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Composition and stability of salts on the surface of Europa and their oceanic origin

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Abstract. We present theoretical models of the composition, the relative abundances, and the stability of hydrated salts on the surface and in the icy shell of Jupiter's satellite Europa and discuss whether those salts have an oceanic origin. The evaluations were done with thermodynamic calculations of (1) salt dehydration equilibria at the conditions of the surface of Europa and its icy shell, (2) chemical equilibria involving solids and water vapor in the Na-K-Mg-Ca-S-Cl-H₂O system at surface temperatures and variable partial pressures of water vapor, and (3) changes in aquatic chemistry and sequences of salt precipitation from freezing oceanic water, using cosmochemical, mass balance, and physical-chemical constraints on the elemental and ionic composition of the ocean. Mass balance calculations of total or partial extraction of elements into an ocean from a carbonaceous chondrite type mantle show that magnesium and sulfate rather than chloride and sodium could be the most abundant solutes in the ocean. Freezing oceanic water of this composition leads to brines that differ in composition from the original water and to deposition of ice and highly hydrated sulfates of Mg, Na, and Ca as well as alkali chlorides. After freezing is complete, highly hydrated salts remain stable in ice-bearing surface materials and throughout the icy shell. For hypothetical surface salt lag deposits, formed through sublimation/sputtering of ice and dehydration of salts, we predict hydration stratification with depth, approaching the highest hydration states in ice-bearing materials in the lowest parts of the deposits. We discuss the effects of fast disequilibrium freezing and variable dehydration rates of salts on the predicted mineral assemblages at the surface. All of our models, which are independent of observations, predict the predominance of Mg and Na sulfates in surface salts, in agreement with spectroscopic models for the nonicy surface material in the near infrared spectral region.

1. Introduction

Galileo spacecraft reflectance spectroscopy in the near-infrared spectral region tentatively indicates the presence of hydrated salts in a non-H₂O ice component on the surface of Jupiter's moon Europa [McCord *et al.*, 1998a, 1998b, 1999]. It was shown that magnesium and sodium sulfates ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, epsomite; $\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, bloodite; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, mirabilite), sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, natron), and mixtures of these salts provide good fits for the near-infrared spectra for the nonicy material [McCord *et al.*, 1999]. The proposed presence of sulfuric acid hydrate [Carlson *et al.*, 1999] is not in contradiction to these interpretations. Sulfuric acid hydrate is probably exogenous in origin, being a product of substitution of protons for Na in sodium sulfate [Carlson *et al.*, 1999]. The presence of sulfates in the nonicy material is consistent with ultraviolet spectroscopy data that indicate the presence of compounds with S-O bond at the European surface [e.g., Lane *et al.*, 1981; Hendrix *et al.*, 1998]. Chlorine-bearing compounds have no spectral features in the available spectral range, and it is unknown if any Cl-bearing salts are present at the European surface.

The strong association of the nonicy material with tectonically disrupted areas (e.g., lineaments and chaotic terrain) on the surface of Europa and the almost uniform spectrum of that material have been interpreted in terms of sublimation/sputtering of salty ice and/or freezing/evaporation of water derived from a global salty water ocean [McCord *et al.*, 1998b, 1999; Fanale *et al.*, 1999a, 1999b, 2000]. The existence of a water ocean beneath the satellite's icy

shell has been predicted theoretically [Cassen *et al.*, 1979; Squyres *et al.*, 1983; Ross and Schubert, 1987] and was recently supported by surface morphology features obtained with Galileo [Carr *et al.*, 1998; Pappalardo *et al.*, 1999]. In addition, the presence of electrolytic solutes beneath the icy shell has been inferred from Galileo magnetic measurements [Khurana *et al.*, 1998; Kivelson *et al.*, 2000]. The presence of solutes in oceanic water is probably unavoidable in the context of water-rock interaction either early in the history of Europa or at present [Kargel, 1991; Fanale *et al.*, 2001; Kargel *et al.*, 2000]. Water-rock reactions should have led to a multicomponent electrolytic solution, which might contain chemical elements that are abundant in terrestrial seawater, although the ratio and concentration may differ considerably from Earth's ocean.

The multicomponent composition of European oceanic water should lead to a variety of salts in the products of freezing and sublimation/sputtering of ice on the satellite's surface. Fanale *et al.* [2001] demonstrated this experimentally by aqueous leaching of salts from a carbonaceous chondrite and freezing of the solution that formed. Here we undertake evaluations of this type from a theoretical basis. In this paper we present internally consistent geochemical and thermodynamic models that describe leaching of aqueous components from a silicate mantle, aquatic chemistry of the ocean, freezing of oceanic water during upwelling in fractures in the icy crust and on the surface, and dehydration of salts on the surface of Europa. The results are compared with observational models for the composition and distribution of the nonicy surface material.

2. Mass Balance Constraints on the Elemental Composition of the Ocean

On Earth, leaching of elements during water-rock interaction and degassing of the interior strongly affect the composition of the

Table 1. Abundances of Elements in an Ocean on Europa Resulting from Total Extraction from a Bulk Silicate Europa of CV Carbonaceous Chondrite Type^a

	Water Shell Thickness/Mass					
	80 km / 2.5×10^{21} kg		100 km / 3.0×10^{21} kg		150 km / 4.4×10^{21} kg	
	Fe	Fe-FeS	Fe	Fe-FeS	Fe	Fe-FeS
Radius of the Core, km	595	814	563	783	376	532
Mass of BSE, kg	3.8×10^{22}	3.4×10^{22}	3.9×10^{22}	3.5×10^{22}	4.2×10^{22}	4.0×10^{22}
Density of BSE, kg m ⁻³	2998	2959	3138	3101	3591	3591
Cl	3.9	3.5	3.2	2.9	2.4	2.3
Na	53	47	44	39	32	31
Mg	2200	2000	1800	1600	1400	1300
S	340	- ^b	280	- ^b	210	9.8
Ca	290	250	240	210	170	170
K	5.6	5.0	4.6	4.1	3.4	3.3
Br	0.025	0.022	0.021	0.018	0.015	0.015
C	83	73	68	61	50	49
Sr	0.23	0.20	0.19	0.17	0.14	0.14
B	0.0047	0.0041	0.0039	0.0034	0.0029	0.0028
F	0.38	0.33	0.31	0.27	0.23	0.22
Li	0.027	0.023	0.022	0.019	0.016	0.016
Rb	0.019	0.017	0.015	0.014	0.011	0.011
P	18	15	14	13	11	10
I	0.0025	0.0022	0.0021	0.0018	0.0015	0.0015
Ba	0.071	0.063	0.059	0.052	0.043	0.042
Cs	0.0014	0.0012	0.0012	0.001	0.00086	0.00083

^a Abundances of elements are in g kg⁻¹ water. BSE, Bulk Silicate Europa. Core radii and densities of the water shell, Fe, and Fe-FeS core are from Anderson *et al.* [1998].

^b The Fe-FeS eutectic core with 26 wt % S contains more sulfur than can be extracted from the BSE of CV type.

ocean [Rubey, 1951; Garrels and Mackenzie, 1971; Walker, 1977]. Likewise, solutes in the ocean on Europa are probably also derived from leaching [Fanale *et al.*, 2001; Kargel *et al.*, 2000] and degassing of elements from the silicate part of Europa. These processes are likely to be responsible for the formation and alteration of the oceanic composition during the satellite's accretion, differentiation, and early and/or subsequent tidal heating and volcanism. The assumption of leaching/degassing provides an opportunity to evaluate limits for elemental composition of the ocean based on the mass and assumed chondritic composition of the silicate part of Europa, and a proposed thickness of the ocean, while keeping in mind terrestrial data on partitioning of elements among the mantle, ocean, and crustal geochemical reservoirs. In this section we present geochemical mass balance calculations that constrain upper and lower limits for abundances of several elements in the ocean on Europa. In addition, we use data on the composition of the Europan atmosphere, charge balance, and salt solubility constraints to get a working model for oceanic aqueous chemistry. In the subsequent sections of the paper this composition is used to model freezing of oceanic water and salt mineralogy in surface lag deposits.

2.1. Mass Balance Models for Oceanic Chemistry

As a starting point for additional modeling, we calculate the consequences of total and partial extraction of elements from the silicate part of Europa into an ocean. The thickness of an outer water shell of ice plus liquid and the masses of silicate mantle and lithosphere (Bulk Silicate Europa, BSE) are taken from a Galileo-based model for Europan inner structure, which assumes either a metallic Fe core or one of Fe-FeS eutectic composition [Anderson *et al.*, 1998]. We consider several models for the interior structure, and our nominal case, shown in Table 1, represents a 100 km thick liquid water shell and a Fe core.

2.1.1. Composition of silicate Europa. Although the composition of the silicate mantle of Europa is unknown, chondrites provide reliable chemical models for terrestrial and Martian mantles [e.g., O'Neill and Palme, 1998; Lodders and Fegley, 1997] and have been used as a model for Galilean satellites

of Jupiter [e.g., Consolmagno and Lewis, 1976]. In addition to carbonaceous chondrites, which are considered as meteoritic analogs for the silicate part of Europa [e.g., Fanale *et al.*, 1977, 2001], we include in our analysis the composition of type H ordinary chondrites and the composition of Earth's primitive mantle. The primitive mantle represents compositions of present mantle, crust, and hydrosphere and is called Bulk Silicate Earth (BSEH) [see Lodders and Fegley, 1998].

Mass balance calculations based on meteoritic compositions from Lodders and Fegley [1998] show that total extraction of water from CI (18 wt % H₂O) and CM (12.6 wt % H₂O) mantles with mass of 3.9×10^{22} kg leads to an ocean 217–152 km thick. However, probably neither CI nor CM carbonaceous chondrites provide the best compositional model for BSE. The majority of hydrous minerals that contain the water in those meteorites formed during aqueous alteration in parent bodies of carbonaceous chondrites rather than in the solar nebula [Zolensky and McSween, 1988; Brearley and Jones, 1998]. This means that parent bodies of carbonaceous chondrites were accreted from a predominantly anhydrous material that was mixed with water ice, which subsequently melted. Although formation of hydrous minerals in a high-pressure Jovian subnebula might not have been as strongly inhibited as in the solar nebula [Fegley, 1993], it is unclear if hydrated minerals in the Jovian system formed this way.

We propose, by analogy to parent bodies of carbonaceous chondrites, that a mostly anhydrous carbonaceous chondrite-type component could have accreted on Europa together with an icy component. The presence of an icy component is likely during accretion of Ganymede and Callisto, which are covered by ice and have lower densities than Europa. The differentiated character of Europa inferred from Galileo gravity data by Anderson *et al.* [1998] and earlier models for the satellite's thermal history [Consolmagno and Lewis, 1976, 1977; Fanale *et al.*, 1977; Cassen *et al.*, 1981] imply that melting of ice, and therefore subsequent water-rock chemical interaction, was unavoidable. Since the mineralogy of hydrous minerals of CI and CM chondrites resulted mostly from aqueous alteration in parent bodies and the formation of hydrous silicates from subnebular gas might have been inhibited, our choice for a nominal BSE is CV carbonaceous

chondrites. Although these chondrites reveal signs of aqueous alteration [Krot *et al.*, 1995], they are much less altered than CM and CI carbonaceous chondrites. Thus a chondritic-type (e.g., CV-type) anhydrous or partially hydrated material could have accreted together with water ice followed by radioactive/tidal heating, ice melting, igneous differentiation, water-rock interaction, removal of elements from anhydrous minerals in the aqueous phase, the separation of a salty ocean, and degassing of oceanic water into space. Escape of hydrogen, which is formed during water-rock (meteorite) alteration, could have led to oxidation of a hydrothermally altered mantle and the formation of oxidized fluids, which form a sulfate-carbonate rich ocean [Zolotov and Shock, 2001a, 2001b].

Note that our choice for CV carbonaceous chondrites as a nominal model for the original silicate material is arbitrary because we have no mineral samples from the Jovian system. Condensation processes in the Jovian subnebula should have been different from that in the solar nebula [Prinn and Fegley, 1981] and remain to be explored in more detail. Correctly speaking, our fixed choice for CV-type carbonaceous chondrites is valid as a means of testing the sensitivity of the results to the choice of starting material. However, as we show below, our choice for original chondritic material does not affect significantly the evaluations of the oceanic composition.

2.1.2. Virtual extraction models. Constraints on the ocean composition can be made by comparing four sets of calculations. In one set, upper limits for elemental composition of the Europan ocean are calculated by a virtual total extraction of elements from a BSE of varied composition and mass. For Europan models of internal structure that involve a Fe-FeS core, we take into account some incorporation of sulfur from BSE to the core. For our nominal case we use 26 wt % of S in the core, which corresponds to the composition of the Fe-FeS eutectic at 30–40 kbar [Ryzenko and Kennedy, 1973].

In the other three sets, compositions are calculated for partial extraction of elements from a chondritic BSE based on terrestrial geochemical data on element partitioning between major geo-

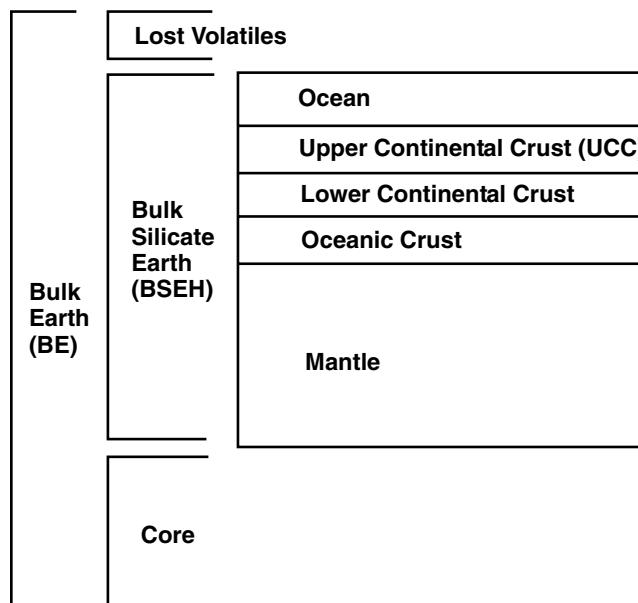


Figure 1. Relations between major terrestrial geochemical reservoirs used in this paper. The virtual reservoir of lost volatiles represents elements that were lost from the Earth in impact processes, including a Moon-forming event. The scheme is dimensionless. See Kargel and Lewis [1993] and Lodders and Fegley [1998] for details.

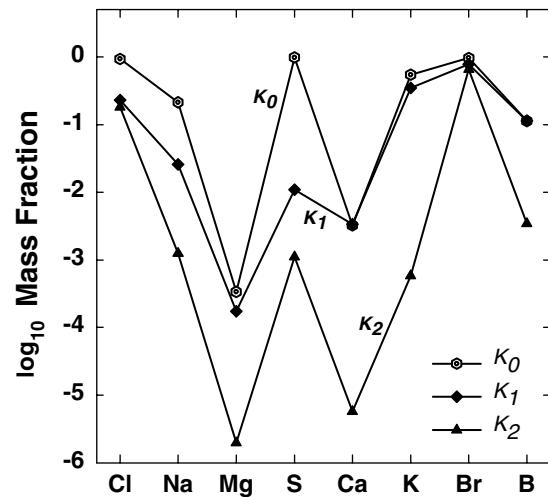


Figure 2. Mass fractions of elements extracted from the terrestrial mantle. K_0 is the fraction of elements extracted into the core, the upper continental crust, and the ocean, as well as being lost from the Earth in impact processes. K_1 is the fraction of elements extracted into the upper continental crust and the ocean. K_2 is the fraction of elements extracted into the ocean from the bulk silicate Earth. Note that 0 on the vertical axis corresponds to total extraction. This figure illustrates numerical data for major elements calculated with equations (1)–(3) using terrestrial geochemical data (see text). These calculations are used as a proxy to evaluate fractions of the elements that might have been extracted to an ocean on Europa.

chemical reservoirs that are shown in Figure 1. For the purpose of discussion, we refer to extraction factors K_0 , K_1 , and K_2 , which represent the fraction of an element that is extracted into the terrestrial ocean, is extracted into other reservoirs, or was lost from the Earth during its formation and early evolution.

The extraction factor K_0 represents the mass M fraction of an element i that is extracted from Bulk Earth (BE) to the ocean (O), the Upper Continental Crust (UCC), and the core, as well the mass lost in impact processes:

$$K_0 = \{M_i(\text{BE}) - M_i(\text{BSEH} - \text{UCC} - \text{O})\}/M_i(\text{BE}). \quad (1)$$

The term $M_i(\text{BSEH})$ corresponds to the mass of an element in the Bulk Silicate Earth (BSEH). The term $M_i(\text{BSEH} - \text{UCC} - \text{O})$ represents the mass of an element that is present in the lower continental crust, in the oceanic crust, and in Earth's mantle (see Figure 1). The term $\{M_i(\text{BE}) - M_i(\text{BSEH} - \text{UCC} - \text{O})\}$ stands for the mass of an element that is present in the UCC, the ocean, and the core or was lost from the Earth in impact processes, including possible impact blow-off of an early ocean. Calculations with the terrestrial factor K_0 provide more reliable upper limits for the oceanic composition on Europa than the model of total extraction.

The extraction factor K_1 represents the mass fraction of an element that is extracted from BSEH to the UCC and the ocean:

$$K_1 = M_i(\text{UCC} + \text{O})/M_i(\text{BSEH}). \quad (2)$$

This factor includes an extraction into salty sediments (e.g., evaporites) and other continental sediments, together with granites. The lack of terrestrial-type evaporitic processes on Europa and a lack of knowledge about granites allow us to consider this extraction factor as a first-order proxy for the Europan ocean at least for Na, Cl, and Br. These elements, by terrestrial analogy and owing to the high solubility of their corresponding salts, probably have small affinities to form chemical sediments on Europa. In other

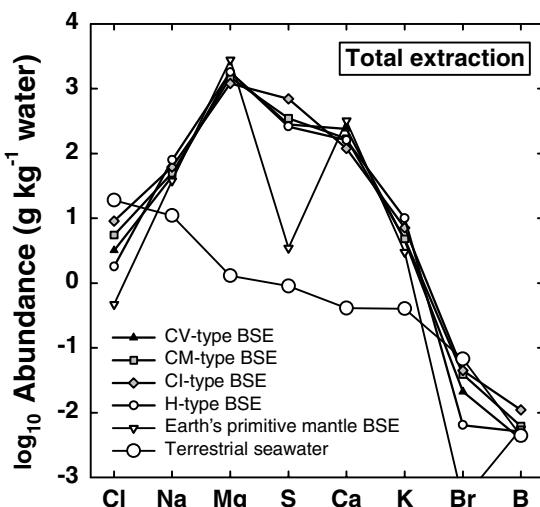


Figure 3. Mass balance models for the bulk composition of an ocean on Europa based on total extraction of elements into a 100 km thick ocean. This figure represents results of total extraction from BSE's of various compositions in comparison with terrestrial seawater. The figure illustrates numerical data for major elements depicted in Table 2 and represents a model of internal structure with a Fe core.

words, Na, Cl, and Br on Europa may accumulate preferentially in the ocean, rather than in chemical sediments and granites. Formation of granites would require a process like subduction of lithospheric plates, which is not known to operate on Europa.

Factor K_2 represents the fraction of an element extracted from Bulk Silicate Earth into the terrestrial ocean only:

$$K_2 = M_i(O)/M_i(\text{BSEH}). \quad (3)$$

We used this factor to set a lower limit for Europan oceanic composition because of the limited chance of evaporative sinks for elements from the ocean. The mass of salts on the satellite's surface and in the icy shell seems not to be significant compared to oceanic abundances.

The calculations were made with elemental abundances in chondrites and terrestrial UCC taken from *Lodders and Fegley [1998]* and *Wedepohl [1995]*, respectively. Data for BE and BSEH were taken from *Kargel and Lewis [1993]*. Figure 2 illustrates results of calculations with the three extraction factors. Note that high extraction values obtained with the K_0 factor for S, Cl, Na, and K could reflect their incorporation into the Earth's core or loss during impacts.

2.2. Results for Total and Partial Extractions

Mass balance calculations for the total extraction of elements from BSEs of several chondritic types are displayed in Figure 3 and Tables 1 and 2. Calculated concentrations (in g kg^{-1} (pure water)) obtained for abundant mantle elements like Mg, Ca, C, and P are greatly overestimated in a calculation of this type. However, the calculations imply that oceanic water can be saturated or supersaturated in these elements. Results obtained for Cl, Br, and B show that even total leaching of these elements from a chondritic mantle cannot reach the corresponding terrestrial values. It is interesting that complete extraction of Na and K from a CV-type BSE leads to oceanic concentrations that are only 4 and 12 times higher, respectively, than those of the terrestrial ocean.

Although the amount of extracted elements generally increases in the H, CV, CM, and CI sequence of BSE's chondritic material, extraction from all these chondritic mantles lead to similar results for many elements, as shown in Table 2 and Figure 3. At a given composition of BSE, greater depth of the ocean leads to lower concentrations of extracted elements in oceanic water, however the variations of the oceanic thickness do not cause significant changes in the oceanic composition, as can be seen in Table 1 for BSE of CV carbonaceous chondrite type.

Variations in the mass of BSE that corresponds to the uncertainties in core composition only slightly affect the amount of elements extracted into the ocean (see Table 1). However, calculations for models involving Fe-FeS eutectic cores show that the mass of S in these cores can exceed the mass of sulfur in the chondritic silicate part of Europa. Mass balances indicate that the presence of sulfur in an 80–140 km thick ocean is inconsistent with the presence of an Fe-FeS eutectic core containing 26 ± 1 wt % S at pressures of 30–40 kbar, appropriate for the core of Europa [*Consolmagno and Lewis, 1976*]. In the case of an ocean with thickness of 80–100

Table 2. Abundances of Elements in an Ocean on Europa Resulting From Total Extractions From BSE of Various Chondritic Compositions^a

	Chondritic Type of BSE					
	H	CV	CM	CI	BSEH ^b	Earth's Seawater
Cl	1.8	3.2	5.5	9.0	0.47	19
Na	79	44	50	62	38	11
Mg	1800	1800	1500	1200	2800	1.3
S	260	280	350	700	3.5	0.9
Ca	160	240	170	120	320	0.41
K	10	4.6	4.8	7.1	3.0	0.4
Br	0.0064	0.021	0.039	0.045	4.5×10^{-4}	0.067
C	27	68	280	440	0.84	0.028
Sr	0.11	0.19	0.13	0.094	0.27	0.0079
B	0.0051	0.0039	0.0062	0.011	0.0056	0.0044
F	16	0.31	0.049	0.77	0.27	0.0013
Li	0.022	0.022	0.019	0.019	0.022	1.8×10^{-4}
Rb	0.030	0.015	0.021	0.03	0.0077	1.2×10^{-4}
P	15	14	13	12	1	6.0×10^{-5}
I	7.7×10^{-4}	0.0021	0.0035	0.0055	1.4×10^{-4}	6.0×10^{-5}
Ba	0.057	0.059	0.040	0.03	0.082	1.3×10^{-5}
Cs	0.0013	0.0012	0.0014	0.0024	1.7×10^{-4}	3.0×10^{-7}

^a Abundances of elements are in g kg^{-1} water. At an ocean thickness of 100 km, the mass of the water shell is 3.0×10^{21} kg, and the mass of the BSE is 3.9×10^{22} kg, which corresponds to a Fe core with a radius of ~ 563 km [from *Anderson et al. 1998*].

^b Bulk Silicate Earth (mantle, crust, and hydrosphere compose the Earth's primitive mantle).

km, CV carbonaceous chondrite mantle, and a S-bearing core, sulfur can be present in the mantle (and extracted to the ocean) only if the core contains less than 6.4–7.4 wt % S. Only internal structures with an ocean thicker than ~145–150 km are consistent with both a small Fe-FeS core and oceanic S extracted from the CV carbonaceous chondrite type mantle (see Table 1). Note that all these mass balance calculations were obtained for the total extraction model and therefore provide upper limits for sulfur content in the core. It follows that observations of sulfur compounds at the surface of Europa might indicate an Fe-rich rather than an Fe-FeS eutectic core.

Calculations of partial extraction of elements from the silicate part of Europa with the three extraction factors are shown in Table 3. Partial extraction with factor K_0 provides a more reasonable upper limit for oceanic composition compared to the model of total extraction. These calculations include incorporation of elements to the core and their loss in impacts. The data obtained with the K_0 factor for S, halogens, and alkalis are similar to results of total extraction.

Partial extraction calculated with the K_1 factor indicates that in addition to Cl, Br, and B, Europa's ocean might also be depleted in Na compared to the terrestrial ocean, as shown in Figure 4. Note that calculations with this factor assume that there are no sinks of solutes into chemical sediments, hydrothermal deposits, or granites on Europa. We believe that for many elements, except Na, Cl, and Br, this is not the natural case and that real abundances might be lower than estimated by K_1 . However, we do not expect that the oceanic abundances are less than those obtained by the calculations with the K_2 factor that lead to significantly lower concentrations for all elements.

2.2.1. A working model for oceanic chemistry. To get a working chemical model for the Europan ocean (K_{1a}) in the Mg-Ca-Na-K-Cl-S-H₂O system, we start our calculations with the K_1 factor and decrease the abundances of K, Ca, S, and Mg on the basis of the following procedures. First, we decrease the potassium concentration to set the oceanic Na/K atomic ratio to 25 to match the value observed in the atmosphere of Europa [Brown, 2001]. Second, thermodynamic calculations of aqueous chemistry, which

Table 3. Chemical Models for the Composition of an Ocean on Europa Based on Partial Extraction of Elements from a CV Carbonaceous Chondrite BSE^a

	K_0	K_1	K_2	K_{1a}
Cl	3.0	0.74	0.58	0.7400
Na	9.3	1.1	0.055	1.129
Mg	0.62	0.32	0.0036	1.525 ^b
S	280	3.1	0.31	2.804 ^c
Ca	0.77	0.80	0.0014	0.3863 ^c
K	2.5	1.6	0.0027	0.0768 ^d
Br	0.02	0.016	0.013	-
C	9.7	9.5	0.0094	-
Sr	0.014	0.0082	2.4×10^{-5}	-
B	4.4×10^{-4}	4.4×10^{-4}	1.3×10^{-5}	-
F	0.058	0.026	6.6×10^{-6}	-
Li	0.0075	7.9×10^{-4}	7.7×10^{-7}	-
Rb	0.011	0.0079	1.1×10^{-6}	-
P	14	0.34	4.2×10^{-6}	-
I	0.0018	7.6×10^{-4}	3.9×10^{-6}	-
Ba	0.017	0.0017	4.0×10^{-8}	-
Cs	0.0012	0.0012	9.0×10^{-9}	-

^a The composition of the Europan ocean is measured in g kg⁻¹ water. The extraction calculations were done for a 100 km thick ocean and a BSE with an Fe core (see parameters in the top part of Table 1).

^b Mg is adjusted to achieve charge balance for the K_{1a} model.

^c Ca and sulfate are set to achieve gypsum saturation in equilibrium with water and ice at -3°C (272.85 K).

^d K is set by the Na/K ratio in the atmosphere of Europa from Brown [2001].

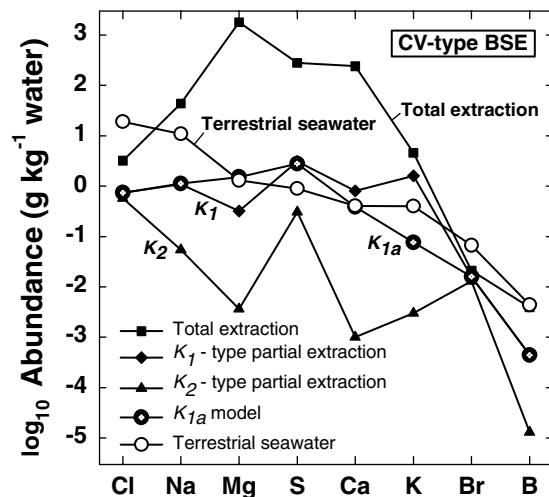


Figure 4. Mass balance models for the bulk composition of an ocean on Europa based on partial extraction of elements into a 100 km thick ocean. This figure represents results for partial extraction (models K_1 and K_2 calculated with equations (2) and (3)) as well as our working model for Europan oceanic water (K_{1a}). The figure illustrates numerical data for major elements depicted in Table 3.

we describe in the next section, show that oceanic water obtained with the K_1 factor is supersaturated with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). To eliminate this state, we decreased the concentrations of Ca^{2+} and sulfate in the K_1 oceanic model in order to achieve stable coexistence of ice and water, which are saturated with respect to gypsum. The resulting concentrations of Ca^{2+} and SO_4^{2-} represent gypsum saturation at the temperature (-0.3°C) where ice starts to form. Finally, the abundance of Mg, which seems to be in excess, is adjusted to achieve charge balance among the ions. The molal concentrations (moles per kilogram of H₂O) of ions that correspond to the K_{1a} model are Mg^{2+} , 6.271×10^{-2} ; SO_4^{2-} , 8.744×10^{-2} ; Na^+ , 4.910×10^{-2} ; Cl^- , 2.087×10^{-2} ; Ca^{2+} , 9.637×10^{-3} ; and K^+ , 1.964×10^{-3} . This corresponds to the following molal concentrations of soluble salts: MgSO_4 , 6.271×10^{-2} ; NaCl , 2.087×10^{-2} ; Na_2SO_4 , 1.412×10^{-2} ; CaSO_4 , 9.637×10^{-3} ; and K_2SO_4 , 9.8×10^{-4} . A total salinity of this model composition is 12.3 g kg⁻¹ of oceanic water, which is ~2.8 times less than Earth's seawater. Elemental and ionic compositions of the adopted ocean model (K_{1a}) are shown in Table 3 and Figures 4 and 5. These estimated compositions are far from exact, but they provide models that can be used to investigate freezing, water-rock interaction, and other processes on Europa.

2.3. Discussion

Mass balance calculations that model extraction of elements into the aqueous phase from a chondritic material show that the concentrations of Na, Cl, Br, B, and possibly K in an ocean of about 100 km thick do not exceed the corresponding values for terrestrial seawater and could be more than one order of magnitude lower. For Na and K this conclusion is consistent with the Na/O and K/O atomic ratios of ~1/300 and ~1/7500 observed in the Europan atmosphere (M. Brown, personal communication, 2001). If these ratios represent corresponding values in oceanic water, they lead to oceanic abundances of Na and K of 4.3 and 0.29 g kg⁻¹, respectively. Note that these values cannot represent the ocean because of uneven sputtering rates for Na, K, and O and because of redistribution of sputtered water molecules that could form a blanket on salt-bearing material.

Our prediction for a low Cl/S ratio in Europan oceanic water provides numerical reinforcement for earlier experimental [Fanale

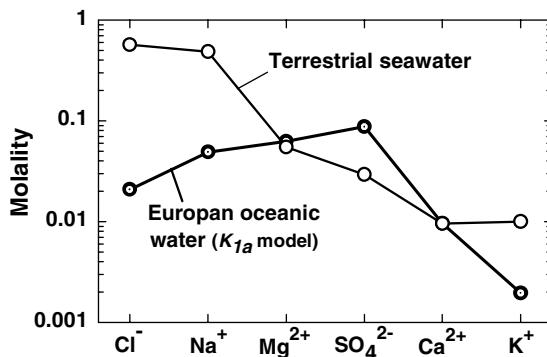


Figure 5. Molal concentrations of major elements in modeled Europian and terrestrial oceanic waters.

et al., 2001] as well as theoretical and speculative investigations [Kargel, 1991; Fanale *et al.*, 1999b; Kargel *et al.*, 2000]. At present, difficulties in spectral detection of chlorine compounds in the surface materials do not allow us to test these predictions.

Sulfur, magnesium, calcium, and potassium may be among the major elements in the ocean on Europa, but the concentrations of the ions are probably limited by the solubility of corresponding minerals that may form chemical sediments on the oceanic floor. Terrestrial and Europian oceanic water at $\sim 0^\circ\text{C}$ becomes supersaturated with respect to gypsum if the solubility product (SP) of this mineral ($\text{SP} = a(\text{SO}_4^{2-}) \times a(\text{Ca}^{2+}) \times a(\text{H}_2\text{O})^2$, where a stands for activity) exceeds $\sim 10^{-4.7}$ (see Marion and Farren [1997] and our calculations below). The low solubility of gypsum limits the concentrations of SO_4^{2-} and/or Ca^{2+} , unless oceanic water is oversaturated with respect to this salt. In addition, oceanic abundances of Ca and Mg may be controlled by equilibria with calcite and dolomite; however, this would require additional considerations of total carbonate and pH. By analogy with the terrestrial ocean, the concentrations of K (as well as Rb, Cs, and Li) and, in part, Mg could be controlled by ion exchange between water and hydrous phyllosilicates in the ocean floor sediments. However, the high solubility of magnesium sulfates leaves the possibility that Mg^{2+} and SO_4^{2-} concentrations are considerably higher than those of other ions. Kargel [1991], Kargel *et al.* [2000], and Spaun *et al.* [2000] favor a model of briny $\text{Mg}-\text{SO}_4$ water that is in equilibrium with ice and crystalline Mg sulfates. Our mass balance calculations of total extraction do not exclude such a case; however, possible precipitation of Mg in carbonates and/or brucite ($\text{Mg}(\text{OH})_2$) could lower the concentration of Mg^{2+} .

Mass balance calculations show that carbon could be in excess in the ocean on Europa: total extraction from the CV-type BSE leads to an oceanic abundance of 68 g kg^{-1} , which is 2400 times higher than in terrestrial seawater. Depending on the efficiency of extraction, Europian oceanic water can be saturated with respect to aqueous (HCO_3^- , CO_3^{2-} , CO_2) and solid (e.g., carbonates of Ca and Mg) species of carbon, which could be abundant solutes and minerals in ocean floor sediments. The likely predominance of sulfate ion over aqueous sulfides (H_2S , HS^-) suggests that Europian oceanic water is relatively oxidized, making elevated concentrations of reduced aqueous species of carbon, such as CH_4 , even more unlikely [Zolotov and Shock, 2001a, 2001b]. Absolute and relative abundances of aqueous carbonate species will be controlled or influenced by several factors, including the existence of carbonates in ocean floor chemical sediments; the solubility of CO_2 as a function of temperature, pressure, and salinity; and the pH of the water. At pH values of 6–10, a range that is a reasonable estimate for the Europian ocean, bicarbonate (HCO_3^-) is the predominant aqueous form of inorganic carbon at 0°C and pressures up to $\sim 1.5 \text{ kbar}$ that represent conditions in the vicinity of oceanic floor [Zolotov and Shock, 2001a, 2001b]. A proposed hydro-

thermal origin of the ocean on Europa [Zolotov and Shock, 2001a] allows us to suggest that originally alkaline oceanic water formed through alteration of olivine-rich mantle rocks. Nonacidic conditions provide favorable conditions for chemical deposition of carbonates, as well as brucite. However, high alkalinity is inconsistent with a predominance of magnesium sulfate in oceanic water and with precipitation of magnesium sulfate salts during freezing [Marion, 1999; Kargel *et al.*, 2000].

The lack of terrestrial-type chemical weathering and formation of evaporites on Europa, and the Earth-like O_2 -bearing atmosphere, would also be responsible for differences in abundance and speciation of several elements (especially S and C) in the ocean on Europa compared to terrestrial values. By terrestrial analogy, the composition of the ocean on Europa would also depend on whether plate tectonics, hydrothermal activity, and microbial life exist on Europa.

3. Freezing of Europian Oceanic Water

A general association of nonicy salty material of a uniform composition with the disrupted areas on the surface of Europa (e.g., linea and mottled terrain, chaos regions) could be caused by freezing of oceanic water followed by sublimation and sputtering of ice [McCord *et al.*, 1998b, 1999; Fanale *et al.*, 1999a]. Freezing of oceanic water is unavoidable during its upwelling in linear fractures of the icy shell, during appearance of water on the icy surface, and after the breaking of the icy shell by meteoritic/cometary impacts or internal tectonic/heating events. The first experimental [Fanale *et al.*, 2001] and theoretical thermodynamic models [Marion, 1999; Zolotov and Shock, 1999, 2000; Kargel *et al.*, 2000] for freezing of representative Europian oceanic water gave some initial insights about the chemical evolution of model solutions. Here we present results of additional thermodynamic calculations and discuss them in terms of the composition and distribution of the nonicy material and oceanic chemistry.

3.1. Models for Freezing Salt Water

We modeled the aquatic chemistry and precipitation of ice and salts during freezing of Europian oceanic water using the assumed composition described above. Thermodynamic models of freezing that include both fractional and equilibrium crystallization were used. During equilibrium crystallization, all components of the system (the aqueous phase, ice, and precipitated salts) are in chemical equilibrium with each other at each temperature. Experimental data for seawater show that such equilibration takes a long time (sometimes months) [Marion and Farren, 1999; Marion *et al.*, 1999] and therefore might not represent very rapid freezing of oceanic water on the surface of Europa and within newly formed fissures in the icy shell. Rapid freezing results in fractional crystallization, in which precipitated salts are separated from an unfrozen solution and do not affect its composition.

Calculations were performed with the FREZCHEM5.2-β code (written by Giles Marion), which provides compositions of the low-temperature aqueous system containing concentrated, strong-electrolyte solutions. This code uses the Pitzer model for activity coefficients of aqueous species and water activity [Spencer *et al.*, 1990; Marion and Farren, 1999]. Testing calculations for freezing of terrestrial seawater show close agreement with the experimental data of Gitterman [1937]. In contrast to the experimental results of Nelson and Thompson [1954], where complete equilibration might have been inhibited, these data may represent the equilibrium pathway of seawater freezing [Marion and Farren, 1999; Marion *et al.*, 1999]. Marion [1999] and Kargel *et al.* [2000] used the FREZCHEM5.2-β code to model freezing of Europian brines. Compared to the FREZCHEM2 code [Mironenko *et al.*, 1997], which we used in preliminary calculations of equilibrium crystallization of Europian water [Zolotov and Shock, 1999, 2000], this code includes Ca sulfates, crystalline $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, and several

other salts. The present freezing calculations were conducted for the Mg-Ca-Na-K-Cl-S-H₂O (liquid, ice) system that corresponds to our working model (K_{1a}) for oceanic water. We model freezing of oceanic water that consists of 1 kg of pure H₂O plus \sim 12.3 g of solutes according to the K_{1a} model. The calculations were done for 10⁵ Pa total pressure. Temperature was decreased gradually below 0°C with a decrement of 0.1°C until a numerical solution was successfully calculated.

3.2. Results of Freezing Calculations

The calculation of fractional crystallization for Europan water of the K_{1a} composition shows that complete freezing occurs below -36°C . At a temperature of -36.0°C , only 0.31% of the initial water remains unfrozen. Once freezing starts, the amount of unfrozen solution decreases rapidly with decreasing temperature, as shown in Figure 6a. Below -10°C the water in the solution represents $<1\%$ of the initial mass of water. In addition to ice, several salts form during freezing. Temperatures of the first appearance of solid phases formed from freezing water are as follows: ice and gypsum (CaSO₄·2H₂O), -0.3°C ; mirabilite (Na₂SO₄·10H₂O), -3.5°C ; magnesium sulfate (MgSO₄·12H₂O), -6.2°C ; sylvite (KCl), -29.1°C ; and hydrohalite (NaCl·2H₂O), -35.4°C . The computation stops at a eutectic temperature of about -36.1°C , when MgCl₂·12H₂O forms. This is almost the same eutectic temperature (-36°C) for terrestrial seawater freezing along the pathway of *Gitterman* [1937]. Figure 6b shows how the molar abundances of various salts change with freezing. One can see that magnesium and sodium hydrous sulfates are the most abundant salts formed. Gypsum is the third most abundant salt, but precipitated chlorides are much less abundant. Once the salts first appear, they form until complete freezing occurs. Note that maximum amounts precipitate once a salt starts to form, as shown in Figure 6c.

Formation of ice during freezing increases the salinity of the remaining solution, which becomes a brine shortly after the ice forms. This is illustrated in Figure 6d, which shows the calculated increases in salinity and ionic strength as temperature decreases. The most dramatic increases in salinity and ionic strength occur until the system cools to -6.2°C , when MgSO₄·12H₂O forms.

Calculated molal concentrations of aqueous species undergo dramatic changes caused by the increase in total salinity and by the deposition of salts. Until mirabilite forms at -3.5°C , the molal concentrations of solutes increase sharply (Figure 6e). This corresponds to an increase in total salinity of the solution caused by extensive formation of ice (see Figure 6a). Likewise, despite the precipitation of gypsum at temperatures between -0.3°C and -3.5°C , the concentrations of Ca²⁺ and SO₄²⁻ increase. The deposition of other salts decreases the abundances of the corresponding components in the aqueous phase, and concentrations of the less abundant components decrease more dramatically. For example, formation of mirabilite decreases the concentration of Na⁺ in the solution, but the concentration of sulfate continues to increase until MgSO₄·12H₂O forms at -6.2°C . Formation of magnesium sulfate causes decreases in abundances of Mg²⁺ and sulfate in the solution and is the dominant sink for sulfate. Extensive crystallization of MgSO₄·12H₂O decreases the total salinity (see Figure 6d) but increases the concentrations of Cl⁻, K⁺, and Na⁺. Concentrations of K⁺ and Na⁺ increase until the corresponding chloride salts precipitate. However, formation of alkali chlorides does not affect significantly the concentration of Cl⁻. The chloride concentration increases throughout freezing, and at temperatures below approximately -8°C , Cl⁻ becomes the most abundant ion in the solution.

Deposition of salts causes changes in relative concentrations among aqueous species during freezing, as one can see in Figure 6f. The Cl⁻/SO₄²⁻ mole ratio increases and the Ca²⁺/Mg²⁺ ratio decreases throughout the calculations. The K⁺/Na⁺ and K⁺/Mg²⁺

ratios increase until -29.1°C , when KCl starts to form. The Na⁺/Mg²⁺ ratio remains almost unchanged after MgSO₄·12H₂O forms.

As a consequence of salt precipitation during freezing, oceanic water rich in magnesium sulfate becomes a brine rich in magnesium chloride. The calculations indicate precipitation of MgCl₂·12H₂O from a eutectic solution. Calculations presented in the next section demonstrate that evaporation of ice from frozen near-eutectic brines would leave salt assemblages rich in magnesium chlorides.

Calculations of equilibrium freezing yield the same results for the aquatic chemistry, the temperatures when salts start to precipitate, and the total amounts of precipitated salts. The only difference is in the amount of salts calculated to precipitate during each temperature step. Therefore all plots in Figure 6 except Figure 6c would represent both fractional and equilibrium crystallization starting with oceanic water corresponding to the K_{1a} composition.

3.3. Discussion

Calculated changes in chemistry of freezing water suggest that the compositions of salts and salty ices in colored disrupted zones on the surface of Europa are not identical to the composition of the ocean. In particular, the surface material in those areas could have higher Cl/SO₄, K/Na, and K/Mg ratios and a lower Ca/Mg ratio compared to the ocean. Note that our calculations correspond to a slow freezing that allows equilibrium to be reached among salts, ice, and the aqueous phase. Faster freezing, which could occur at the contact with the cold surface, should lead to a less profound differentiation compared to our models. One of the reasons for deviation of natural systems from equilibrium or fractional crystallization calculations is trapping of the aqueous phase into defects in rapidly growing ice structures. On Earth this occurs even during relatively slow crystallization of oceanic water in the polar seas. Intense boiling of oceanic water in a low-pressure surface environment on Europa should cause mixing that would obscure significant spatial separation of the aqueous phase from newly formed ice and salts.

Another source for deviation from these models is oversaturation of quickly cooling oceanic water with respect to some salts, for example, gypsum. It is possible that the classical seawater freezing pathway [Nelson and Thompson, 1954] does not include gypsum because of kinetic inhibition of its precipitation [Marion *et al.*, 1999]. If gypsum formation is suppressed in FREZCHEM2 and FREZCHEM5.2-β models, the freezing pathway is in good agreement with the Nelson-Thompson experimental data [Mironenko *et al.*, 1997; Marion and Farren, 1999; Marion *et al.*, 1999]. Our freezing model of Europan water with the FREZCHEM2 code, which does not contain calcium sulfates [Zolotov and Shock, 2000], could represent a situation when precipitation of gypsum is inhibited. However, concentrations of Ca and SO₄ during freezing of terrestrial seawater supersaturated with respect to gypsum do not exceed 0.1 molal (G. Marion, personal communication). Therefore calculations of Zolotov and Shock [2000] for highly concentrated brines are not likely to represent freezing Europan water. Note that all these thermodynamic models are unable to predict to what extent oceanic water can be oversaturated with respect to gypsum. Experiments are required to evaluate the degree of gypsum oversaturation from rapidly freezing oceanic water.

Despite trapping of solution parcels into ice and the effects of oversaturation, the fractionation of freezing water seems to be unavoidable on the surface of Europa when oceanic water ascends through fractures in the icy crust. During water ascent the rate of freezing should increase toward cold surface layers, leading to the supply of partially differentiated water to the surface. The release of latent heat of ice crystallization should prevent rapid freezing, especially of large masses of water that could have been released on the surface from linear and chaotic disrupted zones. When water appears on the icy surface and forms a lake, the profound heat consumption by the surface material should drive the freezing front

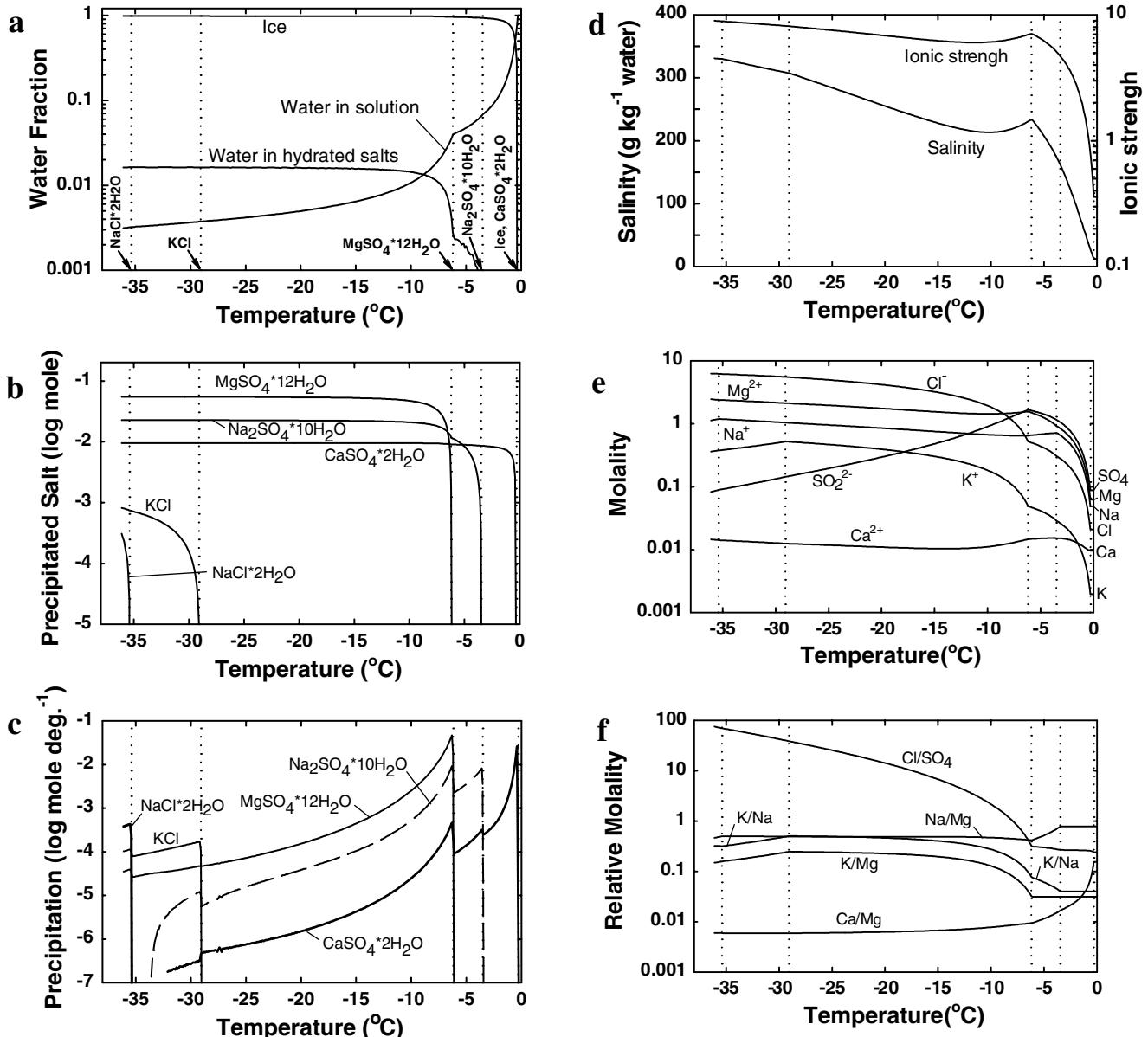


Figure 6. Changes in chemistry and mineralogy during fractional freezing of Europan oceanic water: (a) distribution of H₂O among ice, solution, and hydrated salts, (b) net amount of salt that has precipitated from 1 kg of oceanic water, (c) amount of salt (in moles) that has precipitated in the last temperature interval of 1°, (d) salinity and ionic strength of the solution, (e) molal concentrations of ions in the solution, and (f) relative molal concentrations of ions. The vertical dotted lines represent temperatures at which salts start to precipitate (see Figure 6b). The composition of oceanic water corresponds to the K_{1a} model listed in Table 3.

upward. Of course, downward crystallization of ice from the surface of a water lake could occur, but to a smaller extent than upward crystallization. It follows that the upper parts of freezing water flows and lakes will be enriched in differentiated brines, leading to a salty surface when freezing is complete, or where the uppermost part of the ice is sublimated and/or sputtered. It is possible that the surface coloration in tectonically disrupted zones results from the surface appearance of briny oceanic water, as McCord *et al.* [1998b, 1999] have suggested, but the salts are more likely to result from fractional crystallization of oceanic water during upwelling in the icy shell and upward freezing of water that was released on the surface. Therefore the composition of salts on the surface of Europa can only indirectly represent the composition of the ocean. In addition, we have to take into account fractionation, redistribution, and radiolytic synthesis of surface material

caused by magnetospheric bombardment, sputtering, and implantation [e.g., Cooper *et al.*, 2001].

Ices formed by rapid nonequilibrium freezing of holes in the icy shell generated by impacts or tectonic events may more closely represent oceanic water. It is even possible that the composition of the uppermost ice level in such areas can be identical to oceanic water if it was rapidly quenched and not greatly altered by magnetospheric bombardment, sputtering, and implantation. Deeper ice layers, which can form during downward crystallization of the ocean, can be depleted in salty components because of their partitioning into the ocean.

Relatively pure water ice that occurs over most of the surface of Europa could result from redeposition of sputtered water molecules [see Geissler *et al.*, 1998; Cooper *et al.*, 2001] or, alternatively, may represent quenched oceanic water. If the latter hypothesis is

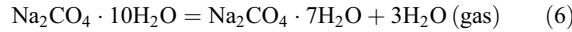
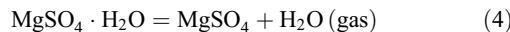
correct, the lack of detection of a salty component in this ice with currently available spectroscopic data is consistent with a moderate salinity of the oceanic water, as in our K_{1a} model. If so, remote or in situ sampling of that ice would give more direct information about the oceanic water composition than would nonicy material in disrupted zones or in frozen water between “icebergs.” However, a comparison of the salt composition in disrupted zones and in areas where oceanic water was frozen instantaneously would help to better constrain models of the freezing fractionation of the ocean.

4. Thermodynamic Stability of Hydrated Salts

The deposition of salts from an aqueous solution should lead initially to the formation of compounds with the highest degree of hydration. On the surface of Europa those salts can dehydrate in contact with space, as shown experimentally under simulated Europan conditions by *McCord et al.* [2000]. The extent of salt dehydration can also be evaluated theoretically by thermodynamic calculations of dehydration equilibria. In this section we apply calculations of this type to estimate the stability and relative abundance of hydrated sulfates and chlorides in ice-bearing materials and ice-free salty lag deposits, which may exist at the surface of Europa.

4.1. Models

Two sets of calculations are described here. In the first set, salt dehydration equilibria like



are calculated from 80 to 140 K to cover the range of observed temperatures of the Europan surface (86–132 K [*Spencer et al.*, 1999]). Standard thermodynamic properties for water vapor [*Gurvich et al.*, 1989] and for solid phases listed in Table 4 are used to calculate equilibrium constants for the dehydration reactions. Heat capacities are extrapolated to the temperatures of the Europan surface. The calculated equilibrium constants are not affected significantly by uncertainties in these extrapolations. The activity of solid phases is taken to be unity, and water vapor is assumed to be an ideal gas. The calculated equilibrium partial pressures of water vapor ($P_{\text{H}_2\text{O}}$) for dehydration reactions like equations (4)–(6) are compared with equilibrium $P_{\text{H}_2\text{O}}$ values over ice [*Lide*, 1998] extrapolated to temperatures of the surface of Europa. These calculations allow us to evaluate the stability of hydrated salts relative to each other and relative to ice.

In the second set of calculations we apply the free energy minimization method [*Van Zeggeren and Storey*, 1970] to evaluate chemical equilibrium in the Na-K-Mg-Ca-S-Cl-H₂O solid-gas type system that is open with respect to water vapor. The values of $P_{\text{H}_2\text{O}}$ were varied from ice saturation conditions to ~ 30 log units lower to cover the range of $P_{\text{H}_2\text{O}}$ that could occur in salty lag deposits. The calculations are performed for temperatures of 100 and 130 K, using Gibbs free energies of formation for water vapor and solid phases at these temperatures that are calculated from standard thermodynamic properties (see Table 4). As a result, the calculations model the degree of hydration and the relative abundances of salts in a cross section of a lag deposit. The nominal bulk atomic composition corresponds to our working model for Europan ocean chemistry (K_{1a} in Table 3). As a contrast, we use another bulk composition representing lag deposits formed through profound freezing differentiation of an aqueous phase derived from the K_{1a} model.

4.2. Results for Dehydration Equilibria

Figure 7 represents dehydration equilibria among magnesium and sodium sulfates, and sodium carbonates, together with the ice-

Table 4. List of Solid Phases in Calculations of Salt Assemblage in Lag Deposits^a

Mineral	Formula	Sources of Thermodynamic Data ^b
-	MgSO ₄	1, 1
Kieserite	MgSO ₄ · H ₂ O	2, 2
Sanderite	MgSO ₄ · 2H ₂ O	2, 2
Starkeyite	MgSO ₄ · 4H ₂ O	2, 2
Pentahydrite	MgSO ₄ · 5H ₂ O	2, 2
Hexahydrite	MgSO ₄ · 6H ₂ O	2, 2
Epsomite	MgSO ₄ · 7H ₂ O	1, 1
Thenardite	Na ₂ SO ₄	1, 1
Mirabilite	Na ₂ SO ₄ · 10H ₂ O	1, 1
Anhydrite	CaSO ₄	3, 1
Bassanite	CaSO ₄ · 0.5H ₂ O	3, 3
Gypsum	CaSO ₄ · 2H ₂ O	3, 1
Arcanite	K ₂ SO ₄	1, 1
Leonite	K ₂ Mg(SO ₄) ₂ · 4H ₂ O	2, 2
Picromerite	K ₂ Mg(SO ₄) ₂ · 6H ₂ O	2, 2
Chloromagnesite	MgCl ₂	1, 1
-	MgCl ₂ · H ₂ O	2, 2
-	MgCl ₂ · 2H ₂ O	2, 2
-	MgCl ₂ · 4H ₂ O	2, 2
Bischofite	MgCl ₂ · 6H ₂ O	2, 2
Hydrophilite	CaCl ₂	1, 1
-	CaCl ₂ · H ₂ O	3, 3
-	CaCl ₂ · 2H ₂ O	3, 3
-	CaCl ₂ · 4H ₂ O	3, 3
Antarcticite	CaCl ₂ · 6H ₂ O	3, 3
Halite	NaCl	1, 1
Sylvite	KCl	1, 1
Gregoryite	Na ₂ CO ₃	4, 4
Thermanotrite	Na ₂ CO ₃ · H ₂ O	1, 1
-	Na ₂ CO ₃ · 7H ₂ O	2, 2
Natron	Na ₂ CO ₃ · 10H ₂ O	2, 2
Magnesite	MgCO ₃	1, 1
Nesquehonite	MgCO ₃ · 3H ₂ O	1, 1
-	K ₂ CO ₃	4, 4
-	K ₂ CO ₃ · 0.5H ₂ O	2, 2
-	K ₂ CO ₃ · 1.5H ₂ O	2, 2

^a Carbonates are not used in calculations performed by the free energy minimization method.

^b The references correspond to standard enthalpy of formation and entropy, respectively: 1, *Robie and Hemingway* [1995]; 2, *Yungman* [1999]; 3, *Garvin et al.* [1987]; 4, *Gurvich et al.* [1989].

water vapor phase boundary curve. Note that pressure decreases upward, so that depth in a lag deposit increases downward. The areas between the curves represent the equilibrium stability fields of salts and ice. Ice should sublime above the dashed curve, which represents the equilibrium conditions for the ice-H₂O (gas) equilibrium. An increase in temperature and/or decrease in $P_{\text{H}_2\text{O}}$ makes ice less stable and leads to the stability of sequentially less hydrated salts. At a fixed temperature, the stable existence of hydrated salts requires lower $P_{\text{H}_2\text{O}}$ values than are needed for the stable existence of ice. This indicates that hydrated salts are more stable than ice and that preferential sublimation of ice would lead to formation of salt lag deposits. In Figure 7 one can see that the conditions of ice saturation, which represent ice-bearing materials, favor the stability of salts with the highest degree of hydration. Calculations show that this is true for the full range of surface temperatures and for higher temperatures that represent the whole icy shell.

Vertical cross sections of phase diagrams in Figure 7 would represent equilibrium isothermal models of a lag deposit. A decrease in $P_{\text{H}_2\text{O}}$, which can occur toward the top of salt deposits, favors dehydration of salts. The stability fields of other salts relative to water ice at 100 K are depicted in Figure 8. One can see that hydrated salts have different stabilities, and at a fixed $P_{\text{H}_2\text{O}}$, highly hydrated salts can coexist with dehydrated compounds of

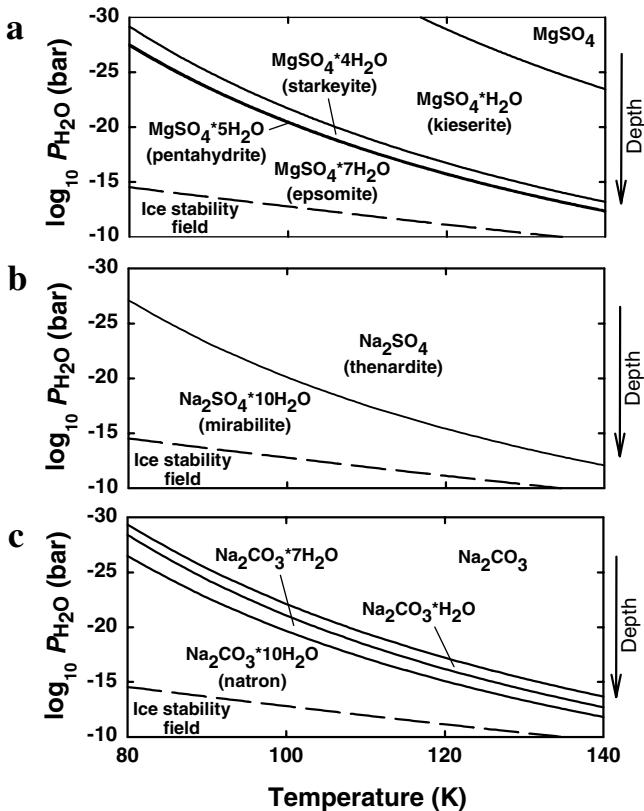


Figure 7. Dehydration equilibria among (a) magnesium sulfates, (b) sodium sulfates, and (c) sodium carbonates at temperatures of the surface of Europa. The dashed curves represent the ice-water vapor equilibrium. Ice is unstable above these curves.

another composition. It is possible that variations of water vapor pressure in lag deposits would lead to a variety of assemblages of salts with variable degrees of hydration.

Relative salt abundances at 100 K and 130 K in a lag deposit calculated from the K_{1a} oceanic water are shown in Figure 9. Magnesium and sodium sulfates compose more than 90% of the

calculated deposit and are less hydrated toward the uppermost layer of the lag deposit. In ice-bearing situations, epsomite (57.8 vol %), mirabilite (33.9 vol %) and antarcticite (7.8 vol %) compose the salt component of the deposits. These three highly hydrated salts are also stable throughout the whole icy shell. Potassium is present in the forms of chloride and sulfate salts, which compose ~0.5 vol %. The results obtained for 100 K and 130 K are similar, except for the proportionally lower stability of hydrated salts at the higher temperature.

Sublimation of ice from frozen brines formed during freezing of oceanic water can generate another mineral assemblage in lag deposits. This is illustrated in Figure 10, which shows the speciation of salts in a model lag deposit derived from the composition of the remaining unfrozen solution at -36°C formed during freezing fractionation of K_{1a} oceanic water. Fractional crystallization increases concentrations of Cl in the unfrozen brine (see Figure 6e), and resulting lag deposits are rich in chlorides of Mg, Na, and K. In ice-bearing deposits formed from these deeply fractionated brines, bischofite (84 vol %), halite (7 vol %), sylvite (4 vol %), and mirabilite (5 vol %) are the dominant stable salts. (Note that several potentially significant hydrated minerals, such as $\text{NaCl}_2 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 12\text{H}_2\text{O}$, were not included in our calculations. We propose that these two minerals rather than NaCl and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are stable phases in ice-bearing mineral assemblages.) Note that the fraction of these Cl-rich brines is small compared to the mass of initial solution (see Figure 6a). Therefore Cl-rich salt deposits should not be a common occurrence on the surface of Europa.

4.3. Discussion

Figures 7–10 show that highly hydrated salts are thermodynamically stable in ice-bearing deposits on the surface of Europa and throughout the icy shell, independent of the temperature gradient inside the shell. This is consistent with earlier investigations by Kargel [1999] and McCord *et al.* [2000] that showed that lag deposits formed through sublimation and/or sputtering of the ice can contain less hydrated salts than ice-bearing materials. This can occur because $P_{\text{H}_2\text{O}}$ values in the lag deposits should be less than those in ice-bearing materials and because the surface of salt deposits could be warmer compared to deeper subsurface layers. Both heating of the surface and a lower albedo of salt deposits compared to ice should contribute to temperature differences between ice-bearing and ice-free deposits. If salt lag deposits are thick enough, salt desiccation can lead to hydration stratification

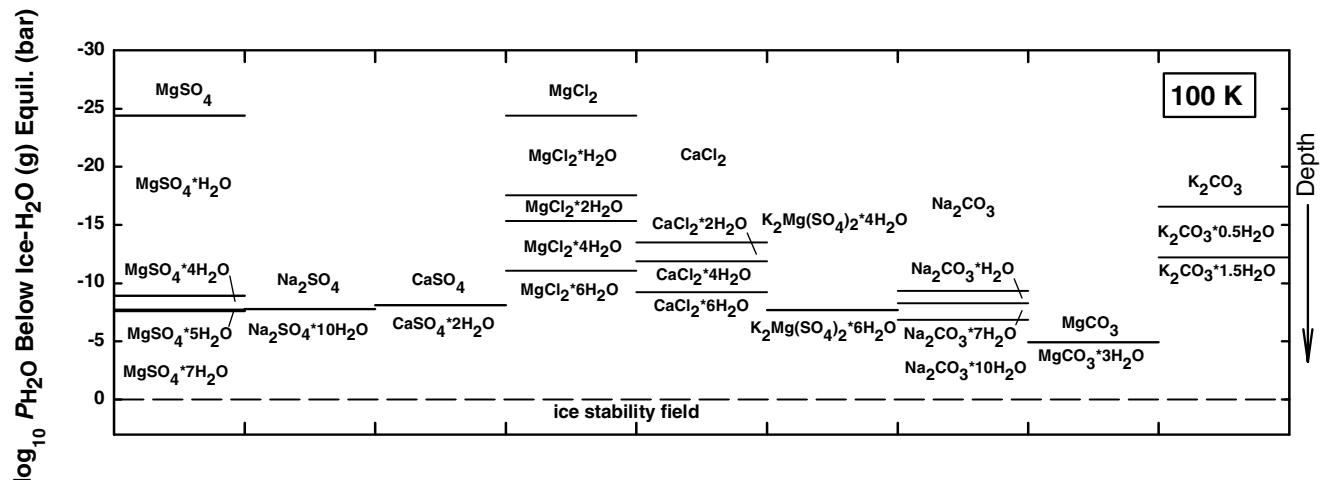


Figure 8. Phase equilibria among hydrated salts at a temperature of 100 K as a function of the partial pressure of water vapor relative to ice-water vapor equilibrium. The dashed line represents the equilibrium conditions for the ice-vapor equilibrium. Ice is stable below this line. In a salt lag deposit on the surface of Europa, the partial pressure of water vapor should increase downward, leading to stability of highly hydrated salts in ice-bearing parts of the deposit.

with depth, approaching highest states of hydration in ice-bearing materials in the lowest parts of the deposits, as can be seen in Figures 8–10. Spatial variation in average surface temperature can also lead to differences in the degree of hydration of the surface nonice materials. Less hydrated salts can be expected in low-albedo and therefore warmer areas.

So far, the presence of highly dehydrated salt deposits on the surface of Europa is not supported by spectroscopic observations. The presumed dominance of highly hydrated salts on Europa [McCord *et al.*, 1998b, 1999] can be caused by several factors. First, ice-free lag deposits could be absent at the surface of Europa.

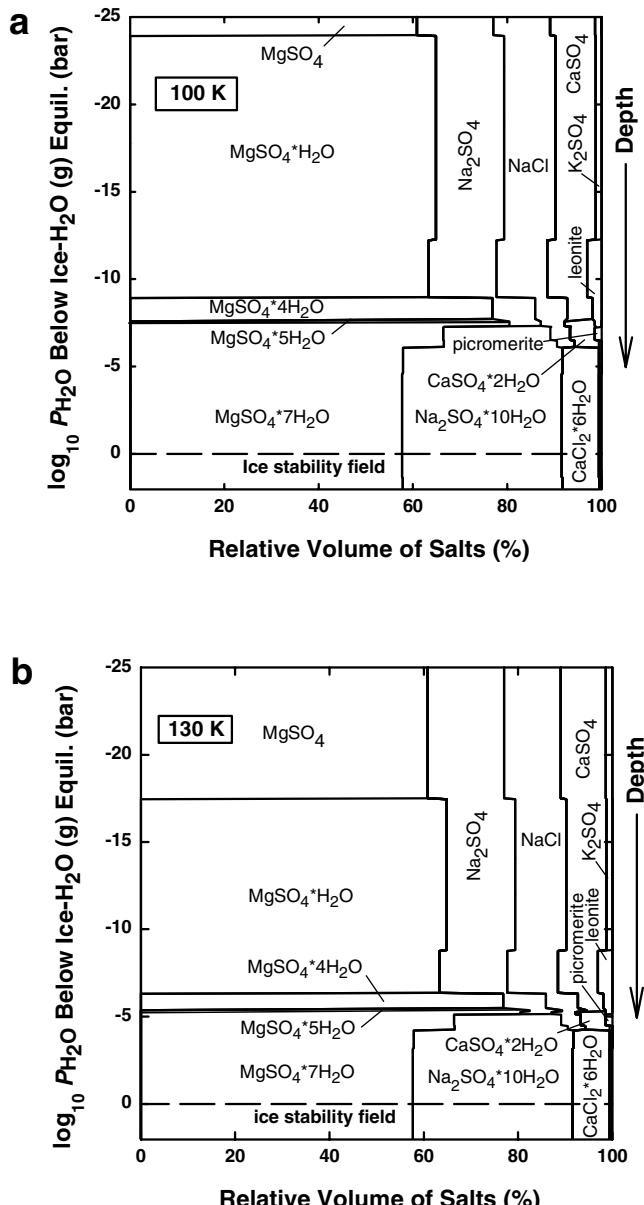


Figure 9. Computed equilibrium stratification of salts in lag deposits on the surface of Europa at temperatures of (a) 100 K and (b) 130 K. Bulk composition of the lag deposits corresponds to Europan oceanic water of K_{1a} composition. The computation models lag deposits formed from sublimation/sputtering of ice from frozen oceanic water. The dashed line represents an upper boundary of ice stability. Partial pressure of water vapor decreases upward from the stability field of ice. A roof of lag deposits can exist somewhere above the stability field of ice. Note that carbonates are not included in these calculations.

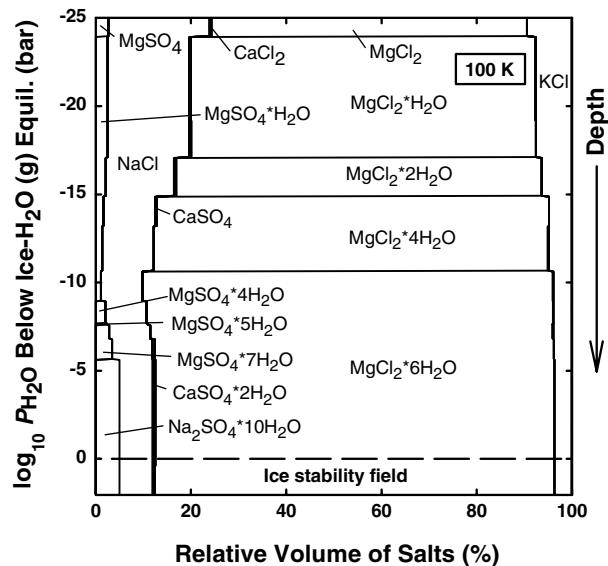


Figure 10. Equilibrium stratification of salts at 100 K in a lag deposit formed from a fractionated brine. Bulk composition (in molal concentrations) corresponds to an unfrozen solution at -36°C that formed during fractional crystallization of Europan oceanic water of K_{1a} composition (see Figure 6e): Mg^{2+} , 2.45; SO_4^{2-} , 8.37×10^{-2} ; Na^+ , 1.14; Cl^- , 6.27; Ca^{2+} , 1.45×10^{-2} ; and K^+ , 0.365.

Indeed, fading of colored disrupted zones through redeposition of sputtered water molecules could prevent both ice sublimation and salt dehydration. Second, in thin lag deposits, the partial pressure of water vapor could be buffered by underling ice, which prevents dehydration of salts. Finally, salts could dehydrate slowly compared to the age of the surface. The high stability of epsomite with respect to dehydration in vacuum, experimentally inferred by McCord *et al.* [2000], is consistent with the latter suggestion.

If ice is locally absent from the surface, salts should dehydrate with various rates. For example, natron and mirabilite dehydrate more rapidly than epsomite [McCord *et al.*, 2000]. It follows that upper layers of ice-free lag deposits can contain both kinetically stable highly hydrated salts (epsomite) and several dehydrated salts (thenardite) that desiccate rapidly. Inside the lag deposits the partial pressure of water vapor and salt hydration states can be buffered by dehydration equilibria among the less kinetically stable salts rather than the most abundant salts. A high kinetic reactivity of mirabilite with respect to dehydration [McCord *et al.*, 2000] leads to the prediction that a thenardite-mirabilite equilibrium in ice-free lag deposits buffers the partial pressure of water vapor. It can be seen in Figure 8 that the thenardite-mirabilite water vapor buffer closely matches several equilibria among Mg, Ca, and K sulfates and maintains the stability of the following salts: $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$, MgCO_3 , and $\text{K}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}$. Alternatively, if water ice is always present, or if the local concentration of sputtered water molecules is high, our calculations predict the stable existence of highly hydrated salts.

5. Concluding Remarks

We present internally consistent models that put constraints on the elemental and ionic compositions of the ocean on Europa, predict precipitation of certain salts during freezing of oceanic water, and imply dehydration stratification of these salts in hypothetical lag deposits on the satellite's surface.

We argue that electrolyte solutes in the ocean are not a result of leaching from a salt-containing carbonaceous chondrite material, but are more likely to have formed through aqueous alteration of

anhydrous chondritic materials. This type of alteration in parent bodies of carbonaceous chondrites led to deposition of secondary salts in the meteorites and is a good analogy for an ocean-forming process on Europa. Aqueous, possibly hydrothermal, alteration during the differentiation of Europa could be a primary contributor to the ionic composition of the ocean.

Mass balance evaluations of bulk composition of the European ocean show that sulfur and magnesium can predominate and that concentrations of Cl, Br, B, and alkalis in oceanic water could be lower than in terrestrial seawater. Abundances of solutes in oceanic water can be limited by aqueous-solid type reactions. Concentrations of Ca can be limited by precipitation of gypsum that can form a chemical sediment on the ocean floor. Concentrations of K, trace alkalies, and Mg can be limited by incorporation in clays in bottom sediments. Salinity of oceanic water on Europa is unknown; our results indicate that it might be lower than terrestrial seawater.

Model calculations show that freezing oceanic water on Europa changes its composition, leading to sequential salt deposition and to uneven enrichment in electrolytic solutes. Hydrated sulfates of Mg and Na can dominate among precipitated salts. However, the remaining solution becomes enriched in Cl, and chloride salts of K, Na, and Mg can precipitate from deeply fractionated brines. Unfrozen parcels of water in the icy shell, if any, may include Cl- and Mg-rich eutectic brines. If oceanic water was fractionated during its upwelling in the icy shell, salts on the surface of linea and other disrupted zones could have higher Cl/S, K/Na, and Mg/Ca ratios compared to oceanic water and will only indirectly represent the composition of the ocean. In the future the oceanic composition can be retrieved using inverse models based on measured compositions of salty ices and salt lag deposits.

Our thermodynamic calculations indicate that hydrated salts at temperatures of the surface of Europa are more stable than water ice. This provides conditions for the formation of salt lag deposits through preferential sublimation of ice. Highly hydrated salts that precipitate from freezing oceanic water are stable in ice-bearing surface materials and throughout the icy crust. In ice-free lag deposits, salts can desiccate, leading to dehydration stratification. Predicted stratification of salts is controlled by the thermodynamic stability and dehydration kinetics of salts. Magnesium sulfates that dehydrate slowly [McCord *et al.*, 2000] can coexist with partially or totally dehydrated salts. However, the possibility exists that redeposition of sputtered water molecules prevents the formation of lag deposits and salt dehydration.

Our models predict the predominance of magnesium and sodium sulfates formed from freezing oceanic water and in lag deposits. This prediction, which is independent of observations, is in agreement with current spectroscopic models for the nonicy material in the near-infrared spectral region [McCord *et al.*, 1998b, 1999], with leaching/freezing experiments of Fanale *et al.* [2001], and with thoughts based on cosmochemical arguments [Fanale *et al.*, 1977, 1999b; Kargel, 1991; Kargel *et al.*, 2000]. However, our prediction does not support the idea of Dalton and Clark [1998] that near-infrared spectral features in disrupted zones could be caused by the presence of pure large-grained ice with bubbles and other scattering centers.

For future work we suggest several investigations that would improve our knowledge about the composition and genesis of salts in the outer shells of Europa: (1) detailed analysis of Galileo NIMS spectra of nonicy material to infer variations in hydration state of the salts; (2) attempts to detect Cl, C, and nonalkali metals in the atmosphere of Europa; (3) experimental study of dehydration of chloride salts at simulated conditions of the surface of Europa; and (4) theoretical evaluations of salinity of oceanic water from Galileo magnetometer data.

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