

AQUEOUS CHEMICAL EVOLUTION AND HYDRATION STATE OF EUROPA'S SALTS.

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Overview. Evidence of hydrated salts on Europa⁽¹⁾ and of magnetic fields at Europa and Callisto probably due to induction in interior brine oceans^(2, 3, 4) has renewed interest in the aqueous chemistry of Jovian satellites^(5, 6, 7). The observational basis of the Europa salt hypothesis rests on NIMS data that seem to require salt-bound water, but little or no water ice, in some terrains⁽¹⁾. The identity of the salt hosts of the bound water is uncertain. Mix-and-match models suggest various mixtures of hydrated MgSO₄, Na₂SO₄, and Na₂CO₃. A nearly perfect reported spectral match of non-ice terrains with a mixture of all three salts unfortunately is flawed because MgSO₄ and Na₂CO₃ are chemically incompatible; they would react readily to form MgCO₃ and Na₂SO₄. Accordingly, Mg sulfates and Na carbonates do not occur together in nature on Earth and are unexpected on Europa in intimate mixtures. All three salts could be present on Europa, but MgSO₄ and Na₂CO₃ must be isolated and may have to be derived from separate aqueous systems. Some chemically compatible mixtures include: (1) hydrated MgSO₄ ± ice, (2) hydrated Na₂SO₄ ± ice, (3) hydrated Na₂CO₃ ± ice, (4) a mixture of hydrated Na₂SO₄ and Na₂CO₃ ± ice, and (5) a mixture of hydrated Na₂SO₄ and MgSO₄ ± ice. Chloride-rich compositions are possible but do not reproduce the NIMS results. The geochemical significance of each possible mixture is distinctive and implies different chemical pathways and distinct geological histories. Despite some claims that hydrated salts would dehydrate on Europa⁽⁸⁾, limited lab and field evidence on vapor pressures suggests otherwise, although more lab data are needed.

Geochemical pathways. Carbonaceous chondrites contain a great abundance and variety of salts— Ca-Mg-Na-rich carbonates and sulfates, plus small amounts of halides. By one class of models, the icy Galilean satellites were initially composed partly of chondritic material, and low-temperature aqueous differentiation initially would have resulted in leaching and emplacement of the most highly water-soluble salts on the satellites' surfaces; these solutes would include primarily Mg-Na sulfates with minor chlorides⁽⁶⁾. From this starting point, one can devise several plausible

geochemical pathways (some are illustrated schematically in Fig. 1):

1. Depending on the ratio of MgSO₄:Na₂SO₄ in the initial rock (which varies among chondrites) and depending on the path and style of melting and crystallization, it is possible to derive solutions and briny ices containing only hydrated MgSO₄, only hydrated Na₂SO₄, or mixed MgSO₄-Na₂SO₄ hydrates⁽⁶⁾.

2. The chondrite leaching experiments of Fanale et al.⁽⁸⁾ confirm that sulfates are more abundant than carbonates and chlorides in the soluble material, but differ from Kargel⁽⁶⁾ in that CaSO₄ (plus MgSO₄ and Na₂SO₄) is abundant in the leachate; the difference is apparently caused by a high water:rock ratio during the chondrite leaching experiments, which is unlikely during the initial aqueous differentiation of the Galilean satellites. However, if low-temperature hydrothermal circulation through a suboceanic silicate crust occurred over an extended time, CaSO₄ could be leached and deposited on the seafloor; Europa's ocean still would be limited by solubility to a low abundance of CaSO₄.

3. High-temperature hydrothermal circulation in an FeO-rich crust would reduce sulfates to solid sulfides, but chlorides and alkali carbonates could remain in solution or form a hydrated Na₂CO₃-rich and sulfate-depleted icy crust.

4. Deep freezing of the ocean and concentration of freezing-point depressants in residual liquid could lead to a chloride ocean.

5. Evaporative fractionation (e.g., due to frequent and extensive rifting of the frozen crust and exposure of oceanic waters) could mimic continental evaporite processes on Earth, resulting in formation of Na-K-CO₃-Cl residual solutions, especially if sulfates are removed by reduction to sulfides. If sulfates are not reduced, the ocean and crust could become enriched in Na₂CO₃ and Na₂SO₄, but any MgSO₄ would react to MgCO₃, which could accumulate on the ocean floor.

In sum, different geologic and geochemical pathways may lead to distinctive brine ocean and briny-icy crust compositions.

Hydration of salts on Europa's surface. The stability of salt-bound water molecules is necessary for the McCord et al.⁽¹⁾ interpretation of NIMS

data. Geochemical and geologic models of Europa rest on this salt hypothesis.

It has been suggested that salts dehydrate rapidly on Europa⁽⁸⁾. Dehydration has been observed in the lab purportedly under European conditions, but details of the experiments are not yet available. Limited data on the water-vapor pressures of hydrated Mg and Na sulfates seem unresponsive of dehydration of salts at European surface temperature and pressure if ice is present. The water-vapor pressures of hydrated sulfates observed in the lab⁽⁹⁾ and the hydration states of sulfates in nature⁽¹⁰⁾ consistently indicate that their vapor pressures are lower than those of pure condensed H₂O (Fig. 2). The difference is about a factor of 1.5 to 5 and depends on temperature and the amount of bound water. The vapor pressures of hydrated salts and of liquid water or ice tend to diverge slightly toward lower temperatures. Lab data extrapolated to European surface temperatures suggest that hydrated sulfates are even more stable (relative to ice) than on Earth. Since ice composes a large fraction of Europa's surface, the tenuous atmosphere ought to be nearly saturated in water vapor with respect to ice and supersaturated relative to hydrated salts. If European ice is not rapidly sublimating, then salts may occur at maximum hydration, e.g., MgSO₄·12H₂O and Na₂SO₄·10H₂O⁽⁶⁾.

Geothermal and solar heating on Europa might cause significant sublimation of ice. If ice eventually is lost completely from the surface layer in any region, and especially if irradiation of the salt residues produces an altered surface of lower albedo and higher temperature, then significant dehydration could ensue. Alternatively, electromagnetic and charged-particle radiation might directly kick water molecules from salt lattices.

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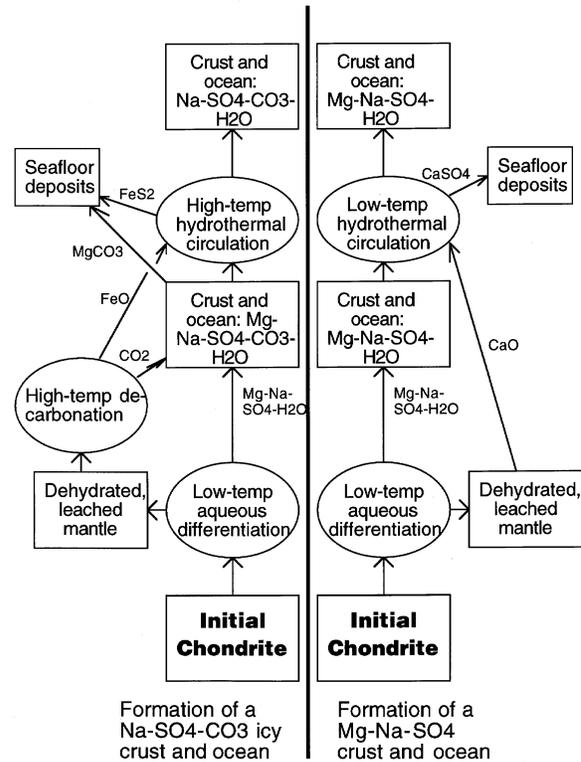


Fig. 1. Simplified schematic of possible chemical pathways of Europa's ocean and surface salts.

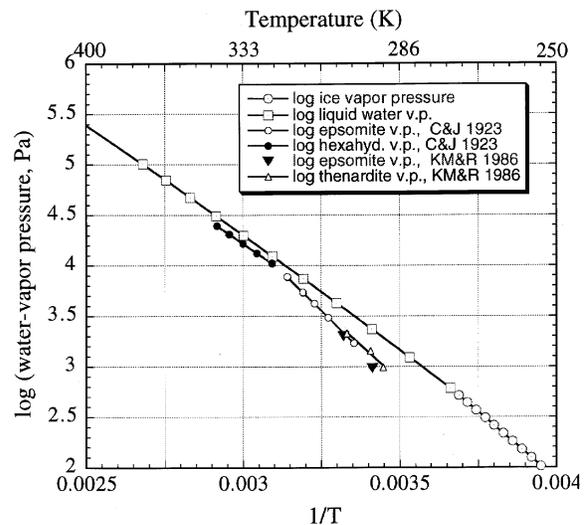


Fig. 2. Water-vapor pressures of MgSO₄·7H₂O, MgSO₄·6H₂O, Na₂SO₄·10H₂O, water ice, and liquid water. Data of^(9, 10).