

OCEANIC CHEMICAL EVOLUTION ON ICY MOONS. M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, e-mail: zolotov@asu.edu.

Introduction: The release of heat from radionuclides led to the formation of water oceans on icy moons. Early oceans could have existed on the Galilean satellites of Jupiter and certain satellites of Saturn, Uranus and Neptune. Some moons (Europa, Ganymede, Titan, Enceladus and Triton) may contain subsurface aqueous fluids at present. The past and present aqueous processes could be manifested in the composition of moon's surfaces, atmospheres and eruptive plumes.

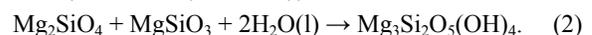
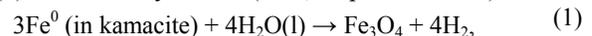
Pathways of oceanic chemical evolution have been affected by bulk composition and thermal history of a moon. The bulk composition constitutes the ratios between rocks, water ice, non-water volatiles and organic compounds. Throughout history, chemical evolution of oceans has been affected by the degree of ice melting, the extent and duration of water-rock chemical interactions, degassing of deep interior and oceanic water, freezing and thawing, and precipitation of inorganic and organic species. A great variety of these factors and processes among icy moons implies diverse pathways of their aqueous evolution.

Bulk Composition of Icy Moons: Moons of giant planets may have formed from a compositionally diverse mixture of grains that slowly accumulated from the surrounding solar accretion disk [1]. Contrary to chondrites, these rocky materials would not have been thermally re-processed in the accretion disk and would have consisted of dust particles ($<1 \mu\text{m}$) without chondrules. A deficiency of chondrules suggests that accreted mineral dust was closer to solar composition than to asteroidal materials. Despite chemical differences, icy moons might have accreted rocky materials similar to those present on asteroids, together with abundant amorphous silicates, ices and organic compounds. The rocky crystalline solids consisted of reduced and anhydrous products of solar nebula processes (mainly Fe-Ni metal, FeS, Mg- and Ca-silicates and Ca-Al oxides) and organic matter. If accreted, cometary-type materials also delivered CO_2 , CO, CH_4 , methanol, ethane, acetylene, HCN, NH_3 and condensed C-H-O-N rich organic species. The initial composition of icy satellites probably graded between that of carbonaceous asteroids and comets with increasing heliocentric distance. Some late-formed moons may have accreted large planetesimals that have been aqueously altered and contained hydrated and oxidized phases and salts.

Formation of Oceanic Composition: Decay of radionuclides, hydration of rocks and deposition of impact energy provided major heat sources for ice

melting. If a moon accretes within ~ 8 Ma after formation of Ca-, Al-rich inclusions, heat from decay of ^{26}Al surpasses heat from long-lived radionuclides. Although less energy is produced by long-lived radionuclides, ice can still be melted on small bodies such as Enceladus [2]. A release of accreted cometary species (CH_3OH , NH_3 , HCl, CO, CO_2) would have led to eutectic solutions at temperatures (T) < 200 K. First solutions could have formed at ~ 175 K ($\text{NH}_3\text{-H}_2\text{O}$ eutectic). Melting of HCl hydrates at ~ 186 K facilitated low-pH dissolution of solids [3] and caused some neutralization of fluids. Melting processes led to growing fluid layers (oceans) underlain by a cumulate of rocky particles. Thin primordial rock+ice crusts could have sunk into early oceans leading to appearance of fluids at moon's surfaces following by trapping of oceanic solutes into rapidly formed ices. Eventually, differentiation led to rocky cores covered by water ice mantles with internal liquid layers. On large moons (Ganymede, Titan) primordial oceans have separated from rocks by high- P ices.

In addition to early-dissolved volatiles and acids, compositions of primordial oceans were influenced by low- T (< 273 K) alteration of rocks. In particular, liquid water participated in oxidation and hydration reactions. Reaction (1) exemplifies oxidation and reaction (2) illustrates hydration (here, serpentinization)



Phyllosilicates (serpentine, cronstedtite, saponite) and tochilinite formed through hydration. Oxidation led to formation of Fe(II) (serpentine, saponite) and Fe(III) (magnetite, cronstedtite) phases, sulfides (tochilinite, pyrrhotite, pentlandite), Ni-rich alloys, chromite and phosphates. Initial aqueous compositions could have fluctuated as primary minerals alter with different rates [e.g. 4]. Acid-base equilibration of oceanic water with secondary minerals stabilized oceanic compositions within 0.1-10 Ma. Early acidic Fe-Mg-Ca-Cl compositions evolved toward alkaline Na-Cl-OH-carbonate solutions [4, 5]. The Cassini detection of salt-bearing particles emitted from Enceladus [6] confirms the prediction for oceanic composition [5].

Oxidized and reduced species of C, S, N and Fe coexisted metastably because of low- T inhibition of redox reactions. Escape of H_2 from small moons contributed to multiple redox disequilibria that provided energy to support metabolisms of chemotrophic organisms [7, 8], if they were present. A limited H_2 escape from larger moons favored stability of reduced S-, C-,

N-species, and limited redox disequilibria and habitability of their oceans.

Chemical equilibrium models [4, 5] demonstrate that early oceans could have been cold (<273 K), alkaline (pH 9–12), rich in Na and Cl, depleted in Mg and S and not saline (<35 g/kg). Sulfur was in sulfide form and its low concentration was controlled by solubility of sulfides [4, 5, 9]. However, sulfate could be present if aqueously altered planetesimals accreted [9,10]. Aqueous C species could have been presented by HCO_3^- , CO_3^{2-} , methanol, and carboxylic and amino acids. Note that abundance and speciation of aqueous C and N species were limited by inefficient low- T oxidation of primary high molecular weight organic polymer. NaCl, methanol and ammonia (if accreted) could be the major solutes that depressed the freezing point and favored longer existence of primordial oceans.

Oceanic Evolution: Pathways of subsequent oceanic evolution were dependent on the scale, timing, and location of heat production in the interiors.

Hydrothermal processes. Continuing heat production could have induced hydrothermal circulation in the rocky interiors, caused dehydration of previously formed minerals and further alteration of organic matter. Dehydration would have affected oceanic masses and compositions. On Europa, hydrothermal circulation could have affected sub-oceanic rocks, and on smaller bodies (Enceladus [11]) circulation may have affected the entire rocky cores. On largest moons, fluid migration has been limited and chemical processes in hot cores may have not directly affected oceanic compositions.

Hydrothermal processes further altered permeable rocks, and favored oxidation and H_2 generation. High- T fluids were rich in sulfide species and mixing of hydrothermal fluids with cold oceanic waters led to precipitation of sulfides. Hydrogen escape on smaller moons (Europa, Enceladus) favored oxidation of rocks and fluids [4, 5, 11]. Sulfide oxidation to sulfate favored partial dissolution of Mg-silicates and led to formation of Mg-sulfate rich oceans on severely oxidized moons, such as Europa [4]. As in CI carbonaceous bodies, an elevated Mg/Ca ratio and precipitation of Ca-carbonates could have limited formation of low-solubility Ca sulfates. As a result, high-solubility Mg sulfates could have become abundant among oceanic solutes. On smaller moons (Enceladus [5, 11]), sulfates may have not formed because of an early cessation of thermal processes.

Hydrothermal conditions also caused further transformation of C- and N-bearing species. CO could have converted to formic acid, C^{4+} solutes, methanol and CH_4 [12]. Hydrous pyrolysis of the high molecular weight polymer [13] caused oxidation of aliphatic

groups, caused some liberation of aromatic molecules and led to the formation of O-bearing species (carboxylic and amino acids, alcohols). Further heating led to oxidation of organic matter to C^{4+} species and N_2 (also from NH_3 [11]). Asteroidal samples do not reveal signs of Fisher-Tropsch type synthesis [14], and a majority of organic species could be presented by transformed primordial compounds. Because of multiple interactions, a variety of aliphatic, aromatic, and N-, O-, S-bearing organic species and CH_4 were delivered into oceans. In contrast to soluble compounds (acids, alcohols), hydrocarbons could have formed floating layers below icy shells. Higher-density aromatic compounds could have accumulated at oceanic floors and may have isolated oceans from rocks.

Low-temperature evolution. Throughout history, changes in tidal heat production due to a variable nature of the orbital resonances should have affected oceanic salinity, composition, temperature and mineralogy of suboceanic rocks. Low tidal activity would cause some freezing of icy shells, increasing oceanic salinities and mineral precipitation. Higher salinity implies colder oceanic water. An intense release of tidal heat would lead to dilution of oceanic water through ice melting. Moderate changes in ice thickness may cause precipitation/dissolution of Ca carbonates and sulfates, sulfides, ferric hydroxides/oxyhydroxides, silica, clay minerals and phosphates without changing concentrations of corresponding solutes. However, concentrations of Cl, SO_4^{2-} , Mg and Na may have not been maintained by dissolution reactions, and concentrations of these solutes would fluctuate along with icy shell thicknesses. Precipitation of abundant salts can only be possible after freezing of a significant portion of oceanic water [4, 5]. If they exist, oceanic organisms may have adapted to changes in salinity, temperature, and sources of nutrients and energy.

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