Europa's Crust and Ocean: Origin, Composition, and the Prospects for Life

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We have considered a wide array of scenarios for Europa's chemical evolution in an attempt to explain the presence of ice and hydrated materials on its surface and to understand the physical and chemical nature of any ocean that may lie below. We postulate that, following formation of the jovian system, the europan evolutionary sequence has as its major links: (a) initial carbonaceous chondrite rock, (b) global primordial aqueous differentiation and formation of an impure primordial hydrous crust, (c) brine evolution and intracrustal differentiation, (d) degassing of Europa's mantle and gas venting, (e) hydrothermal processes, and (f) chemical surface alteration. Our models were developed in the context of constraints provided by *Galileo* imaging, near infrared reflectance spectroscopy, and gravity and magnetometer data. Low-temperature aqueous differentiation from a carbonaceous CI or CM chondrite precursor, without further chemical processing, would result in a crust/ocean enriched in magnesium sulfate and sodium sulfate, consistent with *Galileo* spectroscopy. Within the bounds of this simple model, a wide range of possible layered structures may result; the final state depends on the details of intracrustal differentiation. Devolatilization of the rocky mantle and hydrothermal brine reactions could have produced very different ocean/crust compositions, e.g., an ocean/crust of sodium carbonate or sulfuric acid, or a crust containing abundant clathrate hydrates. Realistic chemical–physical

evolution scenarios differ greatly in detailed predictions, but they generally call for a highly impure and chemically layered crust. Some of these models could lead also to lateral chemical heterogeneities by diapiric upwellings and/or cryovolcanism. We describe some plausible geological consequences of the physical–chemical structures predicted from these scenarios. These predicted consequences and observed aspects of Europa's geology may serve as a basis for further analysis and discrimination among several alternative scenarios. Most chemical pathways could support viable ecosystems based on analogy with the metabolic and physiological versatility of terrestrial microorganisms.

1. INTRODUCTION

Galileo radio-tracking/gravity data require that Europa has a differentiated internal structure, including a dense core of metal or metal sulfides, a rocky mantle, and a low-density icy crust or ice-crusted ocean 80–170 km thick (Anderson *et al.* 1998). Analysis of *Galileo* SSI images and other data offer compelling evidence of interior ductile deformation in Europa, lateral lithospheric mobility measured in several tens of kilometers, and local partial melting in geologically recent times (Belton *et al.* 1996; Carr *et al.* 1998; Greeley *et al.* 1998a,b; Greenberg *et al.* 1998, 1999; Spaun *et al.* 1998; Sullivan *et al.* 1998; Fagents *et al.* 2000; Fanale *et al.* 1999; Head *et al.* 1999a; Head and Pappalardo 1999; Pappalardo *et al.* 1999, Prockter *et al.* 2000). These results confirm suspicions raised earlier by scrutiny of *Voyager* images (Smith *et al.* 1979, Helfenstein and Parmentier 1980, Schenk and Seyfert 1980; Lucchitta and Soderblom 1982, Schenk and McKinnon 1989, Pappalardo and Sullivan 1996) and also support thermal modeling showing that such activity is possible (Lewis 1971, 1972; Consolmagno 1975; Consolmagno and Lewis 1978; Cassen *et al.* 1979, 1980; Squyres *et al.* 1983; Ross and Schubert 1987; Ojakangas and Stevenson 1989; Grasset *et al.* 1996; Yoder and Sjogren 1996). Processes inferred from geology include (1) local effusive and explosive eruptions of icy liquids or slushes (e.g., Lucchitta and Soderblom 1982, Greeley *et al.* 1998a, Head *et al.* 1998, Greenberg *et al.* 1999); (2) more widespread upwelling and shallow intrusion of icy solids or liquids and consequent doming of the surface (e.g., Pappalardo *et al.* 1998); (3) ubiquitous fracturing of a thin icy lithosphere due to tidal disruption (e.g., Helfenstein and Parmentier 1980, 1985, Lucchitta and Soderblom 1982, Geissler *et al.* 1998a, Greenberg *et al.* 1998, Hoppa and Tufts 1999); (4) translation and extension of lithospheric blocks and upwelling of material that fills in the voids thus created (e.g., Sullivan *et al.* 1998, Tufts 1996, Tufts *et al.* 2000, Prockter *et al.* 1999b); and (5) complete local lithospheric disruption and formation of chaotic terrain (e.g., Spaun *et al.* 1998, Williams and Greeley 1998, Greenberg *et al.* 1999). Most visually compelling, chaos regions appear to consist of either (a) masses of icebergs, now frozen in place, that once floated and drifted in a frosty sea jammed with pack ice (Greeley *et al.* 1998a,b; Carr *et al.* 1998; Spaun *et al.* 1998; Greenberg *et al.* 1999) or (b) lithospheric material utterly disrupted by convective solid-state ice diapirism (Pappalardo *et al.* 1998, Spaun *et al.* 1998).

Europa's surface is geologically young—its mean crater retention age is around 10–100 Myr—and Europa probably remains active (Shoemaker 1996, Chapman *et al.* 1998, Zahnle *et al.* 1998, Pappalardo *et al.* 1999). It is even possible that evidence of rapid ongoing resurfacing and high regional heat flow during the era of spacecraft exploration is in hand, although each type of evidence is speculative or ambiguous (Helfenstein and Cook 1984, Domingue and Lane 1998, Geissler *et al.* 1998b, Spencer *et al.* 1999). In any case, Europa clearly possesses a geologically young surface and complex history suggestive of oceanic influences.

Geologic evolution, including a sequential stratigraphic development of the lithosphere, has been documented; this sequence might be related to progressive freezing of an ocean (Head *et al.* 1999b, Prockter *et al.* 1999a), although alternate interpretations exist (Greenberg *et al.* 1999). Recently described evidence for an ancient mega-chaos region (Greenberg *et al.* 2000a), if correct, is consistent with the proposed stratigraphic sequence if an allowance is made for repetition of the cycle and preservation of remnants from a previous cycle (a very exciting prospect). A sequential evolution of lineaments has also been identified (Geissler *et al.* 1998b).

Regardless of the controversy for each geologic interpretation of Europa, it is agreed that Europa has an icy lithosphere that is mechanically isolated from a rocky mantle (Helfenstein and Parmentier 1980; Schenk and Seyfert 1980; Lucchitta and Soderblom 1982; Schenk and McKinnon 1989; Carr *et al.* 1998; Geissler *et al.* 1998a; Greeley *et al.* 1998a,b; Pappalardo *et al.* 1998, 1999; McKinnon 1999). The solid icy shell on Europa should have a plastic, convecting lower part (asthenosphere) and a thermally conductive, brittle upper part (lithosphere) if the solid crust is thicker than 10–30 km (Squyres *et al.* 1983, Ojakangas and Stevenson 1989, Golombek and Banerdt 1990, Ghail 1998, McKinnon 1999). If thinner than 10–30 km, the solid icy shell would be entirely thermally conductive, except for areas that receive anomalous local heating from below that might trigger solid-state diapirism. Possibilities allowed by *Galileo* data include (i) a thin, brittle, conductive icy shell overlying a deep global ocean, or (ii) almost complete solidity of the H_2O-rich crustal layer with a warm, convecting icy asthenosphere beneath a thin, brittle icy lithosphere. Something intermediate is also possible, such as (iii) a thin global or patchy liquid ocean beneath a thick, convecting ice crust and a brittle lithosphere, or (iv) a deep liquid ocean between an outer thick convecting ice crust and surface brittle lithosphere, and an inner layered sequence below the ocean floor. Shoemaker (1996) estimated Europa's crater retention age as 30 Myr for craters >10 km, and found that the cratering record is consistent with a 10-km-thick ice crust overlying a liquid ocean.

As modeled by McKinnon (1999) and others, it is actually very difficult to freeze a Europan ocean entirely due simply to the fact that a stagnant, nonconvecting icy shell is more tidally dissipative than a convecting one. Even without consideration of any tidal heating, Grasset *et al.* (1996) modeled the continuous existence of a liquid ocean since Europa's origin. Very high levels of tidal heating and thinner ice shells are possible in some models, according to Yoder and Sjogren (1996), but they also highlighted the difficulty of ruling out an icy shell so soft that it remains efficiently convective and solid to the base of the crust. However, a salty Europan ocean (Kargel 1991, Fanale *et al.* 1998) would reduce the solidus temperature to less than any likely convective adiabatic temperature (Kargel 1996). Hence, a present-day Europan ocean appears to be a robust theoretical result supported also by geologic observations.

Electrical induction in a hypothetical Europan ocean was first predicted by Colburn and Reynolds (1985). Electrical currents flowing in a salty ocean should induce a magnetic field that would possess certain measureable diagnostic attributes of magnitude, orientation, structure, and temporal oscillation (Kargel and Consolmagno 1996). The discovery by the *Galileo* magnetometer team of what appears to be an induced magnetic field at Europa with the predicted properties suggests that a large fraction of the H_2O layer is a briny, liquid ocean around 100 km deep (Kivelson *et al.* 1997, Khurana *et al.* 1998). If the ocean lacked appreciable solutes, or if it was thinner than a few tens of kilometers or frozen completely, it would not conduct enough current to explain the observed magnetic signature. Uncertainty in the total thickness of the H_2O-rich layer—gravity data permit 80 to 170 km (Anderson *et al.* 1998)—still allows for either a thick (up to ∼70 km) or a thin (few kilometers) frozen crust. Closer scrutiny of the magnetic field data and possible generative mechanisms has supported the brine ocean induction mechanism without revealing strongly compelling alternatives (Kivelson *et al.* 1999). However, a comparable induced field has been discovered at Callisto (Stevenson 1998, Kivelson *et al.* 1999), where there is scant geologic evidence of an ocean. Callisto could have an ocean, especially if ammonia is present (Prentice 1996), but the icy lithosphere would have to be very stable and competent. Possible alternative explanations for Callisto's magnetic signature—that the electrically conducting layer might be some other substance, for instance, graphite—have not been developed in detail. In sum, Europa's magnetic signature supports the existence of a brine ocean, but this support is tempered by Callisto's similar magnetic signature.

Hydroxylated phyllosilicate minerals that are so abundant on Callisto and Ganymede (McCord *et al.* 1998b) exhibit absorption features not seen on Europa (McCord *et al.* 1998a). However, nonice hydrated substances are regionally abundant on Europa. *Galileo* NIMS reflectance spectra of many regions of Europa exhibit highly distorted water absorptions indicating the presence of bound water—and little or no ice—wherever the deep interior has been exposed by deep impact or rifting of the lithosphere or by extrusion of liquids or warm icy masses

(McCord *et al.* 1998a, 1999; Carlson *et al.* 1999; Fanale *et al.* 1999). Consistent with earlier results from telescopic data, NIMS data for other europan terrains reveal nearly pure ice. Two classes of related materials have been suggested to explain observations of Europa's prevalent nonice material: (1) hydrated magnesium and sodium sulfates and/or sodium carbonates (the "salt hypothesis," McCord *et al.* 1998a, 1999a; Prieto *et al.* 1999), or (2) hydrated sulfuric acid with traces of radiolytic sulfur impurities (the "acid hypothesis," Carlson *et al.* 1999). Dalton and Clark (1999) have emphasized ambiguities in attributing the observed distorted water bands to specific hydrates, and they have pointed out slight spectral mismatches between the Europa nonice material and proposed substances. These mismatches likely are due to differences between the conditions or grain size pertaining to lab data and those of Europa. Each of the proposed hydrated sulfates has a strong theoretical backing from cosmochemistry, is highly water soluble, and has an electrolytic nature; therefore, these solutes can explain the electrically conductive nature of a near-surface liquid layer required by magnetic field data. Sodium carbonates are also reasonable for Europa but would require a complex chemical evolution. Below we explore (a) possible physical–chemical scenarios for the origin of these materials, (b) brine evolution from the viewpoint of chemical phase equilibria and chemical compatibility, and (c) relationships of these materials with the physical geology of Europa's icy lithosphere and ocean and possible biochemistry.

We adopt a modified version of the chemical and mechanical/structural terminology of Pappalardo and Head (1999) to describe the layering of Europa. As may be deduced above, any central segregation of metallic or sulfide phases is termed a *core*. A rocky layer surrounding the core is termed the *mantle*; if the mantle is further differentiated (e.g., due to silicate magmatism), the ultramafic residue of partial melting is still termed the *mantle* and a differentiated outer rocky layer is termed the *silicate subcrust*, since it will underlie a volatile crust. The outer layer enriched in H_2O and other volatiles is termed the *crust*. Following formation of a primordial hydrous crust but before separation of a core, the rock-rich material beneath the crust is simply called the *rocky interior*. The volatile crust may further differentiate into (i) a solid upper crust, which we refer to as the *icy shell*; (ii) a liquid interior layer, which we refer to either as the *ocean* or the *hydrosphere* (the latter term may include the ocean plus any liquid inclusions or liquid-filled pods or conduits intruding into the icy shell or leading onto the surface); and (iii) a *volatile subcrust*, which encompasses any layered sequence of salts, sulfur, or other volatile-bearing solids deposited on the seafloor but resting above the silicate mantle or silicate subcrust. The icy shell could further differentiate into various compositional layers. If a surficial layer of ice-free salty material exists, it is termed the *evaporite layer*. The icy shell is divided on a mechanical–structural basis into a cold, brittle top layer termed the *lithosphere* and a warm, solid, convecting interior layer termed the *asthenosphere*. It is possible that no ocean exists (Pappalardo *et al.* 1999) or that convection/diapirism is unimportant in the icy shell

(Greenberg *et al.* 1999, 2000). It seems to us that the evidence strongly supports the ocean/asthenosphere/lithosphere model.

2. FRAMEWORK FOR EUROPA'S CHEMICAL EVOLUTION

What relations exist between the landforms and geologic processes of Europa, the structure of its crust, the composition of any ocean that may exist, and the makeup of its surface? How is Europa's present state related to initial conditions? We seek a reasonable chemical evolutionary framework, compatible with the latest *Galileo* data, upon which possible answers to these questions may be based.

The Mg–Na–sulfate and/or Na–carbonate minerals believed present on Europa (Kargel 1991; McCord *et al.* 1998a, 1999a; Fanale *et al.* 1998) also are widespread in terrestrial continental evaporites (Eugster and Jones 1979, Eugster 1980), suggesting that evaporation and concentration of aqueous precipitates occurred on Europa. The alternative, hydrated sulfuric acid (Carlson *et al.* 1999), raises the possibility that different aqueous equilibria were at work, but still evaporative processes and sulfate chemistry may have been partly responsible. Europa's surface, like the salts of dry lakes, represents an extreme type of water-based chemical fractionation. The surface materials are just the last link in a complex chain of processes. We postulate that, following formation of the jovian system and accretion of the major satellites, the europan chain has as its major links: (a) initial conditions represented by carbonaceous chondrite rock, (b) global primordial aqueous differentiation and formation of an impure primordial hydrous crust, (c) brine evolution and intracrustal differentiation, (d) degassing of Europa's mantle and gas venting into the icy ocean/crust, (e) hydrothermal reactions of brine with the rocky mantle and rocky subcrust, and (f) alteration in the surface environment. These are not strictly sequential stages—some are concurrent and others ongoing. These events are further described and modeled in Section 3.

This conceptual framework is illustrated in Fig. 1, which shows identical chondritic starting material but different end states that depend on details of the chemical pathway. Note that each scenario starts with identical low-temperature incongruent melting of hydrated salts in a CI or CM chondrite (the model of Kargel 1991) and ends up with precipitation of sulfurous compounds on the seafloor; the scenarios differ in compositions of the ocean, crust, and seafloor deposits. The process implications of these and several other possible crust compositions are summarized in a different form in Table I. The compositions and some properties of selected liquids that could arise by these processes are summarized in Table II. In Section 3 we consider some of these processes in more detail. For comparison of our new results and those of Kargel (1991), the reader is referred to the recent work of Spaun and Head (2000), who have modeled the fractional crystallization of a hypothetical europan ocean and formation of a layered crustal sequence in the system $MgSO_4$–H_2O.

2.1. Initial Conditions

We assume that Europa started as hydrated rock formed on the warm side of the Jupiter system's "snow line." Europa is assumed initially to have had solar elemental ratios of involatile and slightly volatile rock-forming elements and an absence of volatile ices. Following Kargel (1991), we take carbonaceous CI chondrites (the most volatile rich, most aqueously altered, and most compositionally primitive class of carbonaceous chondrite) as a reasonable analogue to Europa's initial material. This is merely a convenient assumption that provides (a) roughly the correct amount of water needed for a volatile crust, (b) salts thought to exist on Europa's surface, (c) sulfides for a core, and (d) approximately the correct bulk density. Actually, CIs provide a bit too much water, as we shall see; CM chondrites (another volatile-rich class of chondrite) may be slightly better in this regard but are a bit too dry. Whereas CI and CM chondrites closely bracket the ideal composition, other types of carbonaceous chondrites might also satisfy these conditions if some additional water was provided in the form of ice and then aqueous alteration was allowed (e.g., CV and CO chondrites, both of which are much less volatile rich and less aqueously altered than CIs and CMs). Ordinary and enstatite chondrites (which contain abundant free metal and very little water and carbonaceous matter) lack sufficient water, are too reduced, and would yield too large a core, although heterogeneous accretion of some such material with late accretion of some amount of CI chondrites or comets might work.

The use of hydrated rock similar to CI or CM carbonaceous chondrites is a long-standing assumption by modelers of the Galilean satellites (Ransford *et al.* 1981, Squyres *et al.* 1983, Crawford and Stevenson 1988, Golombek and Banerdt 1990, Kargel 1991, Prentice 1996, Mueller and McKinnon 1988, Hogenboom *et al.* 1995, Fanale *et al.* 1998, McKinnon 1999). Some who have modeled these objects with initial ice plus anhydrous rock (e.g., ordinary chondrites) did so to simplify calculations but acknowledged that carbonaceous chondrites may be a better analogue (Lupo and Lewis 1979). This assumption is rooted in the concept from meteoritics and nebula thermochemistry that rocky nebula condensates just on the warm side of the "snow line" lacked volatile ices but possessed a hydrated mineralogy and solar proportions of refractory and moderately volatile rock-forming elements. There were important differences in nebula processes in the jovian nebula and the solar nebula (Cameron and Pollack 1976, Pollack 1985, Stevenson *et al.* 1986, Prinn and Fegley 1989). Gas pressures, temperatures, condensation, and accretion time scales were different. Gas-phase equilibrium (or lack of) depends sensitively on nebula P–T and nebula lifetime, so assemblages of ices more volatile than water ice depend on where condensation took place. As shown by Lewis (1971, 1972), condensation temperatures depend sensitively on nebula pressures, but condensation *sequences* for solar composition gases are fairly insensitive to nebula pressure. There is relatively little difference in the sequence of condensation
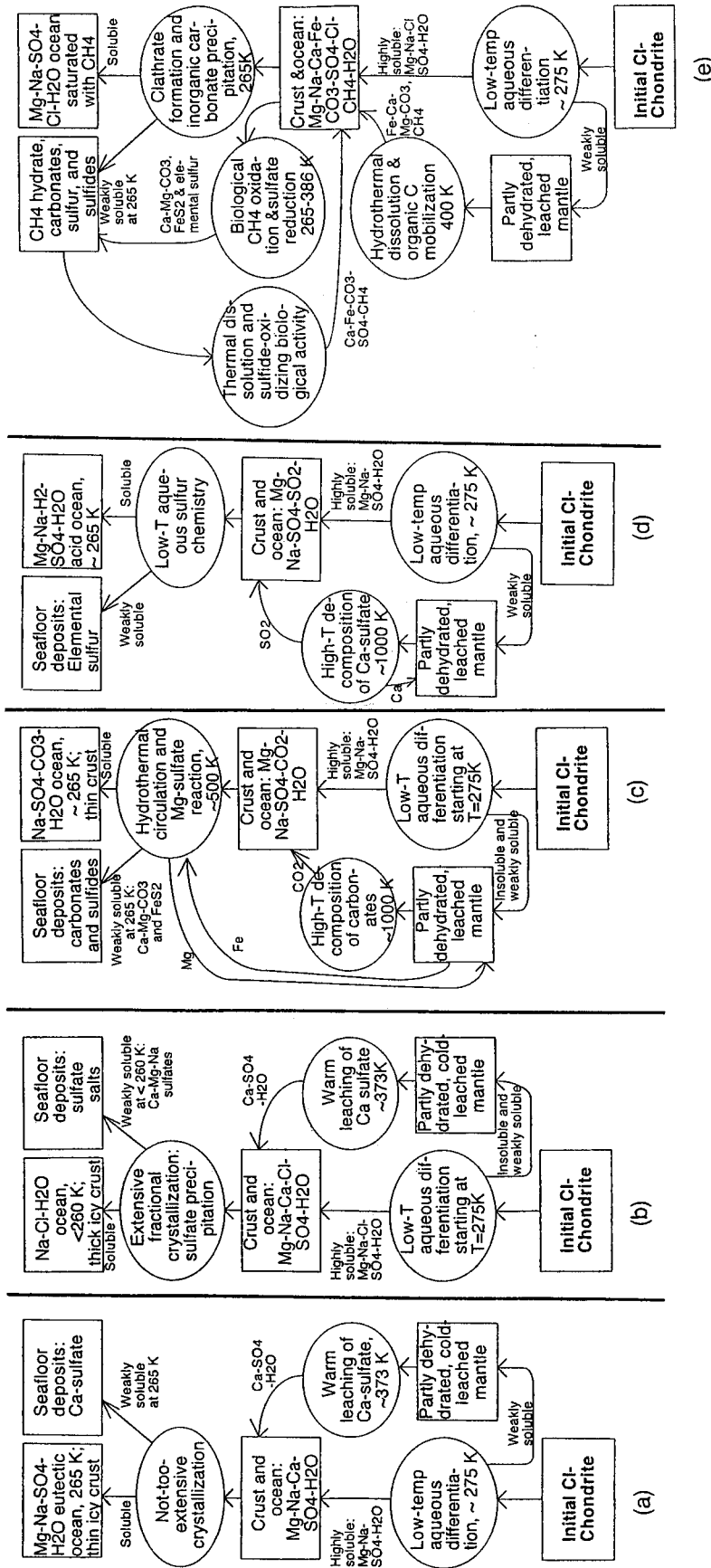
FIG. 1. Schematic chemical evolution of the crust/ocean of a chondritic Europa. (a) Formation of a crust/ocean of a chondritic Europa. (b) Formation of chloride ocean by extensive crystallization of the magnesium-sulfate-rich brine represented in (a). (c) Modified pathway that includes addition of CO_2, which might result in formation of a crust/ocean enriched in sodium carbonate and sulfate. (d) Modified pathway that includes addition of SO_2 or SO_3 and results in formation of an ocean/crust enriched in sulfuric acid and certain salts, such as magnesium sulfate. (e) Modified pathway that includes addition of CH_4, which results in a clathrate-rich, salty crust.

TABLE I
Alternative Surface Compositions and Implications for Europa's Hydrospheric Evolution

Major components of surface	Thermal state of ocean (if it exists) and icy crust	Allowed by NIMS data?	Implications for evolution of hydrosphere
(a) H_2O, $MgSO_4$, Na_2SO_4	Warm ocean Thin icy crust	Yes	Simple evolution by incongruent melting of chondrite salts—Fig. 3, models A5 and B; Fig. 1a. Minimal hydrothermal interaction with basalt subcrust.
(b) H_2O, Na_2SO_4	Warm ocean Thin icy crust	Yes	Incongruent melting of chondrite salts as in case (a). Sequestration of Mg in carbonates or Mg-phyllosilicates and partial reduction of sulfate by hydrothermal circulation in basaltic subcrust.
(c) H_2O, Na_2SO_4, Na_2CO_3	Warm ocean Thin icy crust	Yes	Melting of chondrite salts and sequestration of Mg as in case (b). Addition of CO_2 by pyrolysis of mantle carbonates and organics—Fig. 1c.
(d) H_2O, Na_2CO_3	Warm ocean Thin icy crust	Yes	Similar to case (c), but sequestration of Na by albitization of silicate subcrust due to high-T hydrothermal reaction or fractional crystallization of Na_2SO_4.
(e) H_2O, NaCl	Cold ocean Thick icy crust	No?	Sulfate reduction and sequestration of Mg as in case (b), and fractional crystallization of Na_2SO_4 and Na_2CO_3.
(f) H_2O, NaCl, $MgCl_2$	Cold ocean Thick icy crust	No?	Extensive fractional crystallization. Minimal hydrothermal interaction with basalt subcrust—Fig. 4.
(g) H_2O, $MgSO_4$, Na_2SO_4, H_2SO_4	Warm ocean Thin icy crust	Yes	Similar to case (a) but large additions of S gases due to breakdown of sulfates in mantle or lower crust. Minimal hydrothermal reaction with basalt.
(h) H_2O, H_2SO_4, NaCl, $MgCl_2$	Cold ocean Thick icy crust	Yes?	Similar to case (g) but extensive fractional crystallization of Mg–Na-sulfates.
(i) H_2O, Na_2SO_4, H_2SO_4	Warm ocean Thin icy crust	Yes	Similar to case (g) but sequestration of Mg in carbonates or Mg-phyllosilicates due to low-T hydrothermal circulation (little sulfate reduction).
(j) H_2O, H_2SO_4, NaCl	Cold ocean Thick icy crust	Yes?	Similar to case (h), but extensive fractional crystallization of Mg salts, or sequestration of Mg by hydrothermal processes or carbonate precipitation.
(k) H_2O	No constraint on ocean	Allowed regionally, but not globally	Efficient fractional crystallization and floatation of ice, or diapiric instabilities of ice in icy shell with complete ice resurfacing.
(l) H_2O, CH_4 or organic tholins, + or − salts	Depends on salts	Depends on salts	Deep mantle pyrolysis of carbonaceous components of mantle or reduction of carbonates.

and expected mineralogy down to the point of ice condensation. Therefore, we conclude that although carbonaceous chondrite meteorites are solar nebula materials, basically identical rock should have been formed in the jovian nebula, and that following aqueous alteration it should contain abundant Mg–Na–Ca–sulfate-rich soluble material.

Closed-system, *in situ* aqueous alteration at low to moderate temperatures of high-temperature nebula condensates lacking much free metal produces the mineral assemblages of carbonaceous chondrite meteorites (DuFresne and Anders 1962, Bostrom and Fredrikkson 1964, Richardson 1978, Fredriksson and Kerridge 1988, Anders and Grevesse 1989, Zolensky *et al.* 1989, Burgess *et al.* 1991, Brearley and Jones 1998). Zolotov

and Shock (2000a) have confirmed this result; they modeled the aqueous alteration assemblages resulting from an initial carbonaceous CV chondrite (nearly anhydrous) and obtained salt assemblages somewhat similar to those occurring in CI and CM chondrites. Experimental hydrothermal alterations of chondritic material have reproduced part of the CI and CM chondrite assemblages, including formation of carbonates and phyllosilicates (Scott *et al.* 2000). However, to make the reactions occur on laboratory time scales, the experimentalists found that significant reaction occurred at temperatures much higher than are thought to have been involved in the alteration of CI and CM chondrites; sulfate formation was not reported but probably pertains to the particular oxidation state of the experiments. The

TABLE II
Densities, Compositions, and Solid–Liquid Equilibria of Some Key Liquids Likely on Europa

Substance	Freezing/melting pt. (at 1 atm solidus) (K)	Density at 1 atm: solid (s) liquid (l) (kg m^{-3})	Composition (wt.%)	Derived by melting or incongruent melting of this assemblage	Mineralogy when frozen (wt.%)	The frozen solid yields what liquid upon incongruent remelting?
Water	273.15	917 (s) 1000 (l)	100.0 H$_2$O	ice	ice	100.0 H$_2$O
Eutectic E in system H$_2$O–MS–NS	268.2	1144 (s) 1208 (l)	81.0 H$_2$O 16.0 MS 2.8 NS	ice MS12 mir	48.9 ice 44.7 MS12 6.4 mir	Liquid E
Peritectic P1 in system H$_2$O–MS–NS	275	1235 (s) 1278 (l)	75.5 H$_2$O 20.5 MS 4.0 NS	MS12 eps mir	33.6 ice 57.3 MS12 9.1 mir	Liquid E
Peritectic P2 in system H$_2$O–MS–NS	319	1444 (s) 1361 (l)	65.4 H$_2$O 29.4 MS 5.2 NS	eps hex blo	6.0 ice 82.2 MS12 11.8 mir	Liquid E
Peritectic P3 in system H$_2$O–MS–NS	334	1517 (s) ~1465 (l)	61.9 H$_2$O 33.1 MS 5.0 NS	hex blo MSNS2.5	78.0 MS12 10.6 eps 11.3 mir	Liquid P1
Peritectic P4 in system H$_2$O–MS–NS	337	1530.1 (s) ~1485 (l)	60.7 H$_2$O 34.0 MS 5.3 NS	hex kie MSNS2.5	68.6 MS12 19.4 eps 12.0 mir	Liquid P1
Peritectic P5 in system H$_2$O–MS–NS	344	1869.2 (s) ~1380 (l)	64.6 H$_2$O 15.5 MS 19.9 NS	blo MS·3NS MSNS2.5	17.6 MS12 35.3 MS7 47.1 blo	Liquid P1
Eutectic in system H$_2$O–HS	211	1259 (l) ~1245 (s)	65.1 H$_2$O 34.9 HS	HS6 ice	73.4 HS6 26.6 ice	Eutectic

Note. The liquid and solid mixtures indicated by P1, P2, P3, P4, and P5 refer to the series of peritectics known for the ternary system H$_2$O–MgSO$_4$–Na$_2$SO$_4$ (*International Critical Tables* 1928, Kargel 1991); note that these are not exactly the same peritectics as designated by Kargel (1991) for the binary system MgSO$_4$–H$_2$O. "E" represents the ternary eutectic in this same system (Kargel 1991). Chemical components are designated in short-hand; i.e., water is H$_2$O, MgSO$_4$ is MS, Na$_2$SO$_4$ is NS, and H$_2$SO$_4$ is HS. Minerals are epsomite, eps; hexahydrite, hex; kieserite, kie; mirabilite, mir; thenardite, the; bloedite, blo; MgSO$_4$·12H$_2$O, MS12; MgSO$_4$·Na$_2$SO$_4$·2.5H$_2$O, MSNS2.5; and MgSO$_4$·3Na$_2$SO$_4$, MS·3NS. The densities (in kg m^{-3}) of solid phases are MS12, 1500; eps, 1677; hex, 1745; kie, 2571; blo, 2274; mir, 1490; and the, 2680. Other solid phase densities are not known and were guessed on the basis of data in Hogenboom *et al.* (1995).

water needed for the aqueous alteration of actual chondrite parent bodies could have been provided either by dehydration of hydrous silicates condensed from the solar nebula or by melting of a small amount of ice accreted with an initial anhydrous rock assemblage. Our specific model starts with the salt assemblage known from CI chondrites—closely approximated as 8.8% by mass epsomite, 4.9% by mass bloedite, 1.5% anhydrite, 2.4% dolomite, and 0.7% magnesite (Bostrom and Fredriksson 1964, Fredriksson and Kerridge 1988, Burgess *et al.* 1991, Kargel 1991). The salt assemblages of CM chondrites are somewhat similar. What is most crucially different between CIs and CMs is the amount of water—about 6 wt.% in CMs and up to 18 wt.% in CIs. Our model water content, 18%, is from the H content listed by Anders and Grevesse (1989) for the CI chondrite, Orgeuil. Although details of any model will depend on the initial salt assemblage and the amount of water that is available, the more important results of any such models are fairly independent of these details.

2.2. Primordial Aqueous Differentiation

Progressive heating to temperatures of 268–380 K would have thermally dissociated hydrated salts in a definable staged sequence known from the relevant phase equilibria. Fluids so generated would then have formed a primordial hydrous crust. CI and CM chondrite brines are well represented in the system H$_2$O–MgSO$_4$–Na$_2$SO$_4$—97% of the highly water-soluble fraction of CI chondrites is represented by this system (Kargel 1991, Fredriksson and Kerridge 1988). Calcium sulfate and Ca–Mg carbonates, although abundant in CI chondrites, are not effectively leached during this initial low-temperature stage of evolution because of the low solubility of these phases and the small water : rock ratios involved. Some other components, such as Ni– and Mn–sulfates, can be treated to a first approximation as a part of the MgSO$_4$ component due to chemical similarities. Chlorides would have been present, and although they are highly soluble, they are not nearly as abundant as sulfates in

TABLE III
C-Chondrite Leach Compositions Compared to Seawater (Mass Fractions)

	Major cations (sum = 1.00)			Major anions (sum = 1.00)		
	Mg	Na + K	Ca	SO$_4$	Cl	CO$_3$
CI chondrites, entire salt assemblage[a]	0.438	0.107	0.455	0.603	0.013	0.384
CI chondrites, entire salt assemblage[a] with carbonates subtracted	0.381	0.208	0.411	0.979	0.021	0
CI chondrites, salt assemblage[a] with carbonates and CaSO$_4$ subtracted[b]	0.653	0.351	0.005	0.968	0.032	0
CM chondrite leach obtained by boiling[c]	0.274	0.433	0.293	0.965	0.035	0
CM chondrite leach[c] with CaSO$_4$ subtracted	0.386	0.609	0.005	0.952	0.048	0
"La Mancha" playa evaporitic brine[d]	0.386	0.605	0.009	0.806	0.191	0.003
Earth's seawater[e]	0.100	0.868	0.032	0.125	0.868	0.007

[a] From Kargel (1991); small amounts of Ni and Mn included with Mg.
[b] All CaSO$_4$ subtracted except for enough to saturate the solution.
[c] Fanale *et al.* (1998).
[d] "La Mancha" brine from de la Pena *et al.* (1982).
[e] Seawater composition from Krauskopf (1979).

these aqueous solutions due to the low cosmic Cl : S ratio and low chloride : sulfate ratios of carbonaceous chondrites (Kargel 1991, Fanale *et al.* 1998). The aqueous phases generated by low-temperature dissociation of salts would have been hypersaline and the solutes dominated by magnesium and sodium sulfates corresponding to the series of peritectics in this ternary system (*International Critical Tables* 1928, Kargel 1991). A summary of the eutectic and peritectic compositions in this system is provided in Table II. The salt assemblages in carbonaceous chondrites (Table III) would have yielded the initial liquids indicated in Table II; CIs yield a liquid corresponding to the peritectic P2 that is approximately 65.4% H$_2$O, 29.4% MgSO$_4$, and 5.2% Na$_2$SO$_4$ (there would also have been just over 1% of chloride, not listed in Table II). This is the initial brine composition used in all of our models. A rough validation of the salt assemblage calculated by Kargel (1991) is provided in the CM chondrite leach experiments done by Fanale *et al.* (1998, 1999). By boiling CM2 Murchison they obtained a leachate resembling that used in the modeling here, but this leachate even more closely approximates the ternary peritectic P5 in the system H$_2$O–MgSO$_4$–Na$_2$SO$_4$ (if CaSO$_4$ is subtracted from the leach), which is not surprising considering the temperature of the experiment. However, the CM leach differs most dramatically in that it also contains abundant CaSO$_4$, which is difficult to explain in terms of equilibrium dissolution, but it might be due to use of a large water : rock in those leach experiments. The high opacity reported for the CM chondrite leachate probably was due partly to precipitation of CaSO$_4$, which would have been grossly oversaturated in that mixture.

2.3. Brine and Crust Evolution

Beginning with the first exhalations of aqueous fluids and probably still continuing, Europa's impure crust would have undergone further aqueous differentiation into multiple compositional layers. The development of density stratification during cryomagmatism depends on details of the melt generation processes and eruption mechanisms (Kargel 1991, Hogenboom *et al.* 1995, Wilson *et al.* 1997, Head *et al.* 1998, Kadel *et al.* 1998, Wilson and Head 1999, Fagents *et al.* 2000). Equilibrium crystallization—or quenching with glass formation—might occur in some rapidly cooled cryovolcanic flows and cryoclastic deposits, resulting in frozen layers that would tend to consist of eutectic or peritectic compositions. Layers of pure salts could form by rapid water boil-off of brine lavas, by slow sublimation of ice on the surface, or by fractional crystallization and settling of salt crystals. Layers of nearly pure ice could be produced by recondensation of water vapor at the poles, in shadowed areas, or on cold surfaces adjacent to active brine vents, or by flotation of ice in brine magma bodies (Hogenboom *et al.* 1995, Wilson and Head 1999). Salt–water systems on Europa should have a strong tendency to evolve with fractional crystallization due to the combination of large density differences between solid and liquid phases and the low viscosity of the liquid in salt–water systems (Hogenboom *et al.* 1995). Idealized fractional crystallization might occur in most situations involving slowly cooled, deep-seated magma bodies (brine plutons) or freezing of an ocean on Europa, resulting in massive sills, lenses, and

dikes and thick crustal layers of water ice and segregated salt masses. Interlayering of salts and ice would be gravitationally unstable in the crust. Diapiric instabilities might arise, with ice bodies ascending and salt bodies descending. At one extreme all the ice within Europa's crust eventually could segregate and form a pure-ice upper crust, leaving the salts confined to deeper layers. However, this extreme model does not seem to satisfy the NIMS data, which indicate concentrations of salts on the surface (McCord *et al.* 1998a, 1999a). Various scenarios of brine evolution and crustal differentiation are developed below. NIMS data, which seem to require an abundance of some type of sulfate (or possibly sodium carbonate), tend to rule out models whereby a high degree of crystallization produces a sulfate-depleted chloride ocean (e.g., model 'b' in Fig. 1).

2.4. High-Temperature Degassing of Europa's Mantle and Fluid Reaction in the Hydrosphere

As Europa's deep mantle heated further, hydrous silicates would have undergone progressive metamorphic dehydration between about 500 and 1100 K (Winkler 1979). Aqueous fluid phases would have been generated at each stage. These fluids would have migrated toward the surface, further leaching the silicate interior and carrying additional dissolved salts, thus adding to an already impure crust. Over a similar temperature range, other volatile-bearing phases in Europa's mantle would have decomposed, producing additional fluid constituents. These volatile-bearing phases would likely include Ca–Mg carbonates, Ca sulfate, organic compounds, and sulfides, which are fairly insoluble in water at low temperatures; hence, they primarily remained in the mantle during low-temperature aqueous differentiation. The fluids so generated would have vented into and been trapped by the ice-capped hydrosphere. This situation is different from the Earth, where gases are vented directly into the atmosphere or into the ocean, which is in communication with the atmosphere. Once in the europan ocean and icy shell, gases such as SO_2, CO_2, and CH_4 are then available to react and form other types of brines and solid phases not predicted by the basic low-temperature chondrite evolution model described above and modeled below. Some implications of degassing for ocean and crust composition are briefly explored below, including possible formation of a sulfuric acid ocean. Possibly all of these gases (and others besides) are added to Europa's crust, although in this paper we consider only some possible chemical effects due to separate addition of SO_2, CO_2, and CH_4.

With further heating to temperatures just below the silicate solidus, sulfides would have melted and separated from the mantle, resulting in core formation. As the deep interior of Europa became hotter yet, partial melting of silicates may have yielded basaltic or komatiitic liquids, which then would have formed a basaltic or ultramafic silicate subcrust either composing the seafloor or underlying a volatile subcrust. The emphasis of this work is on the petrological fate of Europa's impure crust, which we model in detail. We make a simple accounting of the separation of Europa's core and do not investigate silicate differ-

entiation at all, other than the removal of aqueous and sulfide phases. Note that our choice of a carbonaceous chondrite precursor means that little or no free metal was available, so that the core would be made of pure metallic sulfides, which are approximated here as FeS. Although crude, this approximation accounts for most of the sulfide component present in CI and CM chondrites (Tomeoka and Buseck 1985, Brearley and Jones 1998) that would exist following dehydration. According to Prior's Rules the rocky mantle and any silicate melts would be extremely enriched in FeO component (hence, significantly denser than the terrestrial planets' mantles for equivalent pressures).

2.5. Hydrothermal Processes in the Seafloor Environment

Hydrothermal circulation of brine in a silicate subcrust could cause chemical reequilibration of solutes. Earth's seawater has evolved a chloride-rich composition partly due to reaction of sulfates with crustal ferroan silicates to form nearly insoluble metal sulfides; magnesium from a dissolved magnesium sulfate component reacts with the rock to form serpentine, chlorite, and other phyllosilicates (Von Damm 1995). A comparable process could occur on Europa under the right conditions, resulting in depletion of the brine in magnesium sulfate and enrichment in sodium chloride. A thick layer of seafloor salts might circumvent or modify any such reactions between silicates and brines.

2.6. Surface Alteration

After all the processes above have had their influence, then material erupted onto the surface or otherwise exposed will be altered by the space environment. Surface alteration includes possible thermal or radiation-induced dehydration and radiolytic processing. Charged-particle implantation and UV radiolytic chemistry are likely to have major effects on salt stability and surface composition (e.g., Carlson *et al.* 1999). Surface processes would not be too effective in altering interior chemistry and structure, and they would not explain geologic associations of nonice material, unless alteration products are buried and somehow recycled deep into the crust. However, surface alteration does affect our view of the surface, which is our best window into the interior.

3. CHEMICAL PATHWAYS AND MODELS

3.1. Chondrite Evolution Models

The salt interpretation of nonice materials on Europa has a short list of suspected components (McCord *et al.* 1998a, 1999a,b). Among them are the types of salts—hydrated magnesium and sodium sulfates—predicted from simple aqueous differentiation of a CM or CI chondrite (Kargel 1991; Fanale *et al.* 1998, 1999). The short list of candidate materials has the unpredicted addition of hydrated sodium carbonate. We note that sodium carbonate and magnesium sulfate are unlikely to occur together, since they are highly reactive and do not occur together on Earth (Eugster and Hardie 1978), although both occur

on Earth in separate evaporite deposits. Sodium carbonate and sodium sulfate minerals occur together, as do magnesium sulfate and sodium sulfate (Eugster and Hardie 1978). Other processes no doubt have affected the composition of Europa, but it is worth considering the chondrite evolution models in some detail as a starting point. According to a widely held opinion among planetary scientists, Europa is probably unique among icy satellites in that ice was not initially present or at least not abundant. Europa may have started as a purely rocky object made of hydrous rock similar to carbonaceous chondrite meteorites (Fredriksson and Kerridge 1988; Kargel 1991; Fanale *et al.* 1998, 1999). The suite of models considered here implies either that Europa accreted carbonaceous chondrite material or that some other chondritic material was accreted but soon underwent aqueous chemistry that resulted in a mineral assemblage similar to that of carbonaceous chondrites—specifically CI or CM chondrites.

Some candidate Europan salts suggested both by chondrite-evolution models (Kargel 1991; Fanale *et al.* 1998, 1999) and by the interpretation of NIMS spectra (McCord *et al.* 1998a, 1999a,b) include epsomite ($MgSO_4 \cdot 7H_2O$), bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$), and mirabilite, $Na_2SO_4 \cdot 10H_2O$. In addition, the NIMS data admit possible sodium carbonates, e.g., natron ($Na_2CO_3 \cdot 10H_2O$). These are common terrestrial evaporite minerals. The unusual compositions of chondritic leachates (compared to terrestrial brines) are highlighted in Fig. 2. Certain rare terrestrial closed-basin brines, such as that of a playa of the La Mancha region of Spain (de la Pena *et al.* 1982), are fairly close approximations to a CM or CI chondrite brine. It is extremely rare to have $Cl : SO_4$ ratios on Earth as low as those expected from chondrite brines. The other main distinction is the extremely magnesium-rich composition of chondrite brines compared to more sodic terrestrial brines, but there are several rare examples here on Earth that come close to the hypothesized europan Mg : Na ratio. The "La Mancha" playa evaporite deposits from Spain are dominated by the same types of Mg–Na–sulfate minerals (de la Pena *et al.* 1982) that are preferred for Europa (McCord *et al.* 1998a, 1999a).

An important sulfate constituent of carbonaceous chondrites, calcium sulfate (anhydrite, $CaSO_4$; and gypsum, $CaSO_4 \cdot 2H_2O$), is not highly water soluble in most naturally occurring waters and so is not expected to be a major constituent of a europan ocean or an icy-salty crust. Calcium sulfate might be leached by hydrothermally circulated water affecting chondritic rock if there is large water : rock ratio (analogous to the CM chondrite boiling experiments done by Fanale *et al.* 1998), but gypsum would readily precipitate upon reaching the ocean, possibly forming extensive deposits near hydrothermal vents.

Chlorides are minor constituents of chondrite leachates (Kargel 1991, Fanale *et al.* 1998) but are very important because they are highly effective freezing-point depressants and would be concentrated in the coldest brines during freezing of an ocean or brine magma body. Chlorides likely would be effective in preventing complete freezing of the ocean.

It is not necessary to think solely in terms of ice containing minor salty contaminants that accumulate only upon severe

evaporation or freezing. For instance, one structural–chemical model produced by Kargel (1991) has a europan crust composed of a peritectic mixture of 84% $MgSO_4 \cdot 12H_2O + 11\%$ $Na_2SO_4 \cdot 10H_2O + 5\%$ ice—ice is the minor constituent. According to that particular model, a 20-km-thick layer made of a peritectic mixture of hydrated salts and ice would be underlain by a much thicker layered sequence of less-hydrated salts totally lacking ice. In another model, Europa has a eutectic crust of 50% ice + 44% $MgSO_4 \cdot 12H_2O + 6\%$ $Na_2SO_4 \cdot 10H_2O$. The main points of this previous modeling were that: (a) salts are major constituents of the crust and ocean derived by chondritic evolution, (b) magnesium and sodium sulfates are specifically predicted as the major salts, and (c) an ocean would probably be hypersaline, with solutes exceeding 17% by mass.

Kargel (1991) modeled the first, coldest stages of aqueous differentiation without evaluating logical progressions of melting and further differentiation at higher temperatures. We have computed many additional models; Fig. 3 shows a selection of alternative chemical structures (or possibly an evolutionary sequence) that might represent a differentiated chondritic Europa. The models all assume that a gravitationally stable structure is achieved. The models differ in the extent of dehydration of the mantle and of aqueous phase segregation in the crust/ocean. Those having an icy shell made of pure ice implicitly involve some process, such as segregation of large ice bodies followed by solid-state ice diapirism. Figure 3 also shows the computed values of C/MR^2 of each structure; C/MR^2 was not used as a constraint on the models, but rather was computed *a posteriori*. A similar set of Europa structure models was recently presented by Spaun and Head (2000); their work is based on fractional crystallization of a putative ocean approximated in the binary system $MgSO_4$–H_2O and took full advantage of Europa's observed value of C/MR^2 as a constraint. Their models resemble some of those presented here in that they show multiple layers of various hydration states and ice content, although in detail the models differ since the modeled processes are different. Modeling results by Zolotov and Shock (2000b) of the equilibrium crystallization of Europa's ocean have a problem with the $CaSO_4$ parameterization added to the FREZCHEM 2 modeling software, and so those results are erroneous. However, more useful is the important result by Zolotov and Shock (2000a) that aqueous alteration of an initial CV chondrite produces a salt assemblage similar to that we have used as the starting point for our models. Their model points out that almost any oxidized chondritic meteorite assemblage could have been used as the starting point for our models and would have yielded a qualitatively similar end result; details, of course, will differ.

Each of the models in Fig. 2 has an identical dense core made of iron sulfide. We approximated the core's mass by calculating the amount of FeS representing the content of sulfide in CM carbonaceous chondrites (Bostrom and Fredriksson 1964, Kargel 1991). In reality, chondritic sulfides are chemically more complex, but it is not our purpose to investigate in any detail the chemical nature of the core. However, considering the strong influence of the existence of a core on C/MR^2, it was necessary
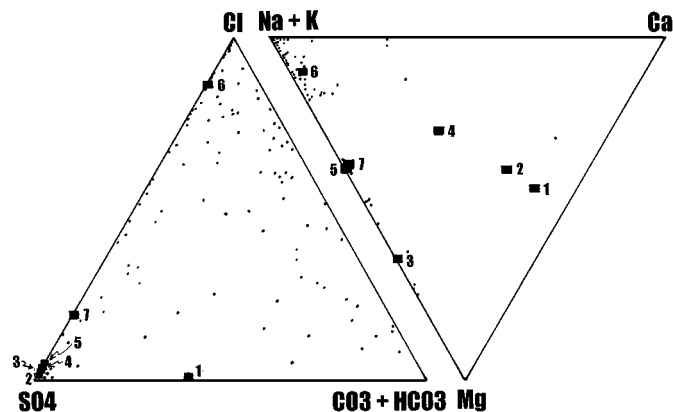
FIG. 2. Triangular plots showing the compositions (mass ratios) of soluble salts of carbonaceous chondrites and terrestrial brines: (left) Major anions, and (right) major cations. Rectangles numbered 1–3 are data for the CI chondrite Orgueil–number 1 is the total salt content, including sulfates, chlorides, and carbonates; 2 is with carbonates subtracted; 3 is with carbonates and calcium sufate subtracted. Rectangles numbered 4 and 5 are for the experimental leachate obtained by Fanale *et al.* (1998) from the CM chondrite Murchison—number 4 is the actual "original leach solution," and 5 is that solution with calcium sulfate subtracted. The most directly comparable points for these two meteorites are 3 and 5. Seawater and a closed-basin playa brine from the "La Mancha" region, Spain (de la Pena *et al.* 1982), are shown as the rectangles numbered 6 and 7, respectively. In both plots dots are closed-basin brines (data from Eugster 1980).

to take a first-order look at how a carbonaceous chondrite precursor could also yield a dense core potentially satisfying the *Galileo* gravity data.

The specific models illustrated in Fig. 3 correspond to the following scenarios, all computed using Europa's observed mass (Anderson *et al.* 1998), a carbonaceous chondrite precursor (Fredriksson and Kerridge 1988), and low-pressure phase equilibria and phase densities in the system $H_2O–MgSO_4–Na_2SO_4$ (Kargel 1991). The model scenarios are briefly described here:

Model A5. Sequential steps of perfect fractional incongruent melting of hydrated salts at a series of peritectics as energy is added to the system. Each peritectic liquid (represented by the frozen crustal layers P2, P3, . . .) is saltier and denser than the solid peritectic assemblage that preceded it (Table II), and so a stable density stratified crust is developed by sequential stages of brine intrusion and underplating. It is assumed that the intrusive layers solidify rather than form an ocean. The amount of water and salts available to the crust/ocean system is determined by phase equilibria during dehydration of salts contained in the primordial europan chondritic assemblage. The mantle of this model, after differentiation, still contains phyllosilicates and the water of hydration of salts that are fairly insoluble and stable at low temperatures, including gypsum ($CaSO_4 \cdot 2H_2O$) and kieserite ($MgSO_4 \cdot H_2O$). The implication is that the mantle has not been heated very strongly, an unlikely situation (considering that Europa has a core). C/MR^2 is far too high compared to Europa's actual value (0.346 ± 0.005; Anderson *et al.* 1998).

Model B. This structure results from multiple stages of efficient incongruent remelting of the hydrated salt layers represented in Model A5—eventually a eutectic crust (or ocean) is formed and all excess salts exist in anhydrous form as a lower crust. C/MR^2 still is far too high compared to Europa's actual value.

Model C. Taking aqueous differentiation yet another step further, it is assumed that the eutectic crustal material of Model B segregates into a buoyant crust of ice and a deeper volatile subcrust of hydrated salts. Segregation may occur by fractional crystallization of an ocean or by solid-state phase segregation and ice diapirism. C/MR^2 still is too high compared to Europa's actual value.

Model D″. More heat is injected into the hydrated salts of Model C, resulting in multiple stages of incongruent remelting. At each stage of remelting the residual salts contain less H_2O than before and the amount of H_2O in the uppermost icy layer is increased. Also, all salts that had remained in the mantle in the models above, including carbonates, gypsum, and kieserite, have now been driven out and added to the crust, but the mantle still retains phyllosilicates. As differentiation of the crust proceeds to completion, the upper crust consists entirely of ice and the subcrust of anhydrous salts. C/MR^2 is much closer to Europa's actual value but still is a bit high.

Model D′. Similar to Model D″, but the amount of water in the crust is increased due to complete dehydration of the chondritic rock's phyllosilicate minerals and all other hydrated phases. We
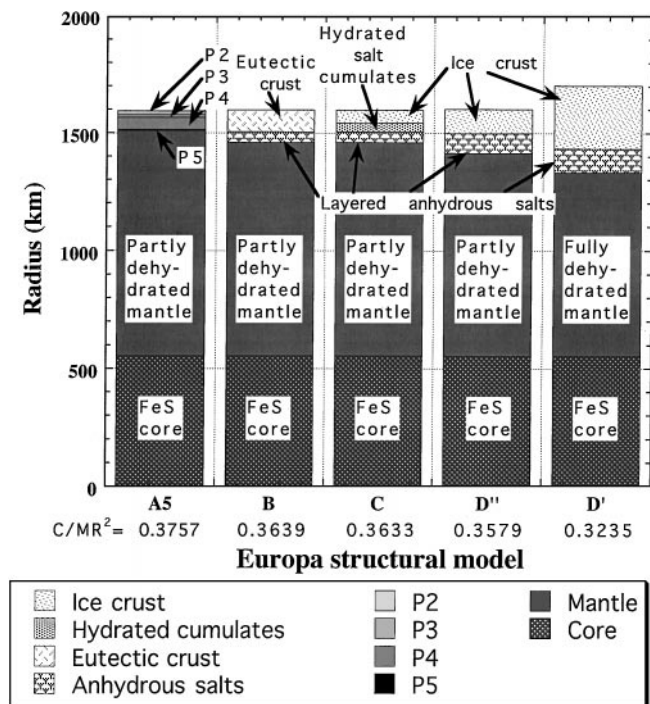

FIG. 3. Five model structures developed from a chondritic Europa (described in text).

assume a toal water content equal to that of CI chondrites calculated from H abundance given by Anders and Grevesse (1989), with the aproximation that all H is in the form of water—H associated with organics is relatively minor. With total dehydration of Europa's interior, C/MR^2 is far too low compared to Europa's actual value (0.347). The radius of the differentiated Europa is also too large and the mean density too low.

The models illustrated in Fig. 3 do not include any complexities caused by addition of other volatiles during heating of Europa's rocky mantle. None of the computed structures in Fig. 3 has C/MR^2 very close to the observed value, but models D' and D'' bracket the observed value (0.347), showing that fairly simple models can evolve into structures consistent with gravitational constraints. Considering that the amount of soluble salts and water in chondrites varies widely (roughly a factor of 3 for CI and CM chondrites), the results would indicate that an ideal solution could be forced with iteration of the amount of salts and water initially present or by iteration of the degree of interior dehydration. Boato (1954) gave a drier estimate of CI chondrite composition ($\sim$12% H_2O by mass) than the 18% value we used (from Anders and Grevesse 1989). Had we used the lower water content, complete aqueous differentiation in model D' would have resulted in C/MR^2 much closer to Europa's actual value.

Our purpose with Fig. 3 is not to present an ideal structure of Europa. Anyway, there is a difference between producing a model that satisfies available constraints (very easy) and producing a model that is uniquely satisfactory (not possible). By showing models that bracket Europa's observed C/MR^2 and mean density, and also presenting a range of other models that do not do so well, we merely wish to point out that a great variety of structures can result from relatively simple chemical models starting with identical chondritic material.

We note that equilibrium petrology would not allow development of an upper crust of pure ice or of pure salts (hydrated or not). An evaporite layer of pure-salt surface would imply sublimation of ice. Any chondritic model that has ice forming the only major constituent of the uppermost crust must involve (a) efficient fractional crystallization of brine flows (whereby salts sink and ice floats), (b) some form of solid-state segregation of phases and diapirism, or (c) water evaporation and frost recondensation. There is strong geologic evidence of and theoretical backing for diapirism (Pappalardo *et al.* 1998, Rathbun *et al.* 1998, Spaun *et al.* 1999, McKinnon 1999) and frost condensation (Squyres *et al.* 1983, Domingue *et al.* 1991), and fractional crystallization of brines is all but inevitable (Hogenboom *et al.* 1995).

The propensity for solid-state diapirism or cryovolcanism to occur, and also the stability of a chemically layered crustal sequence, is greatly dependent on the relative densities of key solid and liquid phases. Table II compiles the densities of important solid phases, solid assemblages, and liquids in the system $MgSO_4$–Na_2SO_4–H_2O. This table also indicates the composition of the liquids formed by lowest temperature melting of each

solid phase assemblage. The listed data do not consider either compression due to elevated pressure or thermal expansion.

3.2. Formation of a Chloride Ocean by Partial Freezing of Chondrite Brines

It is well understood that common chloride salts are more effective as freezing-point depressants than common sulfate salts. In multicomponent solutions containing both chlorides and sulfates it is generally true that partial freezing results in concentration of chlorides and precipitation of sulfates. (A key exception is sulfuric acid, if it is present, as discussed below.) The FREZCHEM 5 model (modified after Spencer *et al.* 1990 by Marion and Grant 1994, Mironenko *et al.* 1997, and Marion and Farren 1999, with modifications including addition of carbonate minerals and improved parameterizations of sulfates to high ionic strengths) was used without carbonate to compute the thermal evolution of chondritic brines. An earlier version of this computational tool was used to investigate the chemical evolution by freezing of Earth's seawater (Marion *et al.* 1999) and a hypothetical martian ocean (Morse and Marion 1999). The FREZCHEM models select the compositions of the solutions and solid phases that minimize the Gibbs free energy of the system. Solid phases formed during evaporation or freezing are assumed to have the potential to subsequently dissolve or react as solution properties change (e.g., the solids can recrystallize and add water of hydration, or lose water). This is equilibrium crystallization, which represents an extreme in that all precipitated phases are assumed to be available for subsequent reactions. Fractional crystallization, which also can be simulated with FREZCHEM 5, represents another extreme in that precipitated phases are buried and thus are unavailable for subsequent reactions.

Figure 4 shows the modeled evolution of a chondrite brine during progressive freezing alternately by equilibrium or fractional crystallization. The initial high-temperature brine in Fig. 4 is that calculated by Kargel (1991) for the Mg–Na–Ca–sulfate components with addition of chlorides in the amounts observed by Fanale *et al.* (1998) in their leachate. In the equilibrium freezing model, magnesium sulfate first precipitates as epsomite ($MgSO_4 \cdot 7H_2O$) but then is completely replaced by $MgSO_4 \cdot 12H_2O$ by reaction with the brine as it cools. In the fractional crystallization model MS7 is preserved and then buried by MS12 and other salts. The calculations show the enrichment of chlorides at lower temperatures and a crossover in chloride and sulfate abundances at about 266 K, which coincidentally is about the temperature where ice begins to precipitate. These computations do not consider effects of elevated pressures in Europa's crust; some pressure effects are considered qualitatively later. Figure 4a shows the thickening of the icy shell (with two alternative assumptions that it is entirely ice or is a cotectic mixture of ice and salts) and thinning of the liquid brine layer as the system cools. Figure 4d shows the difference between fractional and equilibrium crystallization in terms of the final mineral
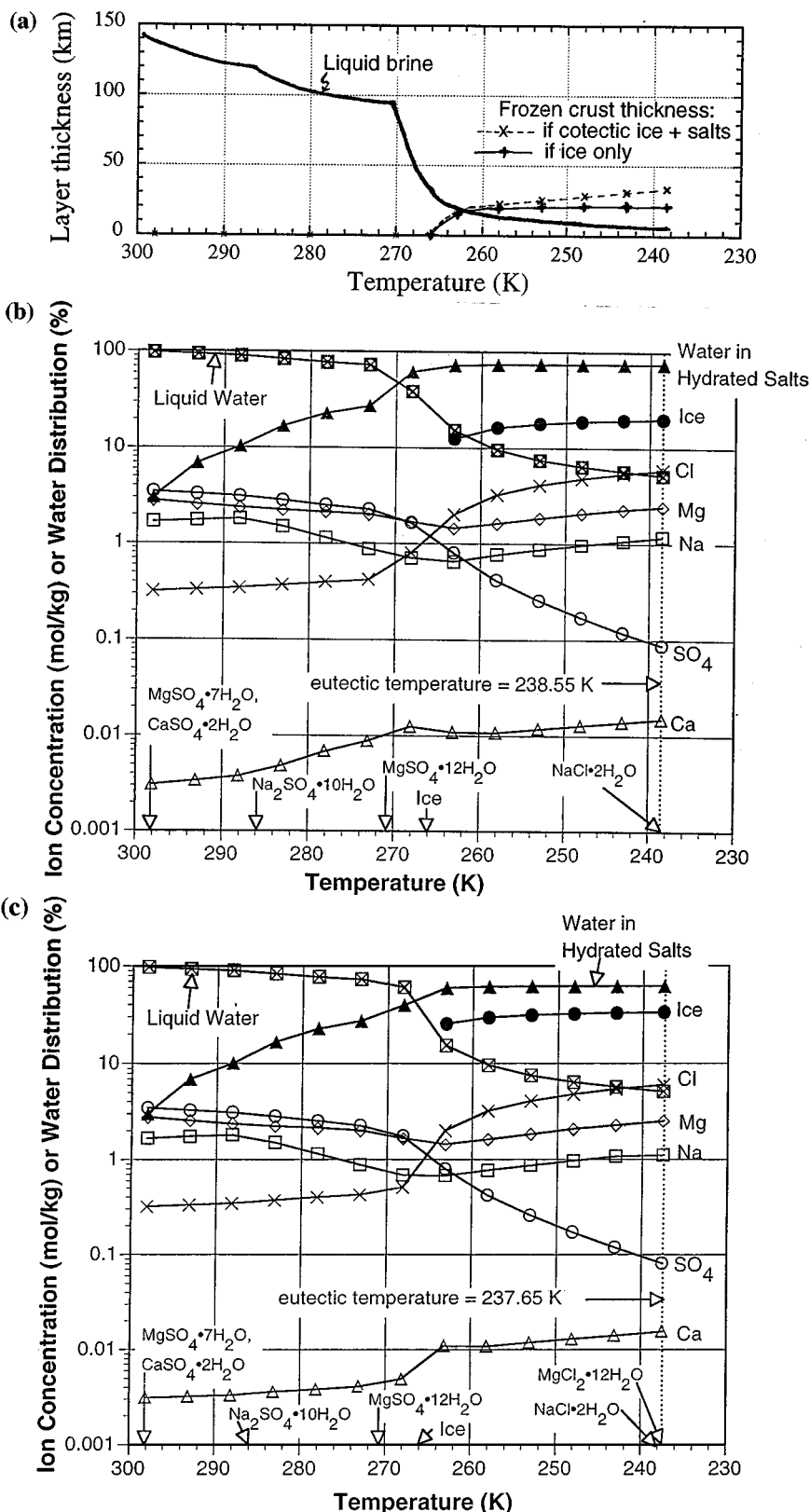
FIG. 4. Freezing evolution of a CI-chondrite-derived brine ocean on Europa. (a) Thickness of liquid brine layer and icy shell versus ocean temperature. (b) Composition of the brine as a function of temperature, calculated with FREZCHEM 5 with the assumption of equilibrium crystallization. The top three curves for liquid water, ice, and water in hydrated salts represent the percentage of the total water in the system that is in those three forms, which add up to 100%. The other curves show the concentrations of each ionic or anionic species. Also shown is the initial temperature at which each solid phase begins to precipitate as the brine is cooled. (c) Same, but fractional crystallization. (d) Completely frozen mineral assemblage produced, alternately, by equilibrium and fractional crystallization. The bar plots show relative abundances of solid phases, not vertical sequences of minerals.

238

(d)

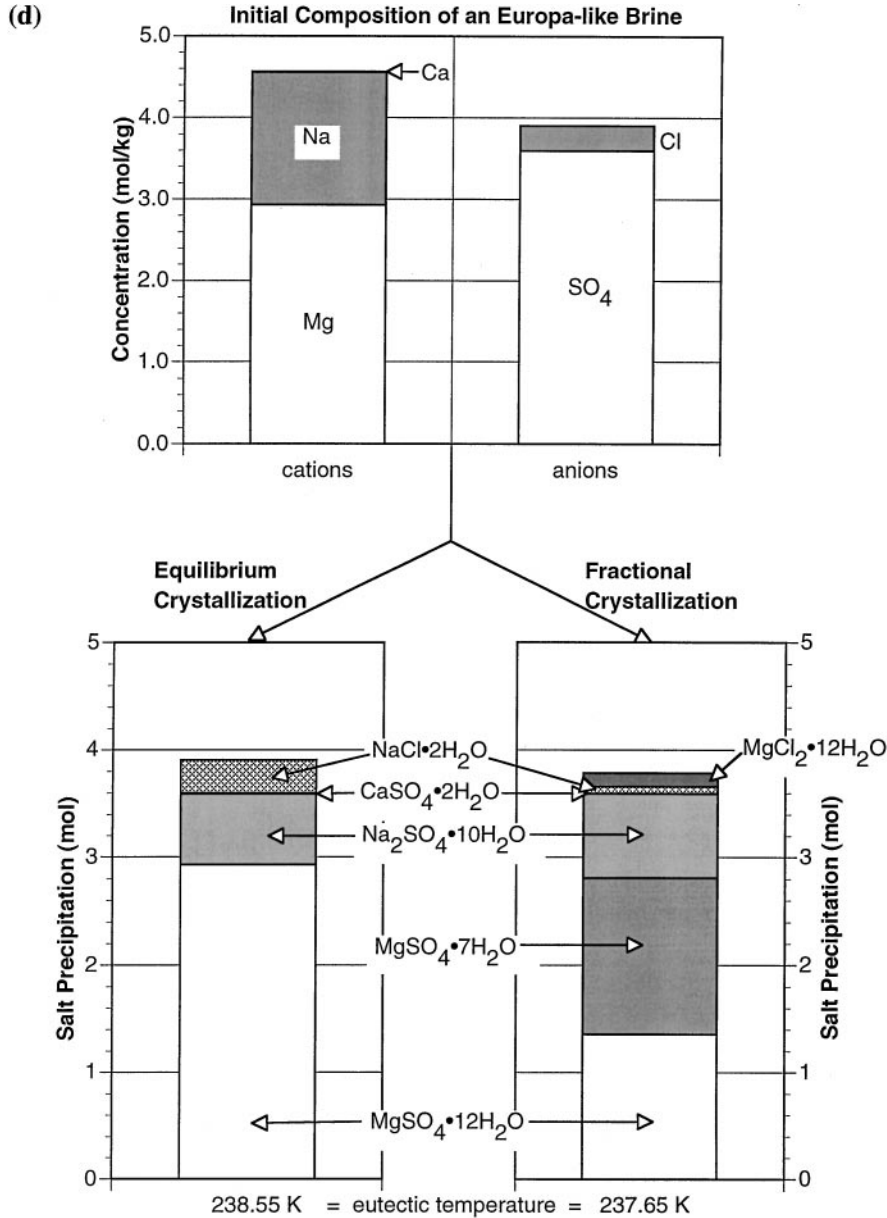### Initial Composition of an Europa-like Brine

FIG. 4—*Continued*

assemblages that are produced. Fractional and equilibrium crystallization produce slightly different lines of brine evolution, but the key point about chloride enrichment at lower temperatures remain qualitatively the same in the two scenarios.

If the initial model brine of Fig. 4 reflects the real Europa, one implication is that any europan ocean in equilibrium with an icy shell would likely have concentrations of chlorides higher than previously believed by Kargel *et al.* (1991). The reason is that the brine starts out with very high solute (especially sulfate salt) contents, and by the time the temperature reaches a point where ice can precipitate, much of the brine's mass has already solidified as hydrated sulfates, causing chlorides to become concentrated in the residual solution. The brine does not completely

freeze until 238.55 K, at which point the sulfates are mostly in solid form already. Considering pressures deep in Europa's crust (to nearly 200 MPa), the actual solidus temperature would be closer to 216 K. This is likely much colder than temperatures of convective adiabats in Europa's icy shell, meaning that it is highly improbable that a europan ocean would be totally frozen or even partly frozen to such an extent that it would consist of a eutectic chloride solution (cf. McKinnon 1999 who uses a temperature of a convecting icy shell of about 260 K). However, even if the temperature is so cold as the chloride eutectic, there is enough chloride in chondritic material to produce a saturated eutectic chloride ocean over 4 km deep (Fig. 4a). For likelier situations having crustal convective adiabats warmer than 216 K

(or >238.55 K if not considering pressure effects), the liquid ocean would be thicker, the icy shell thinner, and the chloride content lower, as Fig. 4 shows. In any event, if the identification of magnesium and sodium sulfates on the surface of Europa is correct (McCord *et al.* 1998a), and if the surface material is in some way reflective of the ocean composition, then it suggests a fairly warm ocean (to keep sulfates in solution). An ocean temperature of 266 K would allow a sulfate-rich ocean to exist and still allow ice to precipitate and form part of the crust (needed to explain surface ice observed spectroscopically). This high temperature would also mean that the liquid mass would be fairly large, the ice mass fairly small (meaning a thin icy shell), and the ocean quite deep—consistent with interpretations of the *Galileo* magnetometer data. Nevertheless, it is difficult to have both a frozen ice-bearing shell and a liquid brine ocean that is quite as deep as the magnetometer team would like; at least 30 km is easily possible so long as the icy shell is very thin. Of course, this is just one chemical model of the ocean/crust. A thin ice crust and deep bring ocean up to 100 km thick (favored my magnetometry results) would require lower initial solute contents than modeled here.
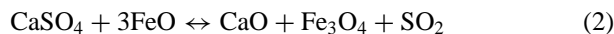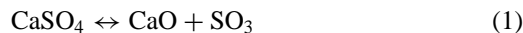
3.3. Addition of SO₂ or SO₃

Stevenson (1982) and Crawford and Stevenson (1988) first considered possible roles of dissolved gases, including CO_2, SO_2, and CH_4, in explosive water volcanism on small icy satellites. An important further advance of our understanding of explosive cryovolcanism has been made by Fagents *et al.* (2000), who have examined in detail the explosive venting of europan aqueous liquids due to exsolution of CO_2, SO_2 and other dissolved gases. On Earth sulfuric acid—an important dissolved species in volcanic crater lakes and acid rain—normally is formed by the introduction of SO_2 gas into aqueous systems (Kargel *et al.* 1999). The fact that SO_2 is so abundant on Io suggests that it may also be vented into Europa's crust, a process that would yield H_2SO_4 (Kargel 1998, 1999a). SO_2 also occurs on Callisto and appears to be endogenic or partly endogenic in origin (Hibbitts *et al.* 2000). This endogenic mechanism is interesting in light of (1) spectroscopic evidence of traces of SO_2 (Lane *et al.* 1981, Noll *et al.* 1995) on Europa, (2) correlation of Europa's UV absorbers (now thought to be a combination of S–O compounds, elemental sulfur, sulfates, peroxides, and ozone) with geologic features in addition to a longitudinal pattern related to exogenic processes (Hendrix 1998, Hendrix *et al.* 1998), and (3) new interpretations by Carlson *et al.* (1999) that Europa's predominant nonice hydrated material is H_2SO_4, which was thought by them to have a mainly radiolytic origin but clearly has some type of partial control by endogenic processes.

Sulfur flux from the volatile subcrust and mantle should generate acidity, which may tend to be neutralized by reactions with silicate rocks. With appreciable sulfur input, a portion of the cations in solution would be charge-balanced by sulfur species rather than by carbonate. In Earth's continental evaporite settings (strongly oxidizing), this scenario naturally leads to neutral Na–

(Mg)–SO_4–Cl brines. The exception of course is when acidity is not neutralized (nonreactive wall rocks) and builds up to produce acid brines. It is valid to ask whether Europan conditions would be sufficiently oxidizing to produce sulfate. Oxygen has been observed in Europa's tenuous atmosphere (Hall *et al.* 1995) but has been attributed to magnetospheric plasma processes occurring on Europa's surface and might say little about deeper conditions. On the other hand, all nonice materials identified on Europa are highly oxidized compounds—SO_2, CO_2, H_2O_2, and one or another type of sulfate. We primarily assume that this oxidized condition persists to deep levels. If we err in making this assumption, then maintaining sulfur in reduced forms (H_2S, metallic sulfides, and native sulfur) should favor Na-carbonates and chlorides as the major "evaporite" products. Thus, the relative amounts and oxidation state/molecular form of C and S compounds are fundamental questions to explore.

Production of copious quantities of SO_2 fits into the sulfate salt scenario just described. The chondrite-evolution models above omit $CaSO_4$ as a major constituent because of its low solubility in water. The bulk of any $CaSO_4$ that would be leached from Europa's interior would promptly saturate and precipitate upon reaching the ocean. Some of Europa's $CaSO_4$ would have settled into a thick layer on the seafloor, but most would never even have been leached from the mantle. We note that Lewis (1982), in evaluating the geochemistry of Io's sulfur under high-temperature, anhydrous conditions, considered $CaSO_4$ to be a major repository of sulfur and a possible source of SO_2. When subjected to temperatures approaching silicate mantle solidus temperatures, $CaSO_4$ may break down and yield free SO_2 or SO_3 fluid by reactions such as these:

$$CaSO_4 \leftrightarrow CaO + SO_3 \quad\quad (1)$$

$$CaSO_4 + 3FeO \leftrightarrow CaO + Fe_3O_4 + SO_2 \quad\quad (2)$$

$$CaSO_4 + FeS \leftrightarrow CaO + FeO + SO_2 + (1/x)S_x. \quad (3)$$

FeO and CaO produced by the forward reactions (2) and (3) would further react with silicates and thus represent components of silicate minerals; the FeS in reaction (3) represents any sulfides still retained in the mantle. A similar process occurs in Earth's subduction zones and regions of basal crustal anatexis, explaining SO_2-rich silicate magmas erupted from volcanoes such as Mount Pinatubo, Lascar, and El Chichón. These volcanoes' S-rich magmas (0.1 to 1 wt.% S in the forms of sulfate and SO_2) is explained by anhydrite saturation at several kilobars (Luhr *et al.* 1984, Luhr 1990, Bernard *et al.* 1991, Mathews *et al.* 1994, Fournelle *et al.* 1996, Rutherford and Devine 1996).

The sulfurous volatiles produced by reaction (3) coincidentally can explain the SO_2 and S_2 gases venting from Io's volcanic plume, Pele (John Spencer, personal communication to Kargel, November 1999). Zolotov and Fegley (1998a,b, 1999), not yet aware of Spencer's findings, modeled the sulfurous volatile assemblage expected from Pele and concluded that volatile interactions with silicate magmas would tend to produce SO_2 and S_2 gases under some likely conditions. On Europa, thick

sedimentary accumulations of magnesium and sodium sulfates in the volatile subcrust also could be subjected to tidal heating; they could dehydrate, and with further heating they might yield SO_3 by reactions analogous to (1), where the metal oxides would form a highly refractory, unsilicated substance. SO_2 or SO_3 would tend to migrate upward and eventually would be vented into the ocean or icy shell. SO_3 would immediately react with water or ice to form sulfuric acid, and SO_2 might also form sulfuric acid under oxidizing conditions; relevant reactions might be

$$SO_3 + H_2O \leftrightarrow H_2SO_4 \qquad (4)$$

$$3SO_2 + 2H_2O \leftrightarrow 2H_2SO_4 + (1/x)S_x. \qquad (5)$$
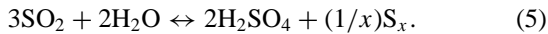
Reaction (5) is important in many terrestrial volcanic crater lakes, as reviewed by Kargel *et al.* (1999). The point is that, by one means or another, copious quantities of SO_2 or SO_3 can be released into Europa's ocean and icy shell from its deeper interior. Radiolytic formation of H_2SO_4 at the surface also is inevitable, and the process apparently works either starting with sulfur in virtually any form, e.g., indigenous Europan sulfate salts or Iogenic sulfur implanted by plasma bombardment (Carlson *et al.* 1999). Hence, there is no shortage of mechanisms by which sulfuric acid can be made.

Unreacted SO_2 in the ocean would dissolve up to a pressure-dependent saturation limit imposed by SO_2 clathrate formation, which occurs by the reaction

$$4SO_2 + 23H_2O \leftrightarrow 4(SO_2 \cdot 5^3/_4H_2O). \qquad (6)$$
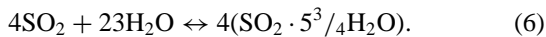
Sulfuric acid also could accumulate until it reaches saturation and forms a hydrate phase:

$$H_2SO_4 + 6.5H_2O \leftrightarrow H_2SO_4 \cdot 6.5H_2O. \qquad (7)$$

Dissolved SO_2 and H_2SO_4 would be available to drive explosive aqueous volcanism, which might also occur by interaction of liquid water with frozen SO_2 hydrate (Stevenson 1982, Crawford and Stevenson 1988, Kadel *et al.* 1998, Fagents *et al.* 2000).

Whatever the precise chemistry behind production of SO_2, if we look to Io's plumes as a model of what may be happening inside Europa, then the amount of SO_2 vented and reacted over time could be substantial. Io is losing mass, apparently mainly SO_2, to the Io torus at a rate of about 1600–3200 kg s^{-1} (from plasma mass loading calculated from plasma corotation lag; Hill 1979, Pontius and Hill 1982, Brown 1994), a quantity roughly consistent with optical and UV observations of escaping S and O ions (Cheng 1984, Brown *et al.* 1983, Shemansky 1987, Bagenal 1994, Wilson and Schneider 1994). There is evidence for interannual variability of this mass loss rate over two decades of observations; there is no way presently to know how this rate may have varied over geologic time. We assume that the recent rate of Io's SO_2 loss is characteristic, which we sum over time to yield the amount of SO_2 that Io has lost and a minimum estimate of the SO_2 with which Io was originally endowed. We

calculate approximately 3.6×10^{20} kg. If Io's rate of SO_2 loss is scaled to Europa's smaller mass (with H_2O subtracted), and if this rate of SO_2 venting from Europa's interior has been constant through time, then in 4.5 Byr 2×10^{20} kg of SO_2 would have been vented into the ocean. This is what we refer to here as the Io model of Europa's SO_2 production. It is simply one estimate of the possible magnitude of SO_2 venting, not an estimate of the precise amount, nor a statement regarding this sulfurous material's present chemical form.

An independent calculation based on reaction (2) and the amount of $CaSO_4$ contained in typical carbonaceous chondrite material yields a similar magnitude of SO_2—4.8×10^{20} kg. We call this calculation the chondritic calcium sulfate model of Europa's SO_2 production. Considering the crudity of the models, the results are in surprisingly good agreement. To put both estimates into perspective, the Io model of Europa's SO_2 production yields an amount of SO_2 equivalent to 0.4% of Europa's mass or 2.5% of its total water mass (according to the CM chondrite model); the chondritic calcium sulfate model produces SO_2 equivalent to 6% of Europa's total water mass. These are substantial amounts, although as several aqueous reactions above suggest, much of the vented SO_2 now would be in other chemical forms, such as sulfuric acid and elemental sulfur.

We calculate the amount of sulfuric acid potentially produced by taking the amount of SO_2 from the chondritic calcium sulfate model and assume that it reacts virtually to completion according to reaction (5). The resulting calculation is 4.9×10^{20} kg of sulfuric acid plus 8×10^{19} kg of elemental sulfur. Elemental sulfur would be deposited on the seafloor; if it formed a single layer of solid rhombic sulfur, it would be approximately 1300 m thick. The calculated quantity of sulfuric acid might react further to form as much as 1.08×10^{21} kg of a solid hydrate phase, $H_2SO_4 \cdot 6.5H_2O$, according to reaction (7). This quantity of sulfuric acid would be structurally and chemically significant for the evolution of Europa's ocean and crust, but to date we have not explicitly included it in our models. Of course the amount of sulfuric acid might be nowhere near as substantial as calculated; some vented SO_2 may have been lost from Europa into space, and some may not have reacted to form H_2SO_4; some of the mantle's $CaSO_4$ may not have decomposed, and some SO_2 or sulfate may have reacted to form metal sulfides instead. On the other hand, some amount of other sulfate salts, e.g., $MgSO_4$, may have decomposed, thus adding to the SO_2 contributions made by $CaSO_4$; hence, the amount of SO_2 and H_2SO_4 could be even greater than calculated. The point is that endogenic contributions of SO_2 and H_2SO_4 could be enormous.

If this model of SO_2 degassing is correct in concept even if not in magnitude, then the amount of endogenic SO_2 and H_2SO_4 in all likelihood would vastly exceed radiolytic and photolytic production of these materials. However, we do not dispute the likelihood that radiolytic/photolytic equilibrium would maintain a high surface abundance of sulfuric acid regardless of the initial form of sulfurous molecules on Europa's surface (Carlson *et al.* 1999). There is good evidence for a global pattern in hydrate distribution consistent with exogenic modulation of sulfuric acid

abundance, but pronounced geologic controls are also evident and require an endogenic process (McCord *et al.* 1998a, 1999a). The oceanic site of sulfuric acid production as modeled above offers a ready explanation for this geologic control. We believe that the evidence supports a prevalent geologic control on the distribution of nonice materials on Europa, but that exogenic compositional patterns are superposed over this endogenic distribution.

The proposed existence on Europa of hydrated salts or sulfuric acid makes sense cosmochemically, and each hypothesis alone is capable of explaining the chief spectroscopic features of Europa's nonice terrains as seen in NIMS data. However, the salt and acid hypotheses are not mutually exclusive from either a cosmochemical or a spectroscopic perspective. As a matter of detail, one would not expect sulfuric acid to coexist with base salts, such as sodium carbonate, but the more general idea of coexistence of dissolved sulfuric acid or sulfuric acid hydrates with some salts, such as magnesium sulfate, is fully acceptable and perhaps inevitable if SO_2 vents into Europa's ocean. Hence, it would not be surprising, and it would be entirely consistent with all available observations, if the nonice hydrate material on Europa consists of hydrated sulfuric acid, magnesium sulfate, and other salts, with variable admixtures of ice.
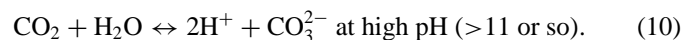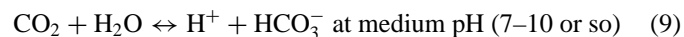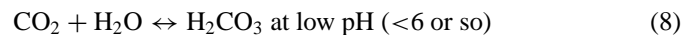
A highly acidic ocean would likely drive much other chemistry. A low-pH regime suggests that a variety of metals, and especially iron and aluminum, would be leached from silicate rocks, especially under hydrothermal conditions, and transported in solution to the ocean and crust. One place on Earth where acid evaporative conditions exist is Lake Tyrrell, Australia. The acidity there has consequences for the stability relations of evaporitic salts; e.g., alunite (an aluminous sulfate containing hydroxyl groups) and jarosite (an hydroxylated iron sulfate) occur in addition to the more usual halite and gypsum (Long *et al.* 1992a,b). This creates a rather different situation from those most common on Earth, where hydrothermal reactions involving neutral-to-basic solutions and ferroan silicates normally lead to sulfate reduction. By analogy, an acidic europan ocean may precipitate extensive deposits of alunite and jarosite. These minerals could occur along hydrothermal circulation paths within the silicate subcrust. They might also form on Europa's surface by freezing and evaporative concentration of erupted brine. High acidity might be maintained in the ocean despite neutralizing tendencies of reactions with silicates if the potentially reactive silicate rocks are sealed off by alteration materials or by accumulation of thick salt deposits on the seafloor. Fracture systems within such layers might permit sulfur gases to continue to be transmitted into the ocean from mantle degassing and thermal devolatilization of evaporites beneath the ocean. The result could be runaway acidification. Further consequences could be rather bizarre, e.g., partial digestion of incoming asteroids by Europa's acid ocean! The indigestible residue—including resilient interstellar/supernova condensates such as diamond and silicon nitride—might settle onto a sulfur-encrusted seafloor.

Alunite and jarosite and some other expected acid alteration minerals contain spectroscopically active hydroxyl and would

be clearly evident in near-infared reflectance spectra (Crowley 1993, Crowley and Hook 1996, McCord *et al.* 1998a). Aluminous hydroxyl minerals, including alunite, have been detected recently in AVIRRIS images (a NIMS-like remote sensing data set) of Mount Shasta despite 50% subpixel coverage by snow patches (Crowley *et al.* 1999). The fact that there is no evidence of these minerals in NIMS Europa spectra may be an important clue to ocean or crustal chemistry. Unlike some minerals that are readily destroyed by solar ultraviolet, hydroxyl phases are highly stable (Yen *et al.* 1999). The apparent absence of these minerals on Europa might be due to any of three possibilities. (a) Acidic brine is not in contact with aluminum and iron-bearing silicate rocks; perhaps a thick accumulation of salts covers the seafloor completely, as modeled above, so that any circulating hydrothermal brines lack opportunities to react with silicates. (b) Efficient neutralizing reactions of oceanic brine with silicates may effectively prevent buildup of high acidity and cause any alunite and jarosite to remain in solid form in the silicate subcrust. (c) The ocean is intrinsically neutral or alkaline, which probably would imply that sulfur gases are not vented in sufficient amounts to overwhelm sources of alkalinity. In any event, it appears on the basis of nondetection of hydroxyl anion either that Europa does not possess a highly acidic ocean or that an unknown mechanism prevents hydroxyl phases from forming or from being exposed at the surface.

3.4. Addition of CO_2

CO_2 is among the materials detected on Europa, Ganymede, and Callisto, albeit in trace amounts (McCord *et al.* 1998b, Hibbitts *et al.* 2000), and sodium carbonate is on the list of candidates for Europa (McCord *et al.* 1998a). Although radiolysis of carbon-bearing ices might produce a variety of carbonaceous species on Europa, including CO_2 (Delitsky and Lane 1998), there is evidence that CO_2 is at least partly endogenic on Callisto (Hibbitts *et al.* 2000). CO_2 is widespread and abundant in the Solar System from Venus out to Triton, so it is reasonable to think that Europa may also possess abundant endogenic CO_2. We shall consider how endogenic processes on Europa might contribute to CO_2 surface frosts and also yield sodium carbonate. In the binary system H_2O–CO_2 the relevant equilibria are described by three reactions, each of which dominates over a specific pH range (given here for equilibria at 298 K, representative of low-temperature aqueous carbonate equilibria, Krauskopf 1979):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \text{ at low pH } (<6 \text{ or so}) \tag{8}$$

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \text{ at medium pH } (7\text{–}10 \text{ or so}) \tag{9}$$

$$CO_2 + H_2O \leftrightarrow 2H^+ + CO_3^{2-} \text{ at high pH } (>11 \text{ or so}). \tag{10}$$

If initial aqueous differentiation yields a Mg–Na-sulfate-dominated crust as considered above, then Ca–Mg-carbonates (also contained in carbonaceous chondrites) would have been left behind in the mantle due to relatively low solubility. This

is similar to the case for calcium sulfate described above. The carbonates may have formed in the first place by oxidation of organics. At some point, intense heating of the mantle would have decomposed the carbonates, and caused degassing of CO_2. This no doubt occurred in Earth, too, but in Europa, the icy shell and possibly an ocean may tend to trap the CO_2, which would be available to drive formation of carbonates, bicarbonates, or CO_2-clathrate. How much CO_2 might this be? There is enough Ca–Mg-carbonates in chondritic material to supply 1.0×10^{21} kg of CO_2 to Europa's crust, if the carbonates entirely decomposed. This compares to a total water mass of 8.1×10^{21} kg in the CI chondrite model of Europa. But there would be some form of chemical sequestration of CO_2. Once the amount of dissolved CO_2 exceeds about 3 wt.% (the exact amount depending on pressure, temperature, and salinity), then CO_2 clathrate hydrate would sequester additional CO_2. However, sodium carbonates and bicarbonates may start to form at much lower amounts of dissolved CO_2. Furthermore, the icy shell over the ocean might be leaky (e.g., fractures through which dissolved gases can escape during eruptions; Fagents *et al.* 2000), in which case most of the CO_2 that goes into the crust ends up being vented to space.

In any case, the amount of CO_2 potentially available to form clathrates, carbonates, and/or bicarbonates is quite substantial and perhaps coequal with SO_2. However, only traces of CO_2 have been detected on Europa (McCord *et al.* 1998b). The chemical nature of aqueous solutions formed by alteration of silicates in the presence of high activities of CO_2 depends very much on the type of rocks. If the rocks contain abundant alkalis and alkaline earth metals (especially K, Na, Mg, and Ca), such as silica-undersaturated mafic volcanic rocks, hydrolysis and carbonation reactions generate weak alkaline solutions (Krauskopf 1979). This type of situation is frequently encountered on Earth in areas of rift volcanism and intraplate hotspot volcanism. Evaporative concentration of dilute alkaline river input in closed basins in such regions characteristically results in concentrated alkaline brines enriched in sodium carbonate or bicarbonate and possessing very high pH. A somewhat similar type of brine could be obtained on Europa, particularly if undersea volcanic rocks had a highly silica undersaturated and alkaline character, such as the mafic feldspathoidal rocks common along the East African rift, the southwestern United States, and many late-stage volcanic rocks capping oceanic island hotspot volcanoes. A controversial but highly regarded hypothesis for the origin of Earth's oceans involves this type of chemistry and an original sodic carbonate composition, which only gradually evolved into a sodium chloride composition (Kempe and Degens 1985).

Under other conditions, with hydrolysis and carbonation reactions acting on acidic rocks, e.g., silica-rich granite, solutions tend to have neutral to acidic compositions (Krauskopf 1979). Extensive hydrothermal reactions involving such silicic, acidic rocks, and chemical sedimentation on the seafloor under highly anoxic conditions could produce rocks similar to banded iron formations (composed of iron oxides, Fe–Mg–Ca-carbonates, and silica phases). Input of excess CO_2 from undersea volcan-

ism or venting of metamorphic fluids could result in a concentrated solution of carbonic acid and formation of CO_2-clathrate-hydrate.

Carbon dioxide might also be consumed by other abiotic and biogenic processes, such as the methanogenesis reaction utilized by some microorganisms:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O. \quad (11)$$
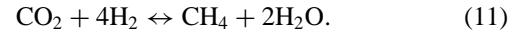
An important reaction on Earth leading to the formation of alkali lakes (Drever 1997) is

$$8SO_4^{2-}(aq) + 2Fe_2O_3(c) + 15C + 7H_2O$$
$$\leftrightarrow 4FeS_2(c) + 14HCO_3^- + CO_3^{2-}. \quad (12)$$
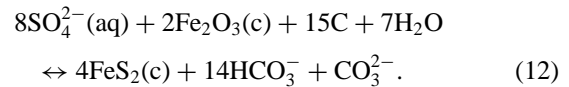
When dissolved carbonate is abundant, this type of sulfate–iron oxidation–reduction reaction removes S as sulfide and Ca and Mg as carbonates, leaving a predominantly Na–K carbonate system. Carbon in the above reaction is either graphite or organic carbon, which on Europa could be primordial organic material initially present in carbonaceous chondrite rock, acquired by impacts of comets or P- or C-class asteroids, or produced by biological activity. Graphite could have originated from thermal metamorphism of original carbonaceous matter.

Other reactions could occur among oxidized crustal and oceanic materials when reduced gases from below percolate into the ocean, for instance,

$$8SO_4^{2-}(aq) + 2Fe_2O_3(c) + 15CO_2(g) + 30H_2(g)$$
$$\leftrightarrow 4FeS_2(c) + 14HCO_3^- + CO_3^{2-} + 23H_2O. \quad (13)$$
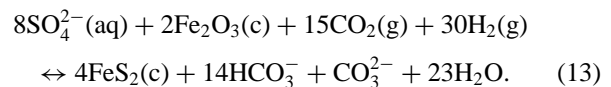
The equilibrium constant for this reaction is extremely large and positive, which would drive bicarbonate formation. The minerals that precipitate from alkaline systems are very much dependent on the assumed P_{CO_2} and brine composition. At $P_{CO_2} = 0.1$ atm for an alkaline carbonate brine (Na–CO_3–SO_4–Cl–H_2O) (G. M. Marion, in preparation), $NaHCO_3$ (nahcolite) precipitates across all temperatures from 298 to 273 K (and probably lower also). The pH of this system is 8.15 at 298 K and 7.87 at 273 K. At $P_{CO_2} = 3.5 \times 10^{-4}$ atm (current Earth value), trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) precipitates at 298 K, which gives way to natron ($Na_2CO_3 \cdot 10H_2O$) below 290 K. The calculated pH of this system at 298 K is 10.15 (cf. measured value is 10.1). If minerals such as natron precipitate on Europa, this would imply a low P_{CO_2}, high pH, and a high alkalinity system; nahcolite would imply more concentrated CO_2-rich systems at lower pH. Since CO_2 is potentially so plentiful on Europa—enough to generate P_{CO_2} exceeding tens of bars if it were not for reactions such as these and for clathrate formation—bicarbonates are likely. In the event that hydrothermal circulation of brine occurs in a basaltic crust, then reduced iron should also react with available carbonate ions to yield siderite, except under conditions of moderate to high acidity, in which case iron compounds

would likely be dissolved in the brine (and in which case we ought to see them at the surface).

Eruption of carbonate-saturated brines could result in explosive activity due to exsolution of carbon dioxide. Alternatively, interaction of liquid water with CO_2 hydrate (Stevenson 1982, Crawford and Stevenson 1988, Fagents *et al.* 2000) or hydrate diapirism could also lead to decomposition of the clathrate structure and explosive cryovolcanism.

3.5. Addition of Hydrocarbon Gases

Hydrocarbon gases may have been introduced to Europa over time by comet and asteroid impacts or may have been derived from Europa's primordial carbonaceous chondrite material (Anders *et al.* 1973) by thermal metamorphism and hydrothermal processes. The CI chondrite Orgueil contains 3.5 wt.% carbon, and CM Murchison contains 2.5 wt.%. The mass ratio of organic carbon compounds to bound water (including hydroxyl) exceeds $1:10$ and may approach $1:5$. Carbon in chondrites is mainly organic, but also forms carbonates, a graphitic phase, and other substances. The perspective of Anders *et al.* (1973) that chondritic carbonaceous materials, including organics, are the abiogenic products of solar nebula and possible presolar processes and subsequent aqueous chemistry is still the prevalent view. Anders *et al.* (1973) reviewed studies of CI and CM chondrites and gave some new analyses that revealed alkanes, aromatic hydrocarbons, fatty acids, porphyrins, and at least 18 amino acids. The more recent review by Cronin *et al.* (1988) tabulates 411 soluble organic compounds, including 74 amino acids, in carbonaceous chondrites. Shock and Schulte (1990) showed that many amino acids and other water soluble organics in carbonaceous chondrites can be produced by low-temperature (373 K) hydrothermal chemistry involving the reaction of simple gas mixtures (O_2, CO_2, and NH_3) with pyrene and other organics believed to occur in interstellar clouds. Reaction of CO_2, H_2O, and N_2 with basalt at 473 K achieves the partial reduction of N_2 and CO_2 and abiotic formation of a complex mixture of aqueous organic compounds (Shock 1990).

Carbon in chondrites is classified as a highly labile element comparable to argon, the alkali metals, and copper; most C is mobilized and lost by heating between 973 and 1273 K (Lipschutz and Woolum 1988), but some is far more readily mobilized. Cronin *et al.* (1988) indicates that about 30% of the organic carbon is in relatively labile forms ranging from C_1 to C_{20} compounds and 70% is in highly resilient macromolecular forms sometimes likened to kerogen. The most labile forms of organic carbon are mobilized by water leaching, and these include amino acids (60 ppm), dicarboxylic acids (>30 ppm), hydroxycarboxylic acids (15 ppm), alcohols, aldehydes, and nitrogen heterocycles. The remaining labile organic compounds are released by crushing or freeze–thaw disaggregation (trapped methane and heavier alkanes), or by leaching with acids, bases, benzene, or methanol (Cronin *et al.* 1988). A small amount of organics is released by heating at 423 K and much more at 573 K when pyrolysis occurs. Pyrolysis of terrestrial sedimentary kerogen

and bitumen, without added oxygen, produced similar results—large yields of methane and higher alkanes, carbon monoxide, hydrogen, and carbon dioxide between 473 and 573 K, with about an order of magnitude more gas released at 573 K than at 473 K (Tannenbaum and Kaplan 1985). Much but not all organic carbon would be volatilized during pyrolysis; some would be graphitized. Heating under oxidizing conditions also produces carbonates.

On the basis of data just summarized, we estimate that organic compounds amounting to about 100 ppm of Europa's mass would have been dissolved in the initial low-temperature brines during primordial differentiation. This low-temperature release of organics from Europa's interior would produce an average of about 1200 ppm of organic compounds in the primordial crust represented by model A5 in Fig. 3. This highly soluble organic matter corresponds to about 4.8×10^{18} kg, and if condensed over the whole surface of Europa it could form an organic layer about 100 m thick. Far greater quantities of carbonaceous fluids—easily two orders of magnitude more—would be produced and released into the crust later as Europa's interior warmed. By the time of core formation, most of Europa's juvenile carbon should have vented into the crust, where it generally would be trapped in the ice, dissolved in the ocean, or precipitated on the seafloor.

A comparatively small fraction of Europa's organics would be dissolved in any ocean that exists; most would be sequestered in various solid or immiscible liquid phases. Methane and other hydrocarbon gases (up to isopentane) form solid ice-like clathrate hydrates under a wide range of high pressures and low temperatures (Sloan 1998).

3.6. Hydrothermal Processes in the Seafloor Environment

If hydrothermal circulation through a basaltic subcrust is significant on Europa, then terrestrial oceanic field data and lab experiments offer a good basis for prediction of the chemical changes in the brine. Lab experiments with artificial hydrothermal systems and studies of altered basaltic rocks and seafloor hydrothermal vent fluids are in good agreement as to the basic processes. For hydrothermal interaction at low water : rock ratios near unity, tens to a couple hundred megapascals, and temperatures between 473 and 773 K—i.e., conditions appropriate to europan seafloor hydrothermal processes driven by basaltic volcanism—some expected trends (Bischoff and Dickson 1975, Mottl and Holland 1978, Seyfried and Janecky 1985, Von Damm 1995, Resing and Sansone 1999) are (1) rapid and almost complete loss of dissolved sulfate due to (a) precipitation of anhydrite or gypsum and (b) reduction of sulfate (with sequestration of sulfur as metal sulfides), and concomitant leaching of calcium (and reprecipitation as anhydrite or gypsum); (2) extremely rapid loss of Mg from solution due to a combination of sulfate reduction and sequestration of Mg by talc, serpentine, tremolite, and other hydrated or hydroxylated alteration phases; (3) much slower loss from solution of dissolved sodium, which reacts to form sodium feldspars and feldspathoids; (4) leaching and gradual enrichment in the solution of Si, K, CO_2, and various

trace constituents such as B and Ba; and (5) marked decrease of pH (greater acidity). At low levels of reaction, magnesium is removed from solution and balanced by calcium uptake; the potential exists to produce a Na–Ca–SO$_4$–Cl brine, where the major cation by far is Na. Calcium increases in heavily reacted brines, but its abundance is sharply limited by anhydrite/gypsum solubility; however, if sulfate is eliminated from the system and calcium continues to be leached, then the possibility exists to develop Na–Ca–Cl brines. Many transition metals—most importantly iron—also are mobilized, then redeposited as sulfides under conditions characteristic of Earth's seafloor hydrothermal systems; as dissolved species the transition metals are never very abundant unless there is extraordinary acidity. The abundance of silica is also sharply limited by solubility unless acidity can reach extraordinary levels. Hence, iron, calcium, and silica are expected to be minor dissolved constituents—but possibly very important in the volatile subcrust—unless brine evolution progresses in ways not encountered on Earth.

Except at very high degrees of reaction and high salinity, sodium, potassium, and chlorine are nearly conserved in hydrothermally reacted brines. Thus, Europa's ocean could resemble Earth's if magnesium and sulfate are eliminated or reduced from levels in typical chondrite brines. There is no evidence for a sodium chloride ocean on Europa, but rather there is good indirect evidence for abundant sulfate on Europa's surface (and presumably the interior), suggesting that terrestrial style hydrothermal processes do not occur or at least do not exert a dominating chemical influence. There are several possible reasons for this. (a) Europa might lack the degree of heat flow needed to drive hydrothermal circulation; considering evidence for recent geologic activity on Europa and perhaps a very thin icy shell, and also considering tidal heat generation, this explanation seems unlikely. (b) The seafloor is not assuredly made of rocks containing ferroan silicates; a thick accumulation of bedded salts or sulfur on the seafloor, as modeled below, would not allow the sulfate reduction process and uptake of magnesium to operate as it does on Earth even if hydrothermal convection is very strong. (c) Perhaps hydrothermally driven sulfate reduction does occur on Europa, but the large quantity of sulfate and other alteration reactants effectively filled cracks and pore spaces with alteration products, thus sealing the rock from further alteration without consuming all the sulfate. (d) Europa might possess a sulfur cycle—inorganic or biologically mediated—that returns precipitated sulfide to sulfate form.

3.7. Silicate Dehydration

We considered above thermal dehydration and incongruent melting of sulfates, production of sulfur and carbon gases by thermal metamorphism and decomposition of sulfates, carbonates and organic substances, and hydrothermal processes in the seafloor environment. Another important high-temperature process is dehydration of hydrated and hydroxylated silicate minerals in Europa's rocky interior (Bunch and Chang 1980, Barber

1985, Zolensky and McSween 1988). Carbonaceous chondrite meteorites contain some of the same hydrous silicate phases known in shales and other sedimentary clay-rich and metamorphic rocks on Earth—tremolite, talc, chlorite, serpentine, montmorillonite, etc.—although in detail there are peculiar aspects of some phyllosilicate phases in chondrites. In addition, they contain large amounts of heavily hydrated salts, such as epsomite, hexahydrite, bloedite, and gypsum (Fredriksson and Kerridge 1988). The total amount of H in the CI chondrite Orgueil is listed by Anders and Grevesse (1989) as 2.02% by mass, equivalent to just over 18% by mass H$_2$O if all H was in the form of water. Some H is in the form of organics, but as the organics are heated, they, too, produce some water. This large amount of water can be understood considering the water content of major phases that make up Orgueil (e.g., septechlorite, 9.7% water; serpentine, 13%; montmorillonite, 22%; epsomite, 51%). Boato (1954) gave a somewhat drier estimate of 12% water in CI chondrites. CM chondrites are less heavily altered than CI chondrites and are drier—typically about 6% water by mass. CV and CO chondrites—even less altered—contain much less water still, but if aqueous reactions are run fully, they would also have water contents similar to Orgueil's (Zolensky et al. 1989).

As Europa's interior is heated to metamorphic conditions, we expect that a stepped sequence of dehydration will occur with formation and expulsion of high-temperature fluid phases, which ultimately should be discharged into the ocean or frozen crust. Although details of the metamorphism of chondritic rocks no doubt would be different than metamorphism of terrestrial rocks, qualitatively the problem is exactly similar. Metamorphism of terrestrial carbonate-bearing ultramafic rocks (Winkler 1979) is a fair analogy to metamorphism of chondrites. At pressures in the vicinity of 100–500 MPa, i.e., in the range of most of Europa's rocky mantle volume, significant dehydration of silicate phases in ultramafic systems begins around 573 K and is virtually complete by 1073 K. For example, in terrestrial ultramafic metamorphic systems, the first major step in dehydration is represented by the breakdown of serpentine between 573 and 773 K, whereupon very H$_2$O-rich and CO$_2$-poor fluids are generated. Another major step is that represented by the breakdown of talc anywhere between 820 and 1000 K for pressures between 100 and 500 MPa and CO$_2$-bearing fluids. The final major stage of dehydration of these rocks is represented by the breakdown of tremolite, typically between about 1000 and 1073 K. In general, metamorphism on Earth results in large water yields at low metamorphic temperatures and fluids that are progressively more enriched in CO$_2$ at higher temperatures. The same is likely to be true in the metamorphism of chondrites and Europa's rocky mantle.

The total amount of water liberated by metamorphic reactions of Europa's interior is likely to be prodigious, if the carbonaceous chondrite petrologic model is any guide. CI chondrites contain more water (including hydroxyl, which is released as water during metamorphism) bound to silicate phases than is bound to salts; CM chondrites do not contain so much silicate-bound

water, but it is still considerable. Hence, the late addition of large amounts of metamorphic water to the salty–icy crust and ocean can be chemically and geophysically very significant. Venting of carbon and sulfur gases, discussed above, occurs over similar metamorphic temperature intervals. Hence, these late-stage fluid additions are apt to be multicomponent aqueous fluids, which are probably enriched also in silica, iron, aluminum, and other constituents.

3.8. Alteration in the Surface Environment

Materials exposed on Europa's surface must be affected by its environment. Although the resulting chemical alteration is only superficial, it has importance for the interpretation of reflectance spectra. Surface pressure and temperature conditions may cause dehydration of salts and amorphization of ice. Europa's tenuous atmosphere does not impede ionizing ultraviolet radiation and energetic charged magnetospheric particles, thus allowing formation of free radicals and appearance of new chemical species that otherwise would not exist. Alteration products might not be only superficial; Carlson *et al.* (1999) have suggested possible burial and endogenic recycling of exogenically produced alteration products.

As mentioned before, NIMS data indicate a high hydration state of Europa's nonice minerals (McCord *et al.* 1998a, 1999a,b; Carlson *et al.* 1999), which suggests that evaporation has not been very effective except perhaps in removing or reducing the amount of ice. When hydrated salts were first suggested, Dalton and Clark (1998) countered that the low atmospheric pressure of the surface may induce dehydration of those minerals. In response, several researchers (McCord *et al.* 1999a,b; Kargel 1999a; Prieto *et al.* 1999; Zolotov and Shock 2000c) have produced theoretical arguments and lab data indicating a stability of hydrated salts greater than that first considered by Dalton and Clark (1998). Nevertheless, hydrate stability and dehydration remains an important issue. Salts appear on Earth with several hydration states, depending on temperature and water vapor pressure, and cycling of hydration state as relative humidity changes is sometimes observed (Keller *et al.* 1986). There are some published data on vapor pressure of both water ice and hydrated salts (Wilson 1921, Clifford *et al.* 1923, Carpenter and Jette 1923, Baxter and Cooper 1924, Matsui *et al.* 1927, Keller *et al.* 1986). These data and estimates of surface conditions on Europa show that the low temperature ought to inhibit the dehydration of the hydrated salts. Accurate vapor pressure data are not available for salts at europan temperatures, and so consideration of this issue requires extrapolation of high-temperature data (Fig. 5).

At ordinary temperatures the water in hydrated salts is bound more tightly than water molecules in ice and liquid water, resulting in vapor pressures lower than that of ice and liquid water. This situation probably persists to low temperatures, although it is not assuredly the actual case for all salts (Fig. 5). The expected situation, wherever ice is present on Europa, is that there should exist a local water vapor pressure that would tend to cause salts to exist in their maximum hydration states. However,
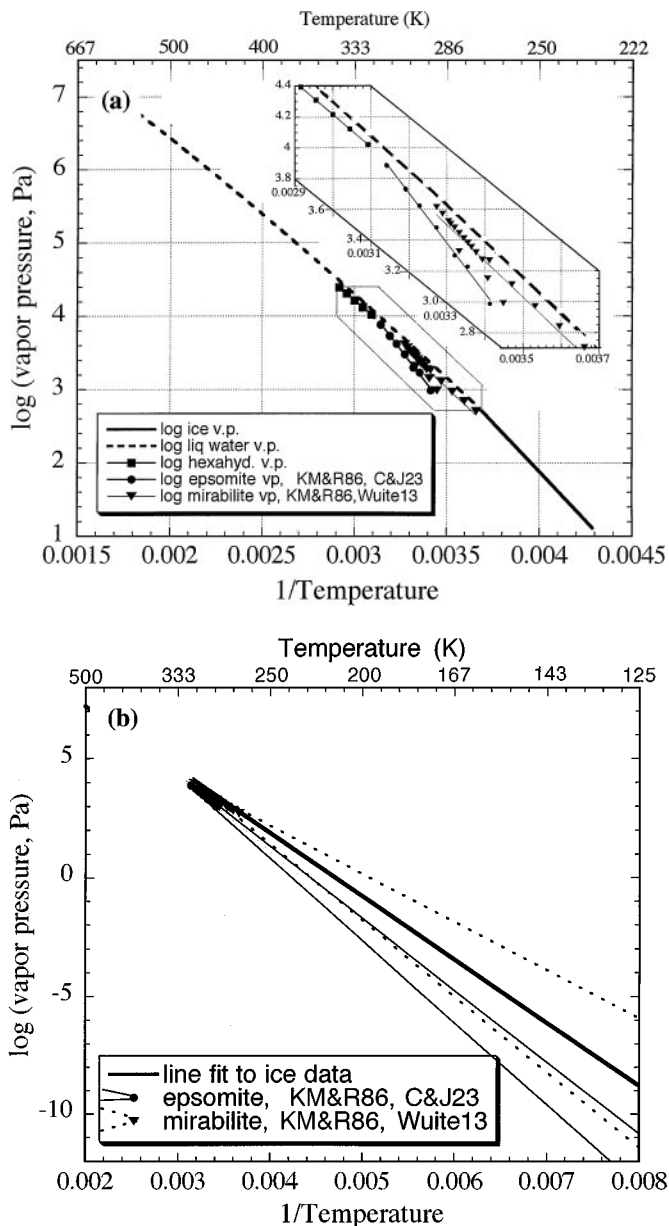

FIG. 5. Water–vapor pressures of $MgSO_4 \cdot 7H_2O$, $MgSO_4 \cdot 6H_2O$, $Na_2SO_4 \cdot 10H_2O$, water ice, and liquid water. (a) Data of Carpenter and Jette (1923) and Keller *et al.* (1986). (b) Extrapolations to low temperatures; error envelopes determined by selectively eliminating outlier points from the least-square linear fits.

ice is not present everywhere on Europa, according to McCord *et al.* (1998b, 1999a); the nonice terrains have a low albedo, and thus are warmer than bright ice terrains. Dehydration or partial dehydration of salts in those regions is possible. New lab data presented by McCord *et al.* (1999b) indicate that even under ultrahard vacuum conditions—where the slightest water vapor is continuously pumped away—magnesium sulfate hydrates would remain metastable for millions of years at temperatures less than 160 K, i.e., over the entire surface of Europa, except

where heated by very shallow brine intrusions (Fagents *et al.* 2000); natron remains hydrated for millions of years at temperatures less than 130 K, i.e., over much but not all of Europa's surface; and mirabilite remains hydrated for millions of years only at temperatures less than 100 K. Thus, magnesium sulfates generally should remain hydrated across nearly all of Europa's surface, but mirabilite generally would dehydrate rapidly except in Europa's polar regions.

Amorphous water ice may be produced by low-temperature (<110 K) quenching from the liquid state, by rapid condensation from water vapor, or by severe radiation damage to crystalline ice (Hobbs 1974, Leto *et al.* 1996, Delitsky and Lane 1998, Hansen and McCord 2000). Water ice normally exists in its hexagonal Ih crystalline phase above about 150 K and as cubic Ice Ic below 150 K. Europa's surface temperature is mainly between around 80 and 130 K (depending on latitude, time of day, and albedo), so amorphous and cubic ice phases are possible when water is frozen on the surface. Interior temperatures and local equatorial surface temperatures in low-albedo terrains are warmer, and freezing may occur slowly in the interior, so hexagonal ice is also possible on Europa. Rapid cooling of brines also produces metastable supercooled and glassy states (Kargel 1991, Hogenboom *et al.* 1995). The reflectance spectra of amorphous briny solid materials are not known but may be different from those of well-crystallized salt hydrates—e.g., absorption bands due to H_2O may be even broader than in the crystalline sulfate hydrates, and fine structural details of the absorption bands may be obscured.

Plasma effects on Europa's surface, especially implantation of energetic magnetospheric sulfur ions derived originally from Io, were thought to be the cause of longitude-correlated ultraviolet albedo variations in *Voyager* and *IUE* data (Lane *et al.* 1981, Johnson *et al.* 1988). Latitude-dependent variations in spectral reflectance may be associated with ultraviolet photolytic alterations. Plasma bombardment and ultraviolet irradiation can induce important changes in salt chemistry and stability. The chemical changes caused by radiolysis and photolysis are very similar, except that the depths of penetration of these ionizing radiations differ greatly (Gerakines *et al.* 2000). Analysis of improved spectra from the Hubble Space Telescope added a wrinkle to the radiolysis/photolysis explanation of Europa's reflectance, according to Noll *et al.* (1995), who favored an internal control of SO_2 venting and deposition. Hendrix (1998) and Hendrix *et al.* (1998), using Galileo UVS spectra, confirm a combination of exogenic and geologic controls on the distribution of UV absorbers but interpret Europa's UV absorptions as due to a more complex set of volatiles that include S–O compounds. The S–O compounds may include the sulfates inferred by McCord *et al.* (1998a) and do not necessarily include SO_2.

Electron bombardment at europan doses effectively destroys salts of singly valent alkali metals, e.g., sodium and potassium sulfates; hydroxides, free metals, and sulfur dioxide are produced in place of sulfates (Orlando *et al.* 1999). Electron excitation is orders of magnitude less capable of generating equivalent

changes in salts of doubly valent magnesium and calcium (*ibid.*). The relative vulnerability of sodium and potassium salts to radiolytic destruction is cited as the explanation for Europa's sodium and potassium atmosphere (Brown 1999).

Plasma and UV radiation also may cause amorphization in water ice, and doubtless radiation affects hydrated salts also. Sulfuric acid hydrate, according to one interpretation, owes their existence to a radiolytic sulfur cycle (Carlson *et al.* 1999). The acid itself is also affected by radiation, but the yields favor a high equilibrium abundance of H_2SO_4 and minor amounts of many other species, including O, O_2, O_2^-, H_2O_2, OH, HO_2, SO, $S(OH)_2$, SO_2, SO_3, and S_x (Carlson 2000). Besides producing dislocations and color centers in ice, radiation acting on sulfates—whether sulfuric acid or sulfate salts—may produce free radicals and result in formation of elemental sulfur, polysulfur oxides, and other colored substances (Carlson *et al.* 1999). Short-chain elemental sulfur and polysulfur oxides produced by irradiation of sulfur-bearing ice is the cause of the reddish/brown color of nonice hydrated terrains on Europa, according to Carlson *et al.* (1999). The high concentration of colored compounds and hydrated material along fractures, rifts, craters, shallow diapiric structures, cryomagmatic intrusions, and cryovolcanic deposits is best explained by endogenic mechanisms that control the distribution of salts and other sulfurous compounds that can then yield the colored photolytic and radiolytic products.

3.9. Influences of Elevated Pressure on Phase Equilibria and Brine Evolution

The pressure at the base of a frozen Europan crust made of pure ice or a pure water ocean some 70–170 km thick, consistent with the *Galileo* gravity data (Anderson *et al.* 1998), would be between 84 and 205 MPa. The higher pressure (corresponding to the thickest possible ice crust) is comparable to the ice I/ice II or ice I/ice III transition pressure, which is around 207 MPa (Bridgman 1912). The pressure at the base of Europa's ice-saturated layer (the ice crust or frozen eutectic/peritectic crust), according to the models in Fig. 3, varies with the particular model, but it is around 140 MPa if this layer is frozen completely. We do not presume that our chemical models or the *Galileo* gravity models are so well constrained that a higher pressure and the possible existence of a stable high-pressure ice polymorph is ruled out, but this seems unlikely unless it is a small amount at the very bottom of the ice layer. The system H_2O–$MgSO_4$ does not exhibit high-pressure phase transitions until far higher pressures are attained (Bridgman 1948a,b; Livshits *et al.* 1963; Hogenboom *et al.* 1995; Sotin *et al.* 1999). Thus, it seems doubtful that Europa's icy shell would contain stable high-pressure polymorphs of ice or magnesium sulfate hydrates. However, pressures in the deep interior of Europa would have greatly exceeded the minimum pressures required for high-pressure phase transitions in solid salt hydrates. Hence, high-pressure polymorphs may have been important during Europa's primordial differentiation. As yet there are not enough high-pressure phase

equilibrium data to make useful constraints on the effects that this may have had on the course of differentiation.

High-pressure polymorphs of ice and salt hydrates might exist metastably in impact crater ejecta due to shock effects, much as high-pressure shocked silica phases occur in terrestrial impact craters. In general, the lower pressures required for solid-state phase transitions in ice and salt hydrates compared to silicates means that impact-shocked high-pressure phases might be far more abundant on Europa than on Earth.

Although high-pressure crustal phases of ice and salts are not likely to exist stably on Europa today, the pressures existing within Europa's crust are sufficient to induce considerable changes in solid–liquid phase equilibria. Even in Earth's ocean, where maximum pressures barely exceed 100 MPa and more typical seafloor pressures are half that, pressure has a controlling influence on carbonate equilibria. Calcium carbonate is strongly supersaturated in surface water of Earth's oceans but strongly undersaturated in deep ocean water (Anderson and Malahoff 1977), a fact that has profound consequences for the depth-dependent mineralogy of marine sediments (Acker et al. 1987). Hogenboom et al. (1995, 1999) found large pressure-induced shifts in the eutectic liquid compositions for the binary systems H_2O–$MgSO_4$ and H_2O–Na_2SO_4; they predicted that the ternary system H_2O–$MgSO_4$–Na_2SO_4 would exhibit a eutectic with a Na : Mg ratio increasing rapidly with pressure at least up to 200 MPa. If so, this would have consequences for the internal chemical structure of Europa's crust and ocean and for its surface composition. For instance, ternary eutectic brines produced near the base of Europa's crust would possess Na : Mg ratios 2 to 3 times greater than those of low-pressure eutectic brines (Hogenboom et al. 1999). Such effects are not considered in the models presented here.

4. GEOLOGIC IMPLICATIONS

The high-resolution image data obtained by *Galileo* for many different areas on the surface of Europa reveal a host of geological features and structures. High-spatial-resolution and low-spectral-resolution imaging data is complemented by high-spectral-resolution and low-spatial-resolution NIMS data. Together, this information can be used to constrain the processes operating in the crust of Europa and to distinguish among the several plausible paths for the evolution of the outer ice layer. This information is twofold. First, such features provide insight into the nature of processes in the recent geological past (e.g., does tectonism indicate expansion, does volcanism involve a buoyant and/or volatile phase, do circular features represent diapirism, does chaos involve a very thin brittle layer overlying an ocean, are impurities in the upper crust associated with specific processes?). Secondly, the sequence of these features and structures can provide information on the evolution of these processes (e.g., is the crust thickening with time, has there been a change in style of convection and resurfacing with time, is there evidence of compositional evolution?). One purpose of this paper is to set the stage for further detailed discussions of these issues.

Initial results from *Galileo* (Greeley *et al.* 1998a,b; Head *et al.* 1999a) reveal the following features and stratigraphic relationships:

(1) Lenticulae (elliptical pits, dark spots, and domes 7–15 km in diameter and spaced about 5–20 km apart) are common and make up much of the texture that characterized mottled terrain at *Voyager* resolution. Diapirism (Pappalardo *et al.* 1998), as well as melt-through of a very thin ice layer (Greenberg *et al.* 1998), have been proposed to explain these features. Lenticulae are observed to cross-cut most other geologic features and structures (e.g., Spaun *et al.* 1999, Prockter *et al.* 1999a) and are some of the youngest features on Europa.

(2) Chaos occurs as irregularly shaped regions tens to over a hundred kilometers in diameter (e.g., Carr *et al.* 1998, Spaun *et al.* 1998, Greenberg *et al.* 1999, Kortz *et al.* 2000), formed by the destruction of preexisting lineated plains, and consists of a distinctive fine-textured matrix and polygonal blocks of background lineated plains that have been rotated, tilted, and translated. Two end-member models for the formation of chaos involve crustal melt-through from an underlying ocean (Greenberg *et al.* 1999) or disaggregation of a thin, brittle lithosphere by ascending solid-state warm-ice diapirs (Pappalardo *et al.* 1998). According to Collins *et al.* (2000), a liquid or partly molten substrate is probably required to form the chaos features. The crustal melt-through model appears to lack sufficient energy to achieve melt-through according to the conventional melt-through model, such that partially molten diapirs may be required (Collins *et al.* 2000). Most chaos regions modify virtually all other features (only a few post-chaos grooves have been observed), and thus is one of the youngest feature types on Europa, apparently similar in age to lenticulae. Greenberg *et al.* (2000a) interpret some degraded chaos regions as much older than others, raising the possibility of a more complex or recurrent geological cycle.

(3) Bands and wedges are regions in which separation and total replacement of background plains have occurred by lateral movement in a manner similar to seafloor spreading (Sullivan *et al.* 1998, Prockter *et al.* 1999b, Tufts *et al.* 2000); strike-slip movment is common (Hoppa *et al.* 1999, Tufts 1996, Prockter *et al.* 2000), and internal structure is often related to distribution of stress due to accomodation to irregular and nonorthogonal separation. Recent evidence indicates that long-wavelength compressional folds affect some bands (Prockter and Pappalardo 2000). Bands and wedges often occur in the intermediate part of exposed europan history, cutting and separating background plains but being crossed by ridges and disrupted by chaos and lenticulae (e.g., Prockter *et al.* 1999a).

(4) Ridges consist of several different types of features (Greeley *et al.* 1998b, Greenberg *et al.* 1998, Pappalardo *et al.* 1998, Head *et al.* 1999b) that extend along-strike for hundreds of kilometers, show different orientations as a function of time in individual areas, and may indicate an evolutionary sequence; theories of origin for the positive topography (see review in Pappalardo *et al.* 1999) include constructional volcanism, linear diapirism, flexure, and intrusion-related deformation. Associated

reddish deposits have been explained by rift-controlled cryovolcanism, by brine mobilization, or by metamorphic dehydration related to heating due to shallow brine intrusions. A review and new evaluation of eruptive mechanisms was recently provided by Fagents *et al.* (2000).

(5) The morphology of cryovolcanic flows varies widely. Smooth plains (Greeley *et al.* 1998b) consist of relatively low-albedo regions appearing to be either emplaced in a fluid fashion (Thomas and Wilson 2000) or partly mantling preexisting terrain (e.g., Head *et al.* 1998). In part these appear to be cryovolcanic in origin and are observed to postdate plains, bands, wedges, and ridges; at least in one area smooth plains are modified by (hence, predate) chaos and lenticulae. One peculiar mitten-shaped lenticula- or chaos-like feature appears to have a cryovolcanic/upwelling origin involving flow of a very viscous liquid or partly molten slurry that formed a towering extruded mass comparable to venusian pancake domes and terrestrial dacite lava domes (Figueredo *et al.* 2000). The very fact that most of Europa's surface is criss-crossed by tectonic lineaments traceable for hundreds to thousands of kilometers shows that (1) cryovolcanic flooding has not been a dominant process since the time of formation of Europa's icy shell (2) or most original cryovolcanic surfaces have been thoroughly overprinted by tectonic features. The relative rarity of cryovolcanism probably attests to the buoyancy of the icy shell.

(6) Background ridged plains consist of terrain highly disrupted by younger ridges, wedges, lenticulae, and chaos. They occur virtually everywhere and form a background of terrain composed of bands, wedges, ridges, and other features in various states of degradation. These plains are the oldest unit in the stratigraphic sequence in each area mapped. Unknown is whether background ridged plains define a specific and valid geologic unit or whether they simply represent our inability to deconvolve the complex record in the early history of each region.

(7) Impact craters, which are relatively uncommon on Europa (Moore *et al.* 1998), can serve as stratigraphic markers (Pwyll and its extensive rays) and as probes to the interior (Tyre and Mannanan). Pwyll rays are superposed on Conamara Chaos and no examples of highly dissected impact craters have yet been reported, although Mannanan deposits are cut by several ridges.

(8) Geologic units: Mottled terrain appears to owe its distinct color and texture to disruption and discoloration accompanying the formation of chaos and lenticulae at the expense of background ridged plains (Greeley *et al.* 1998b, Greenberg *et al.* 1999, Head *et al.* 1999a, Pappalardo *et al.* 1999).

(9) Surface age: Impact crater size–frequency distributions have been interpreted in two very different ways such that the surface of Europa is typically 0.7–2.8 Gyr (Neukum *et al.* 1998) or <0.1 Gyr (Zahnle *et al.* 1998). On the basis of the review in Pappalardo *et al.* (1998) the latter interpretation seems most likely.

In summary, these features, their stratigrapic realtionships, and their ages, indicate that the crust of Europa has been completely resurfaced in the recent geological history, and that this period appears to consist of three phases, during which the following types of activity dominated: (1) background ridged plains formation, (2) band, wedge, and ridge formation, and (3) chaos and lenticulae formation, with some associated cryovolcanism. Interpretation of a large plains area by Greenberg *et al.* (2000a) as an ancient region of heavily modified chaos, if correct, adds a further wrinkle to this three-phase history, perhaps suggesting that remnants of a prior cycle of resurfacing may exist.

Surface geologic features, their interpreted origins and rheological implications, strongly suggest a thin ice lithosphere and a steep near-surface thermal gradient, but at present we cannot distinguish between the presence of (a) a near-surface liquid layer and (b) warm, ductile ice and only local partial melting in a thicker layer. In addition, the apparent change in the characteristics of surface features with time suggests that there may be evidence for thickening of the icy shell with time (e.g., bands and wedges during times of earlier, thinner lithosphere, followed by isolated fractures, and by diapirism as the layer thickened). In addition, or alternatively, heat loss and layer thickness could vary regionally. Present geological analyses are thus focused on several questions: (1) Are these three stages indeed distinctive? (2) If so, how much overlap occurs? (3) Is this sequence seen globally? (4) Do such stages represent a linear geologic progression, or could there be repetitive cycles? (5) Did the latest progression of events, and perhaps each cycle, begin with catastrophic global resurfacing, and if so, what is the nature of this process? (6) What occurred during the first 50–98% of Europa's crustal history? (7) Does the apparent thinness of the outer brittle layer imply a present ocean, and what is its depth and composition today?

How do our models link to these observations and what future work might be productive in further establishing these links and distinguishing among evolutionary models? Evidence of cryovolcanic activity is not common on the surface; this can largely be accounted for by the buoyancy of solid water ice and the difficulty of erupting eutectic brines through eutectic solid crust without involving exsolved gases (Wilson *et al.* 1997, Fagents *et al.* 2000). But some models may favor production of positively buoyant magma. For example, in model A5 (Fig. 3), partial remelting of the bottom of the pile of hydrated salts could form a eutectic brine that is buoyant all the way to the surface. The absence of common and widespread cryovolcanism may be an argument *against* this specific model or may simply indicate that the solidus temperature is rarely achieved.

Regional variation in Europa's geologic styles of surface modification might suggest lateral variations in heatflow and/or thickness of the frozen layer. Stevenson (2000) argued that such thickness variations could not be very significant due to the propersity of ice to flow glacier-style. However, he did not consider rheological effects of an impure crust or of an impure ocean that would cause colder temperatures and a stiffer ice rheology, so we consider lateral thickness variations to be an open issue.

Our models support the possible formation of abundant clathrate hydrates and gas-charged brines due to subcrustal/suboceanic venting of CO_2, SO_2, and hydrocarbons. Stevenson

(1982), Crawford and Stevenson (1988), and Fagents *et al.* (2000) have considered ways in which clathrates might interact with liquid water on Europa and other icy satellites to produce explosive cryovolcanic eruptions. Might clathrates be a common crustal material on both Mars and Europa (and also certain areas of Earth), and thereby play similar geologic roles in the formation of a wide variety of features, including chaos (Milton 1974, Kargel *et al.* 2000)? What similarities and differences would be exhibited by clathrate-related processes on Europa, Mars, and Earth?

Another aspect of our modeling that merits further investigation is the degree of homogeneity of Europa's surface salt assemblages. Early interpretations (McCord *et al.* 1998a, Fanale *et al.* 1999) emphasized the apparent homogeneity as deduced from lack of much variation in the shape and depth of hydrate bands in NIMS spectra of nonice regions. More recent analysis has pointed out possible subtle variations in the fine structure that could relate to compositional differences. Is the salty surface of Europa representative of a homogeneous peritectic or eutectic interior layer, or do compositional gradations exist that might relate to compositional brine evolution produced by progressive freezing of an ocean or of briny diapirs? The possible formation of metastable salt phases of low hydration state (Kargel 1991, Prieto *et al.* 2000) allows for possible subsequent hydration reactions and attendant volume changes that may drive crustal tectonics (Hogenboom *et al.* 1997). How might such volume changes be reflected in the geology of Europa?

There are likely to be several mechanisms for the segregation of ice and salt phases and the production of interesting features and structures. For example, fractional crystallization of an ocean or of smaller intrusive brine bodies could involve "squeeze-out" of interstitial brines during crystallization. Attendant process might be metamorphic recrystallization (analogous to formation of mineral bands in gneiss and formation of coarse crystalline glacier ice from snow) or boiling of brine eruptions with recondensation of water vapor. Heating could cause brine mobilization, collapse of near-surface ice (e.g., Head and Pappalardo 1999), and dehydration of surface and interior deposits (Fagents *et al.* 2000). Vapor–solid fractionation could also occur, with long-term, low-temperature evaporation producing evaporitic salt accumulations in some areas and frost recondensation elsewhere.

Solid-state diapirism might accompany the evolution of the crust. This might involve the ascent of segregated ice and the descent of salts. Further development of our models can yield predictions on the sizes of ice masses or salt layer thicknesses and predictions about the development of Rayleigh–Taylor instabilities in these layers on geologic time scales. Predictions of variations in temperature and composition will provide important information in which to assess observational data and help distinguish among the several models (e.g., Pappalardo *et al.* 1998, Rathbun *et al.* 1998, Spaun *et al.* 1999, McKinnon 1999). In addition, crustal thermal and compositional layering will certainly influence the style of convection and whether it might be layered or inhibited, for example. Compositional information

predicted by models and interpreted from measurements will also have a major influence on distinguishing among the origin of features and different paths of evolution. For example, traces of sulfuric acid occurring as a solid solution within ice single crystals (even less than 11.5 ppm) can induce a drastic lowering of the power-law stress exponent, the effective viscosity, and other rheologic properties (e.g., Baker *et al.* 1999, Trickett *et al.* 1999). Many other naturally occurring trace impurities have similar softening effects on ice. In Earth's polar ice sheets sulfuric acid and salts accumulate at grain boundaries and triple junctions (Fukazawa *et al.* 1998), where the impurities stabilize low-temperature liquid films. These films permit enhanced migration of water molecules and theoretically should allow increased rates of strain recrystallization, thus increasing regelation and flow rates. Thus, soluble impurities (consistent with those predicted by our models) can soften ice by at least two distinct mechanisms. This is expected to cause enhanced "solid-state" deformation rates, making diapirism and solid-state ice extrusions more likely and more rapid than without softening due to soluble impurities.

Many gases expected to percolate from the mantle to the crust are clathrate-hydrate-forming substances. On Earth, the buoyancy of hydrocarbon gases results in their accumulation in anticlinal traps created by salt diapirs, an aspect that has great economic importance. In seafloor sediments methane-rich clathrate hydrates commonly form by the combination of high hydrostatic pressures, low temperatures, high concentrations of hydrocarbon gases, and existence of abundant water (Sloan 1998). Diapiric structures, mud volcanoes, and chaotic terrains with complex faulting, slump, and slide structures are typical of some clathrate-rich seafloor terrains on Earth, such as those in the northern Gulf of Mexico (Roberts and Aharon 1994; Roberts and Carney 1997; Sassen *et al.* 1998, 1999a). A spectacular glacier-like mass flow, some 1500 km^2, on the Mediterranean seafloor, might be related either to deformation of clathrate hydrate or to sediment fluidization related to breakdown of the hydrate phase (Woodside *et al.* 1998). Extrusion of clathrate hydrates or development of clathrate mounds around sites of fluid venting are not uncommon occurrences in some areas of the seafloor where hydrocarbons vent to the deep, cold sea floor. Clathrate hydrates and/or hydrocarbon venting also appear to be associated with development of pingo-like broad-based mounds in terrestrial permafrost (Kargel and Lunine 1998). Similar processes and features may occur on Europa's seafloor and perhaps on the surface of the icy shell.

On Europa the buoyancy of free hydrocarbon gases or of the hydrate phases could result in their concentration in traps at the lower surfaces of the icy shell, in anticlinal traps created by ice plutons, salt hydrate domes, or fold structures within the frozen crust, or in subcrust beneath the ocean. Alternatively, ascension of gases through fractures may result in formation of dikes or veins of gas hydrates cutting through the icy shell, possibly contributing to the formation of structures such as triple bands. If gases are trapped at the base of the icy shell, then gas hydrates may develop a lower chemical layer of a stable icy shell, with ordinary ice I dominating the upper layer. However, if the icy

shell is enriched in salts, then gas hydrate diapirism is possible. Methane hydrate has a low density, 910 kg m^{-3} at 273 K (Davidson 1983), so that hydrate diapirism could occur readily in the icy shell. If the hydrate phase contains a significant fraction of high molecular weight gases such as CO_2 and SO_2, then the hydrate has a much higher density (e.g., $\sim$1100 kg m^{-3} for pure CO_2 hydrate; Davidson 1983), so that diapirism involving these hydrates should be inhibited or may occur only in areas of the icy shell that are composed of extremely salty ice, e.g., a eutectic ice–salt mixture. Decomposition of clathrates because of crustal heating or depressurization in ascending diapirs could result in enormous volume changes, attendant formation of collapse structures, and possible explosive cryovolcanic activity. Escape and evaporation of hydrocarbon gases near clathrate domes may produce residues of heavy hydrocarbons, which could yield detectable organic tholins by solar UV radiolysis. It is possible that such processes contribute to the formation of lenticulae (pits, spots, domes, and microchaos).

In this and all prior work it has been assumed that any europan ocean is homogeneous and in thermodynamic equilibrium throughout—not an implausible situation, but also not necessarily correct. Experience with terrestrial surface brines in warm- and cold-climate desert playas (Last and Schweyen 1983), in ice-covered Antarctic lakes (Torii *et al.* 1975), in coastal marine sabkhas (Brantley *et al.* 1984), and in stratified brine pools on the seafloor (Wallmann *et al.* 1997) indicates that inhomogeneous brines are very common. Strong vertical gradients may develop in salinity, anion and cation ratios, temperature, and density. Stratified brine pools can be amazingly stable against mixing, because normal thermally driven convection is inhibited by density stratification. Heat transfer and compositional homogenization in such situations may occur by diffusion or by forced convection due to tidal or wind-driven water currents or crystal flotation/settling. Since heat input to the base of the brine pool may initially exceed the rate at which heat can be transferred upward, a strong vertical temperature gradient is commonly achieved. In situations where the bottom of the brine pool is covered by salts, any rise in the temperature of the basal layer generally causes further dissolution, thus accentuating the density stratification. In some ice-covered and ice-free Antarctic lakes of the Dry Valleys, heating is by solar radiation and the geothermal heat flux; temperature characteristically rises with depth—the dense bottom water of Lake Vanda reaches 298 K (Torii *et al.*1975). Density-stratified brine lakes in Africa, such as Lake Nyos, accumulate volcanogenic CO_2 to extreme levels. Destabilization and degassing of these stratified lakes can be catastrophic, with exceedingly violent and deadly limnic eruptions (Ladbury 1996).

On Europa, the possibility exists for far more extreme degrees of density and thermal stratification. Any process that can destabilize Europa's oceanic brine column—especially if it produces a strong convective plume or catastrophic turnover—could lead to a heat pulse at Europa's surface or at the base of the frozen crust. Destabilizing processes could include lithospheric fracturing and sudden local degassing, comet impacts, or abrupt

termination of heating at the bottom of the ocean and partial crystallization of bottom water. Geologic activity could ensue, possibly including solid-state convective diapirism, cryoclastic eruptions, crustal melt-through, or even global resurfacing. Although the conventional cold-ocean crustal melt-through models of Europa's chaos lack the thermal energy transfer efficiency needed to achieve melt-through (Collins *et al.* 2000), a high-temperature density-stratified ocean might supply the needed energy.

In summary, the concepts and models offered here provide a framework in which to consider chemical and physical processes involved in the formation of surface features. The continued analysis of data from the *Galileo* mission will help to choose among the several evolutionary pathways for Europa's outer layers outlined here or to develop new concepts and pathways that may better match the observations.

5. ASTROBIOLOGICAL IMPLICATIONS

Speculation that Europa's putative ocean might harbor life or prebiotic conditions has increased since first suggested by Consolmagno (1975) and developed in fictional form by Arthur C. Clarke (Reynolds *et al.* 1983, Lunine and Lorenz 1997, Jakosky and Shock 1998, Chyba *et al.* 1999, Gaidos *et al.* 1999, McCollom 1999, Chyba 2000). Life on Earth requires liquid water, chemical disequilibria, and elemental building blocks; these stipulations may indeed be met on Europa and may have existed continuously or sporadically since Europa's origin. Europa also provides insights regarding the geological and biochemical evolution of early Earth during a hypothetical ice-covered phase (Bada 1996, Gaidos, *et al.* 1999).

Although hydrocarbons are generally considered to be a dispersed biologic resource in ice-covered oceans on Earth (Gaidos *et al.* 1999), in some cases it appears that microbial and macrofaunal chemosynthetic assemblages are associated with localized hydrocarbon vents and concomitant clathrate hydrates (Carney 1994). Molecular and isotopic studies of structure II gas hydrates in lightless chemosynthetic communities of the Gulf of Mexico provide evidence that bacteria can directly oxidize hydrate-bound methane (Sassen *et al.* 1999b). Moreover, hydrocarbons from decomposing gas hydrates appear to drive complex biogeochemical processes in sediments that surround structure II gas hydrate extrusion features, helping to support complex chemosynthetic microorganisms (Fig. 6). The discovery of high concentrations of a new polychaete species on the surface of exposed gas hydrate in the Gulf of Mexico at $\sim$540 m water depth (Sassen *et al.* 1999b, Fisher *et al.* 2000) has additional implications with respect to direct association of relatively complex life (annelids), gas hydrate, and saturated brines (Fig. 6c).

Possible metabolic processes, such as methanogenesis, sulfur reduction, and iron oxide reduction, have been suggested for Europa (Gaidos *et al.* 1999, Chyba 2000) and Mars (Fisk and Giovannoni 1999). Excreted byproducts and decaying material from chemoautotrophic organisms could serve as the basis for a europan ecosystem by supplying carbon and energy sources

to heterotrophic life forms at higher trophic levels. Photosynthesis is unnecessary in this scenario. The potential amount of biomass on Europa has been calculated to be low (Jakosky and Shock 1998), and Gaidos *et al.* (1999) have reinforced this view on the basis of a perceived deficiency of oxidants. Our analysis above suggests otherwise. The availability of chemical energy needed to drive development of a biomass may be far greater than that considered by Jakosky and Shock (1998) according to some geologic interpretations of Europa. The calculations above also allow for the possibility that organic carbon may be much more abundant than that on Earth, such that a dense, well-developed ecosystem might exist. Even in the unlikely absence of endogenic sources of organic carbon, impacts can deliver organics, including amino acids, a fraction of which will survive impact and be retained by Europa (Pierazzo and Chyba 2000). A europan ocean may or may not support a lush ecosystem (or any ecosystem), but it is illustrative to examine the physiological stresses that past or present europan organisms could experience.

The geology of Europa indicates that liquid is probably present and widely distributed; i.e., an ocean probably does exist. If an ocean exists one thing is certain and another extremely likely: first, the top of any ocean must be in equilibrium with ice; second, solute abundances in the ocean are almost certainly extremely high and saturated, suggesting that the seafloor should be covered with precipitated salts. Thermodynamic disequilibria and gradients comparable to those in Earth's ocean and seafloor may exist on Europa and may be exploited as energy sources and provide varied niches for the origin and evolution of life. The ocean's temperature at the base of the frozen layer is constrained by these features to lie between about 216 and 266 K. The exact temperature depends on the pressure and solutes; locally the temperature could be much warmer near a hydrothermal vent. The pressure—up to about 200 MPa—depends on the thickness of the icy shell. Other conditions in Europa's ocean are poorly known: the ocean's pH may be extremely acidic, neutral, or extremely alkaline; concentrations of organic carbon may be extremely low or high; the seafloor could be made of materials as diverse as basalt, elemental sulfur, or salts; the types of solutes in Europa's ocean are uncertain. There is some basis to favor high sulfate concentrations, but the chief cations are debated. Heat flow on Europa due to tidal dissipation may be a small fraction of or somewhat greater than Earth's total heat flow. High tidal amplitudes indicated by Europa's pattern of fractures (Geissler *et al.* 1998a, Hoppa and Tufts 1999) and suggested theoretically (Greenberg *et al.* 1998) would drive tidal currents and circulate nutrients (Greenberg *et al.* 2000b).

Where europan and terrestrial environments overlap in their physicochemical nature, examples from Earth reveal that life can cope and grow under conditions as extreme as most of the range of conditions modeled for Europa's ocean. Possible europan conditions which are not represented on Earth include far colder temperatures (according to some models) and higher pressures, but neither of these extremes is inherently prohibitive to life as long as liquid water is present to allow organisms to grow. Diffusion rates will be slow at cold temperatures, and accordingly life processes may proceed sluggishly relative to those on Earth. Sea ice, hydrothermal systems, and evaporitic salt pans on Earth may provide direct or partial analogues to Europa, so we consider briefly some aspects of life in these environments.

A leading hypothesis for the origin of Earth's life, based on genetic classifications of microbial forms pointing to a hyperthermophilic ancestor to all life, is that it occurred in an environment such as a deep-sea hydrothermal vent (Baross and Hoffman 1985, Baross and Holden 1996, Baross 1998). Such environments not only provide the conditions needed by Earth's most primitive existing life forms to thrive, but they also appear to provide a range of gases and catalysts, such as H_2S, CO, and $(Ni,Fe)S$ particles, that are effective in the activation of amino acids and formation of peptides, which may be a critical step needed for life's origin according to one hypothesis (Huber and Wachterschauser 1998). Since similar conditions are possible on Europa, the same hypothesized origin of life may apply.

5.1. Salt, pH, and Metal Tolerances of Terrestrial Organisms

Halotolerant microorganisms thrive in all briny environments on Earth, including hypersaline lakes, soils, playas, marine coastal lagoons, and marine sabkhas (Javor 1989). Halophilic microbes even require high concentrations of salt for growth (Ventosa *et al.* 1998). These ecosystems, frequently composed of relatively few species (Benlloch *et al.* 1995), are productive despite being saturated in various salts. The Dead Sea, for example, is a hypersaline lake saturated with halite, and it supports thriving populations of heterotrophic archaea (*Halococcus* and *Halobacterium*), cyanobacteria, and sulfate-reducing microbes (Ventosa *et al.* 1999, Evans and Kirkland 1988). One cubic centimeter of Dead Sea brine contains about 10^7 red halophilic archaea and 4×10^4 red algae (Sonnenfeld 1984).

Comparable bacterial and cyanobacterial densities have been found in hypersaline marine bodies along the coasts of the Gulf of Elat and Gulf of Suez. One hypersaline body, the Gavish Sabkha, has a lateral salt gradient ranging from about 5 to >35% (w/v); yet microorganisms thrive over this entire range in a succession of salinity-dependent sedimentary zones (Friedman and Krumbein 1995, Gerdes *et al.* 1985a, Ehrlich and Dor 1985, Kessel *et al.* 1985). The biological community of Gavish Sabkha includes 30 species of halotolerant cyanobacteria in addition to other microbes and a wide variety of halotolerant (up to 14% salt) metazoans: crustaceans, nematodes, and many others (Gerdes *et al.* 1985b).

Extremes in pH pose adaptational challenges but are not problematic in terrestrial ecosystems. Prolific communities of sulfuric acid-producing bacteria are found in acid mine drainage environments with a pH of 0.3–0.7 (Schrenk *et al.* 1998), and one archaeon in pure culture can even grow at pH −0.06 (Schleper *et al.* 1995), equivalent to 1.2 M HCl solution. This hyperacidophile species, *Picrophilus oshimae*, is also moderately thermophilic and occurs naturally in solfatara fields. Remarkably, it grows optimally at pH 0.7 and 333 K. *P. oshimae* appears

to be phylogenetically related to *Thermoplasma acidophila* and other prokaryotes known from burning coal heaps and Yellowstone acidic thermal vents (Darland *et al.* 1970). Microbes undoubtedly reside in a peculiar acid chloride hypersaline brine (pH 3–4) in Lake Tyrrell and some other southeastern Australian salt lakes and playas (Long *et al.* 1992a,b). It is not known how the most extremely acidophilic organisms cope; Schleper *et al.* (1995) speculate that either they possess a strong proton pump or a low proton permeability. Alkaline waters also contain thriving microbial communities; one of the most basic extremes known to allow growth is pH 12.5 (Duckworth *et al.* 1996).

Microbial activity is also robust inside Palaeozoic hydrothermal metallic ores of the Tinto River basin, southwestern Spain. This activity has driven the formation of a complex geomicrobiological system that lowers the pH of solutions between 1.7 and 3.5 along the river up to its mouth. The major energy and mass transfers in the system involve sulfide oxidation and mobilization of Fe^{3+} in acidic solution (Fernandez-Remolar *et al.* 2000).

Viable microbial life at the limit of salt saturation—even inside halite and mirabilite crystals (Wei-Dongyan *et al.* 1998)—is a geologically ancient adaptation. Microbial stromatolite-building communities were often formed in association with halite and imply high levels of ancient biological production at salinities exceeding halite saturation (Friedman 1980). Evaporitic rocks, including halite and potash salts, some over 500 Myr old, normally contain fossilized microbes (Knoll 1985). Sulfate-reducing microbial activity is belived to have been an important part of Earth's sulfur cycle at least back to the Early Proterozoic (2.1–2.5 Ga), when such activity appears either to have evolved or to have finally overwhelmed abiogenic means of sulfer isotope fractionation (Farquhar *et al.* 2000). More recent microbial activity is implicated in the formation of elemental sulfur in the sulfate caprocks of salt domes along the U.S. Gulf Coast. Biocatalyzed reduction of evaporitic sulfates by *Desulfovibrio* probably occurs first by reduction to H_2S and then by oxidation of H_2S to native sulfur caused by remaining sulfate (Feely and Kulp 1957, Sassen *et al.* 1989).

Additional brine environments on Earth include those in sea ice (Bowman *et al.* 1997), oceanic crust (Bischoff and Rosenbauer 1989), and continental crust (Vreeland and Huval 1991). In sea ice, temperatures usually vary between 258 and 272 K, and salt concentrations span 0.1–15% (w/v) total dissolved salt; these habitats harbor diverse assemblages of halotolerant bacteria (Bowman *et al.* 1997). Halotolerant and halophilic microorganisms have also been cultured from coastal oil-well and terrestrial subsurface brines (Huu *et al.* 1999, Orphan *et al.* 1998, Adkins *et al.* 1993, Vreeland and Huval 1991). Brines that exist in the oceanic crust beneath the global mid-ocean-ridge system (Bischoff and Rosenbauer 1989) have likewise been proposed as a suitable habitat for halotolerant microbes (Kaye and Baross 1998, 2000). Extremely halotolerant microbes have also been found in low-temperature Antarctic hypersaline lakes and subglacial environments (Franzmann *et al.* 1987, Franzmann 1991, James *et al.* 1990).

The characteristic high abundance of nutrients in evaporitic settings often comes at the price of having to cope with normally toxic levels of heavy metals (Lyons and Gaudette 1985). Europan brines are likely to be comparably enriched in toxic heavy metals. Millimolar levels of cadmium and cobalt are easily tolerated by some prokaryotes, and frequently these organisms are also halotolerant (Ventosa *et al.* 1998). *Pseudomonas aeruginosa*, a deep-sea vent microorganism, can precipitate and remove extraordinary levels of soluble cadmium in a short period of time (Wang *et al.* 1997). Adaptations to heavy-metal-rich brines in evaporative lakes are thought to underlie the biogenic formation of certain types of metal sulfide ore deposits (Sonnenfeld 1984, Eugster 1985, Krumbein 1985). Lake Tyrrell, Australia, is viewed as a modern analogue for ancient depositional environments of stratiform metal sulfide ore deposits (Fegan *et al.* 1992, Giblin and Dickson 1992). Some species associated with formation of organometallic complexes and sedimentary heavy metal sulfide ore deposits, e.g., the sulfate-reducing anaerobe *Desulfovibrio*, occur in hypersaline marine brines such as that of Gavish Sabkha (Schidlowski *et al.* 1985), in the sulfur–sulfide caprocks of salt domes, and in oil-field brines (Sonnenfeld 1984).

Hypersaline, acidic, alkaline, and metal-rich environments harbor tenacious microbial communities, and it thus appears that organisms are able to exist and thrive under an extraordinary range of conditions wherever fresh liquid water or brines are present. Similarly, brine-filled cracks in sea ice or in the lithosphere provide a suitable habitat for microorganisms, and these types of environments may offer close parallels with the ice and rocky interior of Europa.

5.2. Temperature and Pressure Tolerances of Terrestrial Microorganisms

Conditions in Europa's ocean might include temperatures colder than anywhere on Earth, although it is more likely the ocean may be comparable to Antarctic and Arctic saline lakes. Because life survives (and likely grows) in all of the coldest environments on Earth where liquid is present, even colder conditions may permit biological growth, as long as liquid water is stabilized by solutes. Microorganisms isolated from high-latitude environments have been found to grow at temperatures which dip to 268 K (Franzmann *et al.* 1987, Franzmann 1991), and additional bacterial species grow at temperatures as low as 263 K, albeit slowly (Neidhardt *et al.* 1990); these temperatures are comparable to those of the sulfate-saturated europan ocean modeled above. Microbial activity has been hypothesized to occur in polar sea ice brine pockets at 243 K (Deming and Huston 2000). The permanent ice cover of briny lakes of the Antarctic Dry Valleys is considered an ecological microbial "oasis" (Priscu *et al.* 1998, Psenner and Sattler 1998). Low temperatures come at the cost of a large reduction in metabolic rates (Demin and Hust 2000). Low temperatures and the high solute abundances needed to stabilized brines at low temperatures should markedly increase the liquid's viscosity and thus reduce solute transport rates in the solution.

FIG. 6. Photos of chemosynthetic faunal community on the seafloor of the Gulf of Mexico in association with structure II gas hydrate buildup and associated hydrocarbon venting. (a, preceding page) A hydrate mound in Green Canyon at about 540 m depth partly covered by orange mats of *Beggiatoa*, a sulfide oxidizing bacterium, is shown. Scale of hydrate features is about 1 to 2 m diameter. The leading edge of the hydrate mound reveals exposed gas hydrate. (b, preceding page) Bacterial mats associated with small sediment pockmarks from which hydrocarbons and highly saline, saturated brines issue at about 650 m depth. The floors of pockmarks are partly filled with turbid, saturated brine. (c, above) Hydrate mound with associated tube worms and trains of hydrocarbon gas bubbles. Photos by Roger Sassen.

Temperatures below the freezing point of a brine act to preserve microbes. Though not in a metabolically active state, microorganisms are routinely maintained at 193 K in freezers or at 78 K in liquid nitrogen in the laboratory and subsequently revived after storage for several years. In a natural setting, microbes recovered from an ice core taken above subglacial Lake Vostok, Antarctica, remain viable despite being trapped in frozen lake water for over 100,000 years (Abyzov *et al.* 1998). Brines may freeze on Europa over long time scales as the frozen crust thickens, as brines intrude into cold near-surface ice, or as partly molten briny ice diapirs ascend into the lithosphere (80–120 K) (Pappalardo *et al.* 1998, Rathbun *et al.* 1998), or freezing may occur rapidly due to cryovolcanism (Kargel 1991). The ability of microorganisms to withstand extended periods of extreme cold may be integral to europan life and may provide for future sampling and culturing of surface ices.

At the high-temperature end, the current upper temperature limit for a microorganism in pure culture in the laboratory is 386 K (Stetter 1999). A sulfur-reducing hyperthermophilic archeon isolated from a deep-seavent is capable of adapting to various high temperatures (from 349 to 383 K) by adjusting

the abundances of certain proteins (Holden and Baross 1993), Pledger and Baross 1991). Growth may occur at even higher temperatures in natural systems. As on Earth, thermotolerant organisms on Europa could inhabit subocean environments heated by geothermal sources.

As for pressure, the deepest point in Earth's ocean is under 110 MPa of hydrostatic pressure (over 10,600 m depth) and contains viable microorganisms (Yayanos 1995). Pure cultures of certain bacteria grow at 100 MPa and 275 K as well (Yayanos 1995). Hydrostatic pressure coupled with lithostatic pressure implies that subseafloor and subterranean microbial communities likely experience even higher pressures (Yayanos 1995). Some hydrothermal vent archaea and bacteria, known as barophiles, exhibit affinities for elevated pressure. They can even show an increase in their optimum temperature for growth and an acceleration in growth rates at supraoptimum temperatures (Erauso *et al.* 1993, Pledger *et al.* 1994).

Among the most interesting biological explorations taking place on Earth with pertinence to Europa is the drilling activities at Lake Vostok, Antarctica. The liquid part of the lake is about 600 m deep in places and is covered by up to 200 m of frozen

lake water and about 3500 m of glacial ice above that (Jouzel *et al.* 1999). Pressure at the lake floor is 39 MPa. The ice–water interface exhibits net melting in the northern and western parts of the lake and net freezing in the south (Siegert *et al.* 2000). Drill cores taken from the frozen lake water above the lake has produced evidence of a microbial community (Priscu *et al.* 1999), part of which remains viable and has been cultured after being trapped in the lake ice for thousands of years (Karl *et al.* 1999). These results show that the lake maintains a functioning ecosystem despite being physically isolated from the rest of the planet's biosphere for about a million years.

5.3. Implications for Europa

A review of the adaptive strategies of microorganisms from Earth reveals that most every physiological stress can be overcome so long as the environment contains liquid water. From this physiological perspective, model organisms for a europan ecosystem include members of the versatile bacterial genus *Halomonas*. A halotolerant group, *Halomonas* spp. grow over a wide range of salt concentration (0.01% w/v salt to saturated brine) (Ventosa *et al.* 1998), tolerate high pH (Duckworth *et al.* 1996), grow at temperatures at least between 268 and 318 K (Ventosa *et al.* 1998, Franzmann *et al.* 1987), and tolerate millimolar levels of heavy metals (Ventosa *et al.* 1998). *Halomonas* spp. have been isolated from deep-sea, high-pressure environments at mid-ocean ridges (22 MPa) (Kaye and Baross 1998) and deep-sea sediments (34 MPa) (Takami *et al.* 1999), and they have been found in sea ice brines (Bowman *et al.* 1997) and in brines contained within the continental crust (Huu *et al.* 1999, Orphan *et al.* 1998, Adkins *et al.* 1993, Vreeland and Huval 1991). Moreover, *Halomonas* spp. and other oligotrophic bacteria can grow on low concentrations of organic carbon (0.002% w/v) (Kaye and Baross 1998, 2000; Schut *et al.* 1997).

Some deep-sea vent archaea prefer elevated pressures (Erauso *et al.* 1993, Pledger *et al.* 1994). Accordingly, pressures up to 200 MPa underneath a thick icy shell are not likely to inhibit life processes on Europa. Even though Europa's ocean is in equilibrium with ice, and is therefore predominantly cold, hydrothermal activity in the suboceanic crust may sustain local temperatures that are very high, and so hyperthermophilic traits known from Earth's most phylogenetically primitive microorganisms (Baross and Hoffman 1985, Baross 1998) may be relevant to life on Europa, also.

The physicochemical conditions most likely in Europa's ocean are all surmountable by life based on analogy with the physiological adaptations of microorganisms on Earth. However, one can imagine possible europan chemical evolution scenarios that would result in conditions that might be too extreme for even the most well-adapted life–an ocean of eutectic sulfuric acid solution, for instance, would exceed the low-temperature and low-pH limits known for terrestrial life. On the other hand, Earth does not have such natural environments (though stratospheric clouds come close), and there is no predicting how life

might develop if such conditions were stable. It is yet an entirely different matter whether life could originate in the extreme environments possible in Europa's ocean. The independent origin of life may involve different problems than the sustenance and evolution of life; unfortunately, we know little about the origin of life even here on Earth. Despite uncertainties, we would not discount possibilities for life in Europa's ocean even under the most extreme environments that the ocean might have to offer.

An important aspect of the chemical scenarios for Europa is that a wide variety of carbon and sulfur gases and solids, not all necessarily chemically equilibrated with one another, are produced and mixed or layered in the crust. Chemical and thermal gradients are likely to exist on a range of spatial scales, and the resulting disequilibria is apt to be exploited by any europan life. Hydrocarbon clathrate hydrates and chemical gradients involving sulfur compounds are of special significance, because these chemical situations are similar to some on Earth that life exploits very well. The process of bacterial methane oxidation in gas-hydrate-related environments on Earth appears to occur in the absence of molecular oxygen, along with concomitant bacterial reduction of sulfate (Hinrichs *et al.* 1999). On this basis, if hyrocarbon-bearing gas hydrates are present beneath the ice of Europa, the probability of life capable of methane oxidation and sulfate reduction is increased.

The carbon and sulfur cycles relevant to Earth's marine ecosystems, and the physiology and adaptive strategies of organisms found near cold hydrocarbon seeps (Sassen *et al.* 1993) and seafloor hydrothermal vents (Karl 1995) may offer insights into possible europan ecosystems. Considering that biogenic sulfur formation is so ubiquitous on Earth, we speculate that biogenic sulfur might be produced on Europa, too, and that eruptions of brine-containing organisms or sulfur deposited by them could contribute to the yellowish/reddish color of nonice deposits there.

It is conceivable, if Io once had an aqueous past (Fanale *et al.* 1974, Nash and Fanale 1977, Kargel 1996, 1999b), that its ubiquitous sulfur compounds might bear some relation to biochemical processes in the very distant past. Although sulfurous materials seen in *Galileo* imaging and reflectance spectroscopy of Io and Europa might represent chemical biomarkers, it is improbable that *Galileo* data or other remote sensing could distinguish biogenic and abiogenic sulfur, especially considering that any biogenic sulfur probably has been recycled many times and affected by intense abiogenic processing. *In situ* studies, including stable isotope analysis, offer some hope that we will ultimately elucidate the origin of this material, especially on Europa, where complications due to repeated high-temperature volcanic recycling and fractionations due to global volatile loss have not occurred.

Planned drilling and sampling of the waters and sediments of subglacial Lake Vostok should prove very interesting from a geochemical and exobiological perspective (Bell and Karl 1999). Lake Vostok is probably the closest physical analogue to Europa's ocean that Earth has to offer, though its salinity is

probably much lower than Europa's ocean. The flow of energy and organic matter and the particular adaptive strategies used by life in the Lake Vostok microbial community may be analogous to those of Europa's ocean.

6. IMPLICATIONS FOR FUTURE EUROPA MISSIONS AND OTHER OBSERVATIONS

There are several areas where further observations and analysis would help constrain the chemical composition, structure, and evolution of Europa and prospects for life there. First, existing NIMS data should be scrutinized for minor spectral features within the asymmetric water bands to glean any information on specific identity and hydration state of nonice hydrates. Additional lab data on the spectral reflectivity of hydrated salts and sulfuric acid at cryogenic temperatures are needed to better evaluate the existing spacecraft data. Evidence in NIMS data for minor nonsalt constituents, especially tholins, and their geologic distribution also should be sought. A future orbit-based imaging spectrometer should yield improved spatial resolution, which is needed to understand the geological controls in the emplacement and modification of surface materials, but it should also be designed with improved spectral resolution to help distinguish minor components and the physical state of major constituents. Major gaps in high-pressure physical chemistry data on saltwater systems relevant to Europa exist (Hogenboom *et al.* 1995, Commission on Equilibrium Data 1999) and should be filled. Especially needed are precise phase volume data at elevated pressures relevant to the present state of Europa's ocean (up to 200 MPa) and the primordial differentiation of Europa's mass (up to 2500 MPa).

The Europa Orbiter mission, with its subsurface sounding radar will be invaluable in assessing prospects for an extant ocean (Chyba *et al.* 1998; see also http://www.jpl.nasa.gov/ice_fire//europao.htm). However, the likelihood of multiple reflections and the electrolytic character and freezing-point depression caused by the salty crust will make direct sounding of the ocean's interface with the icy shell difficult (Winebrenner and Sylvester 1996). Dispersed brine inclusions will occur well above the major ice/brine interface and make the ice radar lossy. The possible roles of impurities, including salts, in the interpretation of radar sounding data have been considered by Moore *et al.* (1992, 1994), Corr *et al.* (1992), and Chyba *et al.* (1998). (See also http://outerplanets.larc.nasa.gov/outerplanets/.) In any event, a future Europa orbiting radar should produce data on the depth to a partial melting isotherm. Renewed radar lab work to examine the roles of the specific types of impurities now believed likely, e.g., sulfuric acid, should be conducted. Winebrenner and Sylvester (1996) suggested use of Jupiter's natural dekametric radio emissions as a source of long-wave radio energy for less lossy subsurface sounding.

The variety of morphologic features seen in *Galileo* imaging provide information on the distribution and nature of tectonic and volcanic processes on Europa. Color data provide

high-spatial- and low-spectral-resolution information that can be compared to the high-spectral- and low-spatial-resolution information from NIMS. These data are being used to formulate and test models for Europa's structural and geological evolution. Further acquisition of global high-resolution imaging and altimetry from a Europa Orbiter will be very useful in testing the global significance of geologic processes and sequences that are emerging at the local and regional levels. Taken together, these data may permit one to distinguish among several models for the evolution of Europa's outer layers.

The composition and origin of Europa's atmosphere, now known to contain oxygen, sodium, and potassium (Hall *et al.* 1995, Brown and Hill 1996, Brown 1999), should be examined for any possible controls by sublimation or sputtering of surface materials or direct venting from Europa's interior. Is the lack of magnesium in the atmosphere (Brown 1999) due to a lack of magnesium salts on the surface, or is it an indication of the greater stability of magnesium salts against sputtering and radiolysis? Additional lab data are needed to understand links between surface and atmosphere compositions. New telescopic observations of Europa are needed to search for chlorine and other minor atmospheric constituents. Consideration should be given to flight of an orbiting mass spectrometer.

Additional observations of the europan magnetic field, particularly from orbit, would be especially valuable in reaching a consensus on the origin of the europan magnetic field and in discerning more specific constraints on a possible origin in an ocean. Similarly, higher-resolution gravity data—particularly obtained from the Europa Orbiter—are needed to provide improved constraints on three-layer models and to look for regional heterogeneities in Europa's mass distribution. Surface-based geophysical surveys, including electrical and seismic observations, will also be very helpful in probing the crustal distribution of salts and electrolyte solutions. Perhaps more than anything else, more specific compositional information, especially obtained by surface sample analyses by a landed spacecraft or by a flyby/impactor spacecraft pair, is needed to narrow the range of viable models of Europa's geochemical evolution.

Undoubtedly the most informative and exciting of all possible robotic missions to Europa would be one where the icy shell is penetrated and any ocean that exists would be explored directly. The likelihood that salts are major constituents of the crust poses formidable challenges to any plans to melt through the shell, as some advance planning envisions. Although the salts are soluble in water, the tendency might be for a melting device to induce partial (incongruent) melting, whereby a less hydrated solid salt is generated along with liquid brine. The less-hydrated salt could tend to encrust the melting device. Additional heating would only continue the process of dehydration and partial melting but would not likely remove the encrusting salt residue, which may eventually accumulate into an impenetrable mass. Extremely high temperatures might be required to completely melt this encrustation. The complex thermochemical dynamics of a melting device operating in a very salt-rich,

heterogeneous crust have not been studied to our knowledge but must be evaluated rigorously; testing of such a device in pure ice, polar ice, or even somewhat impure sea ice is not a sufficient engineering test. It may be that a mechanical digger or a combined melter/digger would be a better approach than melting by itself.

The optimism we have for existence of europan life, despite extreme conditions possible in the ocean, also raises a concern. As pointed out by a reviewer, there is a small but possibly not insignificant risk of biological contamination of Europa's ocean if appropriate risk assessments and any needed countermeasures are not taken for future exploration. It could be that the jovian environment reduces this risk to nil, but this is not assuredly so. The *Galileo* team should consider disposing *Galileo*, at end of mission, on Io or Jupiter, rather than take the very small risk that a crash on Europa could result in eventual biological contamination, which potentially could be more harmful to any endemic europan life and our ability to study it in the future than the plutonium aboard *Galileo*. The contamination risk posed by the Europa Orbiter and any future lander should be assessed and risk mitigation strategies implemented if the risk is deemed significant.

7. CONCLUSIONS

CI and CM carbonaceous chondrite meteorites may provide the best analogues for Europa's primordial composition—they can provide sulfides for a core, and salts, water, and other volatiles for the crust/ocean. Europa's value for the gravitational parameter C/MR^2 is bracketed by some highly differentiated chemical–structural models based on CI chondrites. The composition of Europa's crust is very sensitive to the specific evolutionary sequence: magnesium–sodium sulfates are predicted by the simplest evolution from CI and CM chondrites; a sulfuric acid ocean is possible if there was extensive SO_2 venting from the rocky interior or if some sulfate salts thermally decomposed; a sodium carbonate ocean is possible if there was extensive CO_2 venting; and a crust containing many kilometers of clathrate hydrates (including some combination of CO_2, SO_2, CH_4, higher hydrocarbons, or other gases) is possible according to some likely scenarios. Many other possibilities can be envisioned considering Europa's complex evolution, but general predictions are that: (a) there should be extensive precipitation of sulfurous substances on the seafloor, (b) there should exist a strong tendency for mineralogical density layering of the crust, (c) brine volcanism and diapirism are allowed by some chemical–structural configurations of the crust but would be much less likely in other configurations, and (d) most chemical models would present good oceanic habitats, whereas others could be fairly hostile to life as we know it. Foremost, we conclude that realistic chemical–physical evolution scenarios call for a highly impure and heterogeneous crust and a salt-saturated ocean. Definitive identification of the nonice substances on Europa would greatly narrow the range of acceptable chemical–

structural models and would help determine Europa's aqueous chemical history and prospects for life.

In summary, further analysis of present data and future exploration will bring new and clearer insights into the evolution of Europa and its partly liquid outer layer. Europa stands out among the planets and satellites as a distinctive laboratory for the study of the evolution of aqueous systems over geologic time and the study of environments potentially conducive to the formation and evolution of life. Europa's present state might offer a good analogue for Earth's earliest ocean. Io potentially could represent an end state after extreme devolatilization of a Europa-like object (Kargel *et al.* 1999b). Comparative geological, geochemical, and exobiological studies of these objects and others that once may have had oceans, e.g., Mars, may help planetologists develop a deeper understanding of the frequency of and conditions needed by life in the Universe.

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