An experimental estimate of Europa’s “ocean” composition independent of Galileo orbital remote sensing

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Abstract. We have conducted a series of experiments designed to simulate, in the laboratory, the development of any subsurface aqueous phase on Europa. In our theoretical-experimental approach we select a single natural sample (a CM meteorite) that based on cosmochemical considerations, we consider to approximately represent the bulk material that accreted to form Europa. We then subject the sample to a hot water leaching procedure designed to simulate low- to moderate-temperature aqueous alteration. The resulting leach solution was then subjected to a series of sequential fractional crystallization steps producing a series of ices and residual brines. Then all this brines and ices are multiply analyzed for Na, Ca, Mg, Sr, Ba, Fe, Mn, K, Cl, and SO\textsubscript{4}. Results were found to be remarkably consistent between brines and ices in the same stages of crystallization and also between stages. We found that any putative aqueous phase below Europa’s ice crust is probably a brine with cations: Na ~ Mg > Ca, K > Fe and anions: SO\textsubscript{4} >> Cl. Our results are in harmony with inferences drawn from one of the two main current interpretations of the orbital spectral data but cannot definitively rule out inferences drawn from the alternative interpretation. This is so because the mineralogy of the top 200 \textmu m may not reflect the chemical composition of bodies of brine below the solid surface owing to extensive alteration caused by magnetospheric bombardment.

1. Introduction

A primary result of the Galileo orbiter mission has been the discovery of morphological evidence suggesting but not proving the existence of an aqueous layer beneath an icy H\textsubscript{2}O crust [Pappalardo et al., 1999]. Magnetometer studies support the probable existence of an ocean [Khurana et al., 1998]. In addition, spectral evidence from the Solid State Imaging System (SSI) and the Near Infrared Mapping Spectrometer (NIMS) has demonstrated that parts of the optical surface (~200 \textmu m) have spectra that preclude their being composed entirely of H\textsubscript{2}O ice [Granahan et al., 1997; Carlson et al., 1996; McCord et al., 1997].

Finally, coregistration of high spectral resolution images from SSI and false color maps showing distribution of spectral features incompatible with H\textsubscript{2}O ice demonstrated a near-perfect spatial correlation between the “non-H\textsubscript{2}O ice” material and tectonic or impact induced breaches in the solid H\textsubscript{2}O [Fanale et al., 1999, 2000]. Thus it has been assumed that if the mineralogy of the non-H\textsubscript{2}O ice material could be deciphered, the chemical composition of the aqueous phase could be established. In addition to requiring this assumption, the mineralogical interpretations of the orbital spectral data have proven to be divergent.

In the context we have conducted this investigation with the intention of providing a supplementary set of cosmochemically based arguments and related experimental results. Although this approach also requires some assumptions, those assumptions are quite independent from assumptions encountered in the orbital approach. Our procedure involves selecting a natural sample, the Murchison meteorite, which we believe to be a good approximation to bulk Europa-forming material, and then submitting it to a series of processes which we believe may approximate an ocean-creating event on Europa. It could be argued that other meteorite types such as D, P, or CV meteorites would have been a better choice because CMs have been altered mineralogically. We have no acknowledged samples of meteorites derived from D or P asteroids. Both CMs and CVs were altered (CMs more so) during their history on accreted asteroidal bodies. They both, however, retain close approximation to their ‘cosmic’ chemical composition despite mineralogical alteration. Conditions in the early Jovian nebula have been the subject of modeling and speculation. However it is generally accepted that higher temperatures and number densities in the vapor phase than in the asteroid belt were involved (Fanale et al., 1977.) In any event, it should be remembered that Europa is a differentiated body (Anderson et al.) that is still renewing its surface on a geologically short time scale. In this context, it seems likely that the material at the base of any forming ocean would have been altered at least as much as CM or CV meteorites.

2. Procedure

A sample of the Murchison meteorite (a type CM carbonaceous chondrite) was crushed to sizes of a few millimeters. Pieces with evidence of rust or what appeared to be wooly material were set aside. The remainder was crushed to ~1 mm. Then the sample was leached in near boiling distilled H\textsubscript{2}O for 7 hours. The total mass of soluble material leached from the
sample was 342 mg, representing 5.4% of the original sample mass. An aliquot of the “original leach” was set aside for analysis. The rest was placed in a freezer at −10°C for 3 hours. At the end of that time the freezing process had produced nearly equal amounts of ice (“first ice”) and brine (“1st brine”). Then the process was repeated on the “first brine.” Then both the 2nd ice and an aliquot of the 2nd brine were analyzed. The remainder of the “2nd brine” was placed in the freezer until more complete freezing and taken place resulting in 80% of third ice and 20% of “third brine” were produced. All were subjected to analysis.

Thus a total of seven samples was produced. These included the original leach, three “brine” samples and three ice samples. All were analyzed for Na, Ca, Mg, Sr, Ba, Fe, Mn, K, Cl, and SO₄. The sulfate complex was analyzed, and other complexes searched for, with ion chromatography and laser Raman spectroscopy. The other species were determined with atomic absorption. Each analysis was performed three times for determination of the standard deviation. We also determined the visible and infrared reflectance spectrum of an “evaporite deposit” made from the leach. While still partly hydrated, the “evaporite” was not hydrated to the maximum owing to water loss during pump down.

3. Results

All results of chemical analyses and calculations of relevant expressions of those analyses are given in Table 1, which is organized into seven groups of five lines each. Each group of lines represents a sample (original leach, three brines, and three ices). Within each group the first line gives the results of analyses of the sample in terms of mg L⁻¹. The absolute concentrations are not meaningful. Only the relative concentrations are relevant within each line, owing to arbitrary dilutions with distilled H₂O needed for analytical convenience. However, it was noted that 342 mg or 5.4% of the original sample was extracted as solute in the original leach and the water: rock ratio was maintained at ~200:1.

Only relative values apply within each stage. However, the brines and ices were sampled so that within each stage the brine and ice concentrations can be directly compared. This was done in order to directly measure fractionating processes that may have occurred during partial crystallization 50% freezing in the first stage, 30% in the second stage, and 80% in the third stage.

The second line in each group represents the standard deviation on the results based on three analyses. No formal standard deviation was assigned to the SO₄ and Cl⁻ analyses since only one determination was conducted owing to lack of sample. (Lack of a formal standard deviation is represented by the value of zero for the standard deviation). In the case of the third stage brine also, so little sample was left that the results were considered unreliable and did not influence our interpretation. The third line gives the same results recalculated as relative molarity. The fourth line shows the same results recalculated in terms of normality. The last line in each group gives values for the normality of each species divided by the total anionic normality for SO₄²⁻ plus Cl⁻. This is done to evaluate change balance.

Interpretation of these results is aided by the simplified depictions in Figures 1 and 2. There the quotient of the normality of each cation divided by the total anionic normality is plotted for each brine stage (except the third) and for each ice stage. The crosses represents the quotient of the total of all the cationic divided by the total anionic normality (times 10). Thus, if the reported charges balanced, the crosses would all plot at a value of 10. Considering that six individual analytical errors were involved, the scatter of the quotients (5%) is satisfactory. In all cases, Mg ~ Na ~ Ca > K >> Fe and SO₄ >> Cl⁻. In addition, there is no indication of any notable fractionation between the liquid and frozen phases within any stage.

We also measured the diffuse reflectance spectrum from 0.7 to 2.5 µm of an evaporite made from an aliquot of the original leach. This is shown in Figure 3 where it is compared with the spectra of lineae on Europa.

4. Discussion

Two questions concerning Europa have been the focus of intense investigations: (1) Does Europa have a liquid H₂O ocean beneath its icy crust? and (2) If Europa has such an ocean, what is its chemical composition? One approach to the first question has been geological interpretation of surface morphological features. These studies have been thoroughly reviewed and evaluated by Pappalardo [1999] and will not be reexamined here.

Clues to the second question have been derived by examining the diffuse reflectance spectra in the UV, visible, and near IR which indicate the nature of the mineralogy of the top 200 µm or so of the surface. These spectra have been interpreted as being explainable in terms of H₂O ice of varying grain size [Dalton and Clark, 1998]. However, most recent interpretations suggest that they represent a mixture of H₂O ice with a required major component of some hydrated mineral [Granahan et al., 1997; Carlson et al., 1996; McCord et al., 1997]. This second component is characterized by prominent absorption bands at ~1.4 and 2.0 µm. These bands are asymmetric and clearly different from the broader more symmetric bands of H₂O ice. Unfortunately, on Europa, they are always found as an overlay on varying amounts of the H₂O ice spectrum with its generally similar bands. Moreover, the water molecules that hydrate a variety of possible compounds are characterized by bands that resemble each other despite more obvious differences from those of H₂O ice. These compounds with similar water of hydration bands have, however, very different genetic implications and very different implications for the chemistry of any subsurface aqueous phase [Kargel et al., 2000] they also have different possible exobiological implications.

The non-H₂O ice component seems to be quite spectrally similar in the infrared everywhere and it is always associated with coloration in the visible. Therefore we can conveniently refer to it as the “dark” component. There is a near-perfect correlation among (1) the asymmetric bands at 1.4 and 2.0 µm, (2) coloration in the visible, and (3) sites where morphological evidence indicates disruption of the topmost crust [Fanale et al., 1999, 2000]. In fact, coregistration of the distribution of near-infrared spectra with asymmetric bands with images can actually bring out areas of disruption that are not at first obvious on this high albedo, low-topography object [Fanale et al., 1999, 2000]. This, however, is only a secondary motivation for spectral mapping. The primary motivation is derived from the implicit assumption that, since this dark material always seems to be brought up from below, deciphering its mineralogical phase composition will reveal the chemical composition of any putative aqueous phase below, with possible exobiological implications.
So far, results of such investigations have pointed in two different directions, indicating that the dark material is either (1) $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ mixed with various polymers of $\text{S}$ [Carlson et al., 1999], or (2) a mixture of sulfate salts, of Mg and Na [Fanale et al., 1998; McCord et al., 1998; Fanale et al., 1999, 2000]. These two interpretations are obviously quite different. If one follows the motivation to use the surface as a key to the interior, they also have obviously different implications for any aqueous phase and its possible hospitality for origination or sustenance of life. The reason for such dichotomous results is that they are almost entirely based on interpretation of two broad bands, and these bands are also inconveniently similar in a variety of hydrated compounds in $\text{H}_2\text{O}$ ice. In terms of spectral “matching” alone, however, and, in the absence of other information, both compositional interpretations are justified. The difficulties of extending either set of conclusions concerning the composition of the optical surface ($\sim 200 \mu\text{m}$ thick) to any subsurface aqueous phase are great.

We will now discuss the assumptions linking the surface with the interior and compare them with a list of assumptions inherent in our current approach. Our contention will be that the value of our approach lies not in the fact that less assumptions are involved in our approach but rather that the two sets of assumptions have little in common.

The two sets of assumptions are illustrated diagrammatically in Figure 3. Starting “from the top,” there are several major

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Table 1. Composition of Brines and Ices

<table>
<thead>
<tr>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Ba</th>
<th>Fe</th>
<th>Mn</th>
<th>$K_+ $</th>
<th>Cl</th>
<th>$\text{SO}_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.112E+04</td>
<td>0.802E+03</td>
<td>0.758E+03</td>
<td>0.850E+00</td>
<td>0.000E+00</td>
<td>0.350E+00</td>
<td>0.280E+00</td>
<td>0.790E+02</td>
<td>0.179E+03</td>
<td>0.636E+04</td>
</tr>
<tr>
<td>0.260E+04</td>
<td>0.600E+01</td>
<td>0.400E+01</td>
<td>0.300E-02</td>
<td>0.700E-02</td>
<td>0.227E+00</td>
<td>0.200E-01</td>
<td>0.900E+00</td>
<td>0.000E+00</td>
<td>0.000E+00</td>
</tr>
<tr>
<td>0.487E-01</td>
<td>0.200E-01</td>
<td>0.312E-01</td>
<td>0.970E-05</td>
<td>0.000E+00</td>
<td>0.627E-05</td>
<td>0.510E-05</td>
<td>0.025E-02</td>
<td>0.050E-02</td>
<td>0.626E-01</td>
</tr>
<tr>
<td>0.487E-01</td>
<td>0.400E-01</td>
<td>0.624E-01</td>
<td>0.194E-04</td>
<td>0.000E+00</td>
<td>0.125E-04</td>
<td>0.102E-04</td>
<td>0.020E-02</td>
<td>0.050E-02</td>
<td>0.132E+00</td>
</tr>
<tr>
<td>0.534E+00</td>
<td>0.291E+00</td>
<td>0.454E+00</td>
<td>0.141E-03</td>
<td>0.000E+00</td>
<td>0.914E-04</td>
<td>0.742E-04</td>
<td>0.014E-01</td>
<td>0.367E-01</td>
<td>0.963E+00</td>
</tr>
</tbody>
</table>

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Footnote: Read 0.245E+04 as $0.245 \times 10^4$. The results of the analyses discussed in the test are presented. There are seven groups of lines. They correspond to the seven samples: the original leach and three ice-brine pairs resulting from three fractional crystallization steps performed on the original leach. Within each group, the first line gives the mass in mg L$^{-1}$ of each chemical species. The absolute values are irrelevant as they result from dilution for convenience of aliquoting and analysis; however, the relative concentrations are relevant. The water rock ratio during leaching was very approximately, 200:1. The second line in each group gives the standard deviation of three repeat analyses of each sample. The third line gives the same relative values recalculated in terms of relative molarity. The fourth line gives the same results recalculated as relative normality. The fifth line gives the same relative values normalized so that the total anionic charge ($\text{Cl}^+ + \text{SO}_4^-$) equals unity. The essential aspects of these analyses are presented in simple form in Figures 1 and 2.
alteration processes operating on the optical surfaces which are strictly exogenic and are not caused by endogenic influences. They derive completely from impact of magnetosphere particles on (and into) the optical surface. These include (1) the effect of permanent implantation of magnetosphere particles such as $S_1$ and $S_{11}$ as well as protons into the optical surface, (2) effects of sputtering and subsequent redeposition of sputtered constituents, and (3) the effects of radiolysis; such as the polymerization of sulfur.

There is ample evidence that all these processes cause major alteration of the optical surface; there is abundant observational evidence for implantation of S [Lane et al., 1981; Hendrix et al., 1998]. There is also evidence that the fading of geologically recent lineae is caused by sputtering and redeposition of H$_2$O molecules. This is the reason why they brighten in the visible while simultaneously darkening in the infrared [Fanale et al., 2000]. Finally, polymerization of S has been attributed to radiolysis and used to explain the visible coloration of the “dark material” [Carlson et al., 1999]. In addition, any “ocean” derived material could be altered before it even makes its way to the surface. The nature of the alteration will, if aqueous initially, depend on the rate of cooling. If salts are present, precipitation will occur which will determine the assemblage of minerals, which initially forms from the ions in the solution. This will affect not only the visible mineral assemblage but even the elemental mass balance. There is a comparable assemblage of assumptions involved in the direct approach to prediction of ocean chemistry we present here: Starting from the bottom, there is a choice of starting material. Models of the preplanetary and early Jovian nebula and remote sensing of the asteroids suggest that carbonaceous meteorites greatly dominate the outer part of the main asteroid belt and beyond [Lewis, 1972; Johnson and Fanale, 1973]. The most thorough theoretical discussion of possible aqueous activity on asteroids

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**Figure 1.** The results from Table 1 are plotted for the major cations and anions for the original leach and each brine. (Diamonds, Na; asterisks, Ca; triangles, Mg; squares, K; plus signs, $E_i = E(\text{Na}) + E(\text{Ca}) + E(\text{Mg}) + E(\text{K})$). They are in terms of relative normality (equivalence) and are normalized so that the sum of the anionic normality is unity. The ordinate shows the resulting values for each cation according to the symbols given above. The crosses represent the ratio of the sum of all the cation normalities divided by the sum of all the anion normalities (unity) times 10. Data from runs where paucity of sample precluded accurate determination of the standard deviation are not plotted.

**Figure 2.** The results from Table 1 are plotted for the three ice stages and the original leach. The results for the ice stages are plotted above 1, 2, 3, and the results for the original leach are plotted above 0 for easy comparison. (Diamonds, Na; asterisks, Ca; triangles, Mg; squares, K; pluses, $E_i = E(\text{Na}) + E(\text{Ca}) + E(\text{Mg}) + E(\text{K})$).

**Figure 3.** A diagrammatic presentation of the numerous processes that may have occurred on Europa and that preclude completely secure identification of the mineralogy of the optical surface (~200 µm) with the chemistry of any putative aqueous phase below.
and satellites was given by Kargel [1991] and that study supports the basis for this investigation. Thus the carbonaceous meteorite Murchison may be a good choice. Nonetheless, it suffers from its singularity and alternatives were discussed in the introduction.

In addition, our approach suffers from all the same unknown effects of all the composition-altering processes that cause separation between our predicted ocean and the top 200 μm of the surface which plague the “top down” approach. These include (see Figure 3) freezing at an unknown rate either in a freezing mantle or in passage through a conduit to the surface or following spewing onto the surface. For example, one of the first things that could happen under some conditions is removal of Ca as gypsum, possibly directly on release to the ocean [Kargel, 1991].

In considering all these difficulties, we reiterate that the purpose of this investigation is to predict directly the composition of the ocean, not the surface, on the basis of cosmochemical theory and a single series of experiments. Then, we argue that comparison with results based on the top down approach which requires a different set of assumptions will be a valuable test of credibility for both approaches. Alteration of our projected composition may occur either on introduction to the base of the putative ocean or during its residence therein. We should point out that even if alteration in composition occurs immediately, the composition in the immediate vicinity of any submarine vents may have it own exobiological significance since, on earth, primitive forms of life, perhaps the possible genetic parents of both animal and plant life, tend to cluster and form biological communities in the immediate vicinity of vents. We believe that any ambient ocean would retain the composition input mass balance shown in Table 1 and Figures 1 and 2 (with the important exception of the Ca which may be essentially missing, having been deposited on the seafloors [Kargel, 1991]). Nonetheless, we found that cooling the leach and brines to −10°C and freezing first 50 then 80% or more produced no notable differences in concentration of any of the components between the brines and ices, probably because very low concentrations characterized the experiment would still be able to produce the coloration in the visible that outlines the lineae. However, the speed of freezing in the experiment may be very important and quite different than occurs on Europa.

It should also be remembered that on exposure to the magnetosphere, sputtering will preferentially remove H₂O ice. Also, the images of Europa are normally color enhanced in order to outline the features. It could be argued that the cooling and partial crystallization in the study was done too rapidly or too slowly to represent conditions on Europa. Either or both could be true, by several orders of magnitude. For example, if freezing occurs at the base of a crust that thickens over geologic periods of time, then our simulation was orders of magnitude too fast. It should be noted, parenthetically, that Europa is not a Kelvinistic object or one which cools and freezes on the timescale of U, Th, and K decay. Instead, it is an object in which tidal heating is asymmetrically imposed on a nonsynchronously rotating crust [Geissler et al., 1998]. Thus, at any spot on Europa at any time the ice crust may be either thickening or thinning, in either case orders of magnitude more slowly than in our simulation. On the other hand, if the brine were simply spewed out upon the surface at 100°C, then our simulation of freezing could be orders of magnitude too slow. This could affect partition of elements between ice and water, especially if crystallization was much slower on Europa.

The objective of this investigation is an assessment of the probable composition of any subsurface aqueous phase on Europa. This assessment is designed to be as independent as possible from those which attempt to deduce that composition from matching spectrally the diffuse reflectance spectrum of the top 200 μm of Europa’s surface. We have pointed out that the latter approach is vulnerable to many surface alteration effects caused by exposure to magnetospheric particle fluxes. Nevertheless, some attempt to compare the spectral reflectance of our “evaporate” made from a small aliquot of our first leach to the dark material of Europa is intuitively mandated. Figure 4 shows the 0.7 to 2.5 μm spectrum of our leach evaporite in linear combination with an equal amount of H₂O ice. It is compared with spectra of lineae, within dark terrain and those outside dark terrain [Carlson et al., 1996]. Note that differences between our evaporite spectrum and the lineae are not notably greater than differences among the lineae themselves. Note also that the sharp, asymmetrical bands at 1.4 and 2.0 μm are evident in all spectra and that the coloration in the visible matches as well (without benefit of assumed radiolysis effects). Finally, we note that this spectrum was derived by a single experiment performed on a natural sample believed theoretically to be a reasonable simulation of Europa-forming material and treated in a way designed to represent likely alteration processes on Europa as opposed to being a spectrum of a single chemical reagent or computer-matched combinations of several reagent spectra.

5. Conclusions

1. Any subsurface aqueous phase on Europa probably consists of a brine in which, among the cations, Mg >> Na >> Ca, K, Fe, and among the anions, SO₄ >> CI

2. The non-H₂O ice portion of the optical surface is probably also dominated by a mixture of sulfates of Mg and Na. This conclusion is in agreement with one of two current divergent mineralogical interpretations of Europa’s infrared spectra from 0.7 to 5.2 μm as measured from the Galileo orbiter [McCord et al., 1998]. It does not totally refute the other in-
interpretation [Carlson et al., 1999] since almost all of our evidence and interpretation applies directly to the aqueous phase. Many surfaces processed that we describe, most resulting from magnetospheric bombardment, can cause discrepancies between the composition of originally extruded material and the current optical surface.

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References


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