ escape from primordial atmospheres, and the formation of a layer of high-pressure ices above cores upon cooling terminated oxidation reactions involving water. High fugacities (*f*) of highly non-ideal H₂ ($f_{\text{H}_2} \gg P_{\text{total}}$ at high P_{total}) and low *T* limited the oxidation of Fe-rich metal and favored the formation of secondary Fe-Ni alloys (as in Earth's serpentinites [13]). The alloys could have catalyzed the high-*P* hydrogenation of carbon species, forming CH₄ and other light hydrocarbons. This mechanism is consistent with observations of CH₄ on Titan [14,15]. On Europa, the lack of CH₄ could be explained by significant H₂ escape caused by periodic melting and disruptions of the ice shell, low gravity, elevated surface *T*, and Fe⁰-FeS core formation.

Hydrothermal processes. Heat production in rocky cores induced dehydration of early-formed hydrated minerals (e.g., phyllosilicates, tochilinite) and upward migration of hydrothermal fluids, which affected the mass and composition of oceans. Again, the composition of ocean-forming fluids was chiefly controlled by interactions in the uppermost rock layers. During and after core dehydration, hydrothermal processes took place as oceanic water circulated through permeable rocks below the ocean-rock boundary. The release of tidal heat and/or magmatic activity in subjacent rocks enhanced the circulation.

Our models show that hydrothermal circulation altered the mineralogy of permeable rocks and promoted oxidation (e.g., Fe-silicates and Fe-Ni alloy to magnetite and pentlandite) and H₂ generation. High-*T* fluids were rich in sulfide species (e.g., H₂S), and the mixing of hydrothermal fluids with oceanic water led to the precipitation of metal sulfides at ocean-rock interfaces. The upward transport (bubbling, diffusion, convection) and escape of H₂ oxidized icy satellites. High-*T* and low-*f*H₂ conditions increased the carbonate (CO₂ + HCO₃⁻ + CO₃²⁻) and sulfate (HSO₄⁻ + SO₄²⁻) concentrations of hydrothermal fluids [c.f. 17]. The oxidation of sulfides favored the partial dissolution of Mg-silicates, which led to the formation of Mg-sulfates in severely oxidized satellites, such as Europa. Presumably, the slow escape of H₂ allowed mineral assemblages to control the oxidation state (*f*H₂) of hydrothermal systems. On early Enceladus, sluggish hydrothermal circulation might have led to CH₄-CO₂ and NH₃-N₂ equilibria at ~250-300°C in a buffered environment [16,18]. Our calculations suggest that H₂ escape drove the oxidation state of hydrothermal systems on early Enceladus to the pyrrhotite-pyrite-magnetite (PPM) buffer. Reactions in the C-N-O-H system could have been catalyzed by magnetite and/or sulfide minerals.

The high-*T* transformation of accreted aromatic polymers with aliphatic, N-, and O-bearing side chains led to the partial oxidation and release of O- and N-bearing species (e.g., carbonate species, methanol, carboxylic and amino acids) into buoyant fluids. NH₃ (if present) might have been oxidized to N₂ [19,16], except in reduced oceans such as Titan's. The accumulation of soluble oxidized C (i.e., carbonate species, organic acids) in oceans, precipitation of carbon-

ates at ocean-rock boundaries, and escape of relatively insoluble CH₄ (if formed) contributed to satellite oxidation.

Summary: The composition of early oceans on ice-rock bodies was a consequence of low-*T* (~0°C) dissolution, hydration, and oxidation reactions between minerals and liquid water during ice melting and gravitational separation of water and rocks. Subsequent heating of rocky cores affected oceanic chemistry by contributing water from dehydration reactions in cores and promoting hydrothermal circulation of water through permeable rock layers. The escape of H₂ led to the oxidation of minerals, hydrothermal fluids, and oceans. Thus, H₂ escape drove the redox evolution of icy satellites. Restricted H₂ escape favored the mineral-catalyzed hydrogenation of carbon species and formation of CH₄.

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Appendix: We use the modified GEOCHEQ code [20,21] to calculate chemical equilibrium in gas-water-solid multicomponent systems at *T* = 0-400°C and *P* < 5 kbar. Input data include the thermodynamic properties of one-component crystalline solids and non-ideal solid, gas, and aqueous species. Isobaric and isochoric conditions can be explored. Sophisticated models account for rates of mineral dissolution and oxidation. We use these codes to quantify aqueous geochemistry on early asteroids, Europa, Enceladus, and Mars [7,11,12,18,22].

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