WHAT AFFECTS THE OCEANIC COMPOSITION ON EUROPA? M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, e-mail: zolotov@asu.edu.

Although an existence of a subsurface water ocean on the Jovian moon Europa is supported by diverse observations [1], the composition of oceanic water remains poorly constrained [2, 3]. Here we refine the indirect knowledge about the oceanic chemistry and discuss some factors that influenced the composition of oceanic water in the history of the moon.

Insights on the oceanic composition: A possible presence of Mg salts, mainly sulfates and/or chlorides, in colored endogenic surface materials inferred from several near infrared datasets implies Mg-bearing oceanic water [4-8]. Contrary to S, O, Cl, Na and K species, Mg compounds have not been detected in ionian materials that affect the surface. Although S³⁺ compounds form through the implantation of ionian species and radiolysis of reduced S compounds [5], sulfates in colored endogenic features could be oceanic. First, reduced S species (HS⁻, H₂S) should not be abundant in the water because of a solubility control by Fe sulfides [3]. Radiolysis of trace sulfides in frozen oceanic water may not lead to sulfate features seen in near infrared spectra of colored materials. Second, Mg should not be abundant in a sulfate-less ocean owing to low solubility of Mg silicates [cf. 3]; and a [Mg+Na]Cl type ocean suggested from the spectroscopy data [6, 7] may not be possible. In water-basic/ultrabasic rock environments suggested on Europa, Mg-rich solutions form only in sulfate-rich systems where the amount of Na⁺ is insufficient to compensate SO₄²⁻ [cf. 3]. The high solubility of MgSO₄ plays a major role in formation of corresponding fluids. Third, Mg sulfates could have been leached from CI/CM chondrites which are considered among the building blocks of Europa [2, 3, 9].

Although the reported presence of CI bearing salts in surface endogenic materials [7] needs verification [8], CI is the most likely anion leached through water-rock interactions [2, 3, 9-11]. A presence of Na carbonates [4, 5] and CO₂ [12] in endogenic surface features needs confirmation. However, the Na/K ratio in the Europa’s exosphere differs from the ionian value and suggests sputtering of the alkali elements from frozen oceanic water [13]. Abundant Na⁺ and CO₃²⁻/HCO₃⁻ ions in a high-pH ocean do not contradict to water-CI chondrite interaction models [10], and to the data on Ceres [14] and Enceladus [11, 15]. The detected CO₂ could form through radiolysis of organic matter (oil) delivered with or instead of oceanic water [3]. In summary, Mg²⁺, Na⁺, SO₄²⁻, Cl⁻ and HCO₃⁻/CO₃²⁻ are probably among major oceanic solutes but their concentrations and corresponding pH are uncertain. The [HCO₃⁻/CO₃²⁻]/Cl⁻ ratio could be more (the Ceres’ case [14]) or less (the Earth’s ocean case) than unity.

Europa’s bulk composition: The composition of the moon is the main factor affecting the ocean chemistry. It determines pathways of thermal evolution, and the composition of suboceanic rocks and ocean-forming fluids. Europa’s density (3 g cm⁻³) and gravity imply a rocky differentiated body [16] but the composition of the moon’s interior is uncertain. Discussed rock analogs vary from CI carbonaceous [2, 3] to LL ordinary chondrites [17]. The accretion of solids to the Galilean moons from the both sides on the solar nebula [18] and a subsequent cross-migration of planetesimals formed from both sides of Jupiter [19] could have delivered a mix of carbonaceous, icy, hydrated, anhydrous, reduced and oxidized (sulfate bearing) solids. Some of these compositions could be similar to Jupiter’s Trojans, and D, P and C asteroids.

Carbon species in endogenic surface materials [4, 5, 12] do not exclude accretion of sulfate-less organic/CO₃/CO/NH₃ solids that contributed to the composition of Ceres [14, 20] and outer solar system bodies (Titan, Enceladus, KBOs, comets, etc.). A significant fraction of the ‘cometary’ component in the Europa’s composition would suggest a low-density interior, a thin H₂O envelope, and carbonatization-silification of rocks which could be separated from an alkaline Na₂CO₃ rich ocean by an organic layer [cf. 3, 10, 21]. In turn, a major contribution from Cl/CM chondritic materials will be consistent with the presence of Mg in endogenic surface features and with endogenic sulfates.

Ocean’s formation scenarios: In one scenario (I), the ocean formed through a low-temperature water-rock separation during accretion and early thermal evolution. Initial low-pH solutions formed via dissolution of CO₂, CO, HCl and H₂S were neutralized by rocks. CO₂ and CO converted to HCO₃⁻, CO₃²⁻ and HCOO⁻ in forming neutral/alkaline solutions. A primordial ocean was enriched in accreted volatiles (inorganic C species, Cl⁻, NH₃/NH₄⁺), water-soluble organic compounds (e.g. methanol) and leached Na⁺. Accretion of planetesimals similar to Cl/CM chondrites [2, 3] and/or irradiated ices with trapped oxidants (O₂, H₂O₂) [22] led to a MgSO₄ bearing ocean. Mg²⁺ leached from rocks because unabundant Na⁺ did not compensate SO₄²⁻ and other anions [cf. 3, 22]. Ca²⁺ may not be abundant because of low solubility Ca sulfates. This scenario is likely if Mg is abundant in endogenic surface materials.

In another scenario (II), the ocean formed by hydrothermal solutions released through the thermal dehydration of rocks prior to igneous differentiation of the moon [3]. Sulfates could have been reduced through high-temperature (> 200 °C) reactions with...
organic compounds and/or H₂ formed via oxidation of Fe⁺ metal and ferrous silicates by water. S and C species were trapped in Fe sulfides and Ca-Mg-Fe carbonates, especially in suboceanic rocks that avoided much heating and silicate melting. Ocean-forming NaCl type reduced (H₂-bearing) solutions with some sulfide and carbonate species were depleted in Mg, Fe, Ca and Al because of low solubility of suboceanic phyllosilicates (chlorite, saponite, serpentine, etc.). Although hydrothermally-formed organic species could not be abundant or present, the fluids could have contained species (e.g. CH₄) formed via a thermal processing of accreted organic matter [3].

**Ocean evolution pathways:** The ocean formed by scenario (I) could have been altered by reduced NaCl fluids formed by the pathway (II). Throughout history, the oceanic chemistry was affected by the thermal-tidal evolution of the body and by related fluctuations of the shell thickness and endogenic processes at the ocean floor [23]. The young age of the icy surface (< 10⁶ Ma) and surface features suggest a major melting(s) of the shell followed by freezing(s) that may characterize the current epoch [3, 24]. Major melting(s) and ice-penetrating impacts caused partial degassing of low-solubility neutral species (N₂, H₂, CH₄ and Ar) from the ocean, though inorganic C and S compounds were preserved as ions. Melting(s) did not supply much surface oxidants (O₂, H₂O₂, CO₂) to the ocean because of a vigorous boiling at the water-space interface [3].

The current heat flow can be explained by the tidal heating in the shell, and no endogenic processes could occur at the ocean floor. Although periods of silicate volcanism could have supplied fresh rocks to the ocean floor, both magmatic degassing and post-magmatic hydrothermal circulation are limited at the pressure of ocean floor (150-200 MPa). The composition of suboceanic rocks (basalts, komatiites, alkaline rocks or chondrites [3]) may not have a strong effect on the major ocean chemistry if permeability is low.

**Permeability of suboceanic rocks:** The permeability determines the mass of rocks which may affect the oceanic composition. Rocks become impermeable at ~300 MPa [25] and a thin rock layer could interact with water. Carbonaceous chondrites are porous but impermeable rocks [26]. On Europa, altered suboceanic rocks with phyllosilicates, settled interplanetary dust grains, chemical sediments (SO₂ phases, clay minerals and low solubility salts) and organic matter (tars, oils and kerogen-like materials) could seal the rocks [cf. 3].

**Ocean’s thickness:** The apparently changing oceanic thickness directly affects the ocean salinity. In turn, salinity affects the ionic strength, activities and concentrations of solutes. In some cases, changing salinity affects relative concentrations of solutes through precipitation of a new phases or complete dissolution of a phase at the ocean floor. The later processes were important at major freezing or melting of the icy shell.

**Aqueous solubility control:** The degree of water-solid solubility control of the oceanic composition depends on the salinity and the water/reactive rock) ratio. In today’s low-salinity ocean [3], Mg²⁺, SO₄²⁻, Na⁺ and Cl⁻ may not be buffered by solids. At low permeability (a high water/rock ratio), the only low-solvability solids may control concentrations of abundant elements (Si, Al, Fe, Ni, Co, Cr, Ti, etc.) in oceanic water.

**Summary:** The composition of solids that formed Europa was the main factor affecting the major ion composition (Na⁺, Cl⁻, Mg²⁺, SO₄²⁻ and HCO₃⁻/CO₃²⁻) of the ocean. Water-rock interactions at the ocean floor and ice melting/freezing cycles were less important. The abundance of Mg in surface endogenic features informs about the oxidation state (SO₄²⁻ content) of the ocean and the bulk composition of the moon.

**References:**