Cryovolcanism is among the foremost processes responsible for modifying the surfaces of icy satellites. Volcanic brine petrogenesis in ammonia-deficient satellites should mainly involve eutectic melting in relevant salt–water systems. Carbonaceous chondrites provide useful insights into the compositions of salts and aqueously altered rock in icy satellites and asteroids. C1 chondrites contain about one-fifth by mass of salts in various states of hydration. Many aspects of the petrogenesis and physical volcanology of icy satellite brines should be well described in the system H2O–MgSO4–Na2SO4. Minor components include sulfates of K, Ni, Mn, and Ca. Chondrites also contain abundant carbonates, but these are probably not very important in brine magmatism due to their low solubilities under expected conditions. Chlorides are also unimportant under most circumstances because of the low cosmic abundance ratio of Cl/S. Soluble salts may have profound effects on the geology and structure of icy satellites and asteroids. In some models late episodes of water volcanism are facilitated by high buoyant forces due to the relatively high densities of sulfate-rich mantle and crustal layers. In other models early hypersaline brine volcanism quickly yields to plutonic magmatism due to low crustal densities.

Europa probably has a layered crust composed of anhydrous Mg–Na sulfates near the base and a frozen or partially molten eutectic mixture of ice and hydrated Mg and Na sulfates near the surface. Ganymede may have a crust about 300 km thick composed of a 10:1 ratio of ice:mirabilite, and a mantle 500 km thick composed of 50% ice phases plus 50% hydrated Mg and Na sulfates.
ward equilibrium, possibly yielding hydrated phyllosilicates and soluble salts. Thus, regardless of whether salts were initially present, partial melting probably would yield brines rather than pure water. The composition and salinity of a particular brine would depend on the oxidation state of sulfur in the rock, solution pH, and other factors.

This contribution will: (1) constrain the probable compositions of brines generated in chondritic asteroids and icy satellites; (2) present an objective rationale simplifying these compositions to a minimum of components; (3) examine some physical properties of simple salt–water mixtures; and (4) discuss possible planetological consequences of salt–water magmatism.

This paper is restricted to physical chemistry data appropriate to 1 atm due to a paucity of relevant data taken at elevated pressures. The planetological applications at this juncture are exploratory and qualitative. The author and co-workers have recently initiated experimental studies of high-pressure phase equilibria in salt–water systems necessary for more quantitatively realistic planetological applications (Hogenboom et al. 1991).

Previous publications from this laboratory related to cryovolcanism have dealt mainly with the densities and viscosities of ammonia–water liquids (Croft et al. 1988, Kargel et al. 1991). A review of published and original physical chemistry data for a broad range of plausible cryovolcanic liquids and general applications to the geology of icy satellites were presented in the author’s dissertation (Kargel 1990).

The compositions of volcanic brines may vary within broad limits. These compositions dictate the temperatures of partial melting and the likelihood that melting can occur in convecting satellites. These compositions also determine the quantities of brine and the thicknesses of briny crusts and mantles that might form, the surface compositions of icy satellites, the physical properties of erupted brines, and the morphologic characteristics of landforms and landscapes produced by brine volcanism.

2. IMPLICATIONS OF CHONDRITE SALTS FOR EXTRATERRESTRIAL BRINE COMPOSITIONS

Aqueous alteration of carbonaceous chondrites. Carbonaceous chondrites offer valuable insights into the nature of low-temperature water–rock chemical interactions in chondritic asteroids, and the composition of watersoluble material produced during such alteration events. Aqueous alteration in carbonaceous chondrites is shown by a great abundance of aqueously precipitated salts, of secondary phyllosilicates including montmorillonite, saponite, chlorite, and serpentine, of certain sulfides and hydroxides including tochilinite and brucite, and of spherulitic magnetite (DuFresne and Anders 1962. Bostrom and Fredriksson 1964, Kerridge et al. 1979, Zolensky and McSween 1988, Bunch and Chang 1980, Barber 1985, Keller and Buseck 1990). In a general sense, most salts and alteration products in chondrites are similar to the phases produced by chemical weathering, diagenesis, and low-grade metamorphism of common terrestrial rocks. Since primary phases in chondrites are also generally similar to terrestrial crustal phases, including olivine, pyroxenes, feldspars, and sulfides, one reasonably infers that many of the aqueous reactions in carbonaceous chondrite parent bodies were probably similar to common terrestrial weathering and low-grade metamorphic reactions involving combinations of oxidation, carbonation, hydrolysis, and hydration.

Formation of secondary epsomite, magnetite, and serpentine can be represented by a composite reaction involving the oxidation of troilite and hydrolysis of forsterite in an aqueous medium:

$$12\text{Mg}_2\text{Si}_2\text{O}_5 + 6\text{FeS} + 54\text{H}_2\text{O} \rightarrow 130_2 \rightarrow 6[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4] + 6[\text{MgSO}_4 \cdot 7\text{H}_2\text{O}] + 2\text{Fe}_3\text{O}_4 \quad (1)$$

Planetologists commonly assume that the rock in icy satellites closely resembles carbonaceous chondrites chemically and mineralogically. Quite incompatibly, another common assumption is that the rocky fraction of icy satellites does not participate in low-temperature magmatic processes except as a stable inert component of the residuum of partial melting. While few would argue that the first assumption is unlikely, the second assumption, that rock is inert, is generally invalid. Either the rock contains abundant water-soluble salts if it resembles type 1 or 2 carbonaceous chondrites, or, if it more closely resembles type 3 carbonaceous chondrites or unequilibrated ordinary chondrites, then the rock contains unstable anhydrous minerals that normally would break down and yield soluble components upon reaction with water. As shown in Fig. 1a, the quantities of soluble matter present in extensively altered type C1 chondrites and less altered C2 chondrites are considerable. Commensurate with these abundances are the effects that the salts would have on the igneous and geological evolution of differentiated icy satellites and asteroids.

Theoretical modeling of cryomagma generation and evolution in salty icy satellites and asteroids is much more complex than in the simplistic salt-free case, since the number of chemical components, and free parameters, becomes very large. However, several factors justify consideration of simplified chemical systems.

Salts dominated by MgSO_4. Salts in C1 and C2 chondrites are dominated by metal sulfates (Fig. 1b), particularly the hydrated magnesium sulfate, epsomite (MgSO_4 \cdot 7H_2O). Other important salt components include sulfates...
FIG. 1. Compositions of chondritic meteorites (derived from Fredriksson and Kerridge 1988, Burgess et al. 1991, and Dodd 1981). (a) Relative mass proportions of salts (dehydrated sulfates and carbonates), aqueously altered rock components (mostly phyllosilicates and hydroxides), and unaltered anhydrous minerals (including olivine, pyroxene, sulfides, and metal). (b) Relative mass proportions of sulfates, carbonates, and chlorides (assuming all chlorine occurs as chlorides). Evaporated seawater for reference. (c) Relative mass proportions of magnesium sulfate, sodium sulfate, and all other sulfates combined. The composition of all highly soluble material, ignoring the chlorides, is given by the point "without CaSO₄" in (c).

of Ca and Na (Fig. 1c), and carbonates of Ca, Mg, and Fe. Minor components include sulfates of Ni, Mn, and K. Chlorides have not been widely reported in chondrites, a fact attributed to a cosmic abundance ratio Cl/S ~ 0.01, and, according to one reviewer, possibly also reflecting the relative stability of Cl-rich chlorapatite and sodalite during low-temperature aqueous alteration. MgCO₃ and BaSO₄ have been reported from interplanetary dust particles. (Reitmeijer 1990, Richardson 1978, Bostrom and Fredriksson 1964, DuFresne and Anders 1962, Nagy and Andersen 1964, Fredriksson and Kerridge 1988, Burgess et al. 1991).

The relatively large fraction of sulfates, especially magnesium sulfate, and the exceedingly low abundance of chlorine in chondrite salts contrast sharply with most terrestrial brines and evaporite deposits (Fig. 1b). Terrestrial salts are most often dominated by NaCl and are relatively deficient in MgSO₄. This distinction is easily explained. The Earth's continental upper crust, from which most terrestrial brines ultimately derive their solutes, has been greatly enriched in Na and depleted in Mg by multistaged igneous fractionations, and was derived from a mantle that had previously seen severe chalcophile element depletions apparently related to core formation. Na is a
factor of 6 less abundant and magnesium a factor of 7 more abundant in Cl chondrites relative to the average continental upper crust (Anders and Grevesse 1989, Taylor and McLennan 1985). Sulfur, 40% of which is oxidized in the form of sulfates in the Cl chondrite Orgueil (Fredriksson and Kerridge 1988), is well over an order of magnitude more abundant in chondrites than in the Earth’s upper crust, while the condritic abundance of chlorine is similar to its abundance in the upper crust.

One could usefully consider scenarios where SO$_4$ or Mg are unimportant in chondritic brines, or where Fe$^{+2}$ is as abundant as magnesium. For example, chemically reducing conditions during aqueous alteration could stabilize S in the form of relatively insoluble metal sulfides. Reducing conditions could also allow high concentrations of dissolved Fe$^{+2}$; in view of the chondritic ratio Fe/Mg $\sim 2$ (Anders and Grevesse 1989), dissolved Fe$^{+2}$ easily could be as important as Mg under these conditions. Strongly alkaline conditions, perhaps caused by a high NH$_3$ content, could sharply curtail hydrolysis, thus slowing the rates at which major cations enter solution; furthermore, sufficiently alkaline conditions would stabilize Fe and Mg in the form of solid Fe- and Mg-hydroxides (Brookins 1988), preventing significant concentrations of these metals in aqueous solution. Strongly acidic conditions could favor significant solution of carbonates. While these are not a priori unlikely situations, the author maintains a more conservative approach is assuming the prevalence of conditions and mineralogies represented by available aqueously altered cosmic material (i.e., carbonaceous chondrites). Thus, a substantial fraction (40%) of S is in the form of sulfate, particularly highly soluble MgSO$_4$ and Na$_2$SO$_4$; carbonates and CaSO$_4$ are nearly insoluble; and the abundances of dissolved CI$^-$ and Fe$^{+2}$ are negligible.

Over one-fifth of the mass of the Cl chondrite Orgueil consists of salts in various states of hydration (Fig. 1). Calculated entirely on an anhydrous basis, salts constitute 14.6% by mass of this meteorite, of which about two-thirds of the salts (by mass) are highly water soluble under normal conditions. MgSO$_4$, constituting nearly three-fourths of the highly water-soluble fraction, is clearly the single most important salt in chondritic brines, followed by Na$_2$SO$_4$.

Minor and weakly soluble salt components. MgSO$_4$ and Na$_2$SO$_4$ together account for 97% of the highly water-soluble fraction of Orgueil. The remaining 3% consists primarily of the sulfates of K, Mn, and Ni. As shown in Fig. 1b Ca–Mg–Fe carbonates are important solid components of chondrites, but are normally nearly insoluble, and could not normally constitute important components of magmatic brines. The same is true, to a slightly smaller degree, of CaSO$_4$. The high abundance of carbonates and gypsum in carbonaceous chondrites is a result of localized and essentially isochemical aqueous alteration and in situ chemical reprecipitation. Therefore, these phases would remain with the solid rocky residue during anatexis and melt removal. Brine magmatism, as considered in this report, is a fundamentally different process in that it involves open-system transport of highly soluble components, resulting in gross chemical fractionations on large spatial scales.

3. PHASE EQUILIBRIA

Aqueous binary sulfates. Figure 2 shows solid–liquid phase equilibria in binary aqueous systems involving MgSO$_4$, Na$_2$SO$_4$, CaSO$_4$, K$_2$SO$_4$, MnSO$_4$, and NiSO$_4$, all at 1 atm pressure. These binaries include all the major and minor sulfate components reported in carbonaceous chondrites, listed in order of abundance (Fredriksson and Kerridge 1988). The system H$_2$O–MgSO$_4$ is by far the single most important of these binaries. Under unexpected conditions, not examined in this work, aqueous FeSO$_4$ or (NH$_4$)$_2$SO$_4$ could also be important components, and might yield very different types of petrological evolution than considered below.

The phase equilibria shown in Fig. 2 probably should remain valid, as a first approximation, to pressures up to 2 kbars, since none of the substances are extremely volatile or unusually compressible. Higher pressures should progressively introduce qualitative changes, particularly solid-state phase changes. Kargel (1990), drawing on published data, showed that solid–liquid equilibria in the system H$_2$O–NaCl remain qualitatively unchanged, except for the stable ice polymorph, under pressures ranging from 1 atm to 12 kbars. The system H$_2$O–MgSO$_4$ currently is being studied experimentally under pressures up to 4 kbars; early results (Hogenboom et al. 1991) indicate no major surprises. However, subtle pressure-dependent aspects may have significant planetological consequences. These results will be presented elsewhere.

Metastable magmatic phenomena often occur in nature, particularly in quenched lavas. Supercooling, glass formation, and precipitation of metastable sulfate solids occur regularly under laboratory conditions, and indeed are avoidable only with considerable patience. Metastable phenomena, analogous to those which occur in the laboratory and in silicate volcanic flows, are especially likely during rapid solidification of the surfaces of aqueous sulfate flows. Persistence of these metastable phases over geologically lengthy periods is possible, a speculation supported by the occurrence of metastable magnesium and calcium sulfate minerals in terrestrial evaporite deposits. More often, terrestrial evaporite minerals revert to their stable forms when held at normal temperatures for a few hours or days (the surfaces of icy satellites are not “nor-
mal," however). Solidification of the interiors of extraterrestrial aqueous sulfate flows would likely occur over sufficiently long intervals (hours to days) that equilibrium solid assemblages probably would be produced. More importantly, melting processes in asteroid and satellite interiors would occur over very lengthy periods and major departures from equilibrium are unlikely. Thus, despite the likelihood that flow surfaces would be metastable (an aspect with possible spectroscopic significance), most magmatic phenomena probably would involve essentially equilibrium processes.

The recognition that MgSO$_4$ is probably the most important solute in extraterrestrial volcanic brines invites examination of multicomponent phase equilibria when other chondrite sulfate components are added to aqueous MgSO$_4$. These ternary phase equilibria are illustrated in Fig. 3 and are discussed below.

**System H$_2$O–MgSO$_4$–Na$_2$SO$_4$.** Nearly all Na in Orgueil is in the form of Na$_2$SO$_4$, the second most abundant sulfate component in Orgueil after MgSO$_4$. It is fruitful to consider phase equilibria of these components together in aqueous solution (Fig. 3a). This system includes 97% of the highly water-soluble material in Orgueil (Fredriksson and Kerridge 1988).

Solid solution between magnesium and sodium sulfates is negligible. This system exhibits a large number of hydrous and anhydrous phases, including several stoichiometric double salts. epsomite (MgSO$_4$ · 7H$_2$O), hexahydrate (MgSO$_4$ · 6H$_2$O), kieserite (MgSO$_4$ · 1H$_2$O), and bloedite (MgSO$_4$ · Na$_2$SO$_4$ · 4H$_2$O) apparently occur in carbonaceous chondrites. A eutectic liquid (81% H$_2$O, 16% MgSO$_4$, 2.8% Na$_2$SO$_4$ by mass) coexists near –5°C with water ice, mirabilite (Na$_2$SO$_4$ · 10H$_2$O), and MgSO$_4$ · 12H$_2$O. Melting and crystallization sequences of ice-free and ice-rich model assemblages are modeled and discussed in a planetological context in Section 5.

**System H$_2$O–MgSO$_4$–CaSO$_4$.** The high abundance of CaSO$_4$ in carbonaceous chondrites (Fig. 1c) seems at first to suggest that this also may be an important component in cryomagmatic brines. However, CaSO$_4$ is sparingly soluble in water (Fig. 2c), indicating a very limited capacity of chondritic brines to transport CaSO$_4$. This contrasts with the Earth’s hydrologic cycle where enormous quantities (water : rock ratios ~ 10$^5$–10$^6$) of dilute, unsaturated solutions of CaSO$_4$ and other salts are transported to the sea or inland basins; evaporative concentration results in extensive precipitation of gypsum and anhydrite in basins distant from the points where the solutes originated. Analogies and magma migration in icy satellites and asteroids occur just once or a few times, involving water:rock ratios ~ 1. This quantity of brine can dissolve only an insignificant fraction of the gypsum present in carbonaceous chondrites. Large amounts of CaSO$_4$ are formed by aqueous activity in icy satellites and asteroids, but nearly all is precipitated in situ.

Figure 3b shows the solubility curve exhibited by gypsum in magnesium sulfate solutions. This type of solubility curve is shared by other multicomponent aqueous sulfate solutions and is explained by nonideal solution properties and ionic complexing (Cameron and Bell 1905, Harkins and Paine 1919). The ternary eutectic liquid contains about 17% MgSO$_4$ (essentially the same as in the binary system H$_2$O–MgSO$_4$) and only 0.06% CaSO$_4$. Clearly this result warrants neglecting CaSO$_4$ as a soluble component for most purposes.

**System H$_2$O–MgSO$_4$–K$_2$SO$_4$.** As with Na, nearly all K in Orgueil is in the form of sulfate. The potential importance of K$_2$SO$_4$ is sharply limited by the low cosmic abundance of K. K$_2$SO$_4$ constitutes 0.13% of Orgueil and less than 2% of the total sulfates (Fredriksson and Kerridge 1988). However, K is even less abundant in Earth than in Orgueil. Even so, terrestrial silicate igneous fractionations yield major quantities of potassic phases in the continental crust, a fact with many important geological consequences. One cannot rule out analogous complex igneous fractionations in aqueous sulfate systems in differentiated satellites and asteroids.

The system H$_2$O–MgSO$_4$–K$_2$SO$_4$ (Fig. 3c) is somewhat similar to the system H$_2$O–MgSO$_4$–Na$_2$SO$_4$, as one might anticipate from the geochemical similarities of K and Na; the most notable distinction is that K$_2$SO$_4$ lacks a hydrated equivalent of mirabilite. Among the similarities, solid solution between Mg and K sulfates is negligible, and a series of double salts occurs. One of these, schoenite (K$_2$SO$_4$ · MgSO$_4$ · 6H$_2$O), coexists with ice, MgSO$_4$ · 12H$_2$O, and the ternary eutectic liquid. In asteroids and icy satellites, however, K$_2$SO$_4$ probably occurs in solid solution, substituting for Na$_2$SO$_4$ in various salts.

**System H$_2$O–MgSO$_4$–MnSO$_4$.** MnSO$_4$ constitutes less than 1% of the highly soluble fraction of Orgueil and only 0.06% of the whole meteorite. Even so, MnSO$_4$ is worth considering as a minor component. Figure 3d illustrates phase equilibria in this system. Solid phases exhibit substantial but incomplete solid solution, reflecting the identi-
FIG. 3. Ternary aqueous phase equilibria involving third components added to the system H$_2$O-MgSO$_4$. (a) H$_2$O-MgSO$_4$-Na$_2$SO$_4$. (b) H$_2$O-MgSO$_4$-CaSO$_4$. (c) H$_2$O-MgSO$_4$-K$_2$SO$_4$. (d) H$_2$O-MgSO$_4$-MnSO$_4$. (e) H$_2$O-MgSO$_4$-NiSO$_4$. Data sources: Binary phase diagrams and sources listed in Fig. 2 caption; Levi (1923), Blasdale (1927), Starrs and Storch (1930), Starrs and Clarke (1930), Benrath and Blankenstein (1934), Benrath and Neumann (1939), Soboleva (1960).

Cal valence states of Mg and Mn and their roughly similar ionic radii. Among the hepta- and hexahydrates, the solid phases have higher contents of Mg, lower concentrations of Mn, and higher Mg/Mn ratios than coexisting liquids. In silicate petrological vernacular, Mn is moderately incompatible.

System H$_2$O-MgSO$_4$-NiSO$_4$. The chondritic ratio Ni/Mg ~ 0.12 (Anders and Grevesse 1989), nearly two orders of magnitude greater than in Earth’s upper crust (Taylor and McLennan 1985), allowing the possibility that Ni could be an important constituent of cryovolcanic brines. Indeed, Mg-Ni-Na sulfates in Orgueil include up to 28% NiSO$_4$, although on average NiSO$_4$ is minor (Fredriksson and Kerridge 1988). Figure 2f shows binary phase relations of aqueous NiSO$_4$. Comparison with the H$_2$O-MgSO$_4$ system shows that sulfate solubility curves and the series of hydrated solids are very similar, except that NiSO$_4$ hexahydrate forms crystallographically distinct monoclinic and tetragonal polymorphs, whereas MgSO$_4$ forms only the monoclinic variety. The apparent lack of a Ni counterpart to MgSO$_4$ · 12H$_2$O might reflect kinetic problems in forming Ni dodecahydrate, rather than its lack of existence, as Mg dodecahydrate is also more difficult to form than heptahydrate.

The hydrates of MgSO$_4$ and NiSO$_4$ form complete solid solutions, analogous to the behavior of Mg and Ni in silicates. This is not unexpected since the valence states of Ni and Mg are the same and their ionic radii are nearly identical. The literature sources used in the construction of Fig. 3e did not find Mg dodecahydrate, so the three-phase cotectic between ice and sulfate involves the heptahydrate. This cotectic is a simple thermal trough running almost isothermally across the phase diagram from one binary to the other. The stability field of tetragonal NiSO$_4$ · 6H$_2$O terminates at a peritectic upon the addition of just 4% MgSO$_4$ to the binary H$_2$O-NiSO$_4$ eutectic liquid. Therefore, except for this small tetragonal hexahydrate field occurring only for very Ni-rich compositions, the aqueous MgSO$_4$ and NiSO$_4$ systems, and ternary mixtures of them, are isomorphic.

Two sets of representative three-phase triangles in Fig.
3e connect the compositions of solid sulfates with their equilibrium liquids on the sulfate–ice cotectic. These data indicate that the partitioning behavior of Ni and Mg among the sulfates and liquid are very similar and of order unity, in accordance with these metals' chemical similarity. In other words, the ternary phase equilibria are insensitive to the Mg/Ni ratio of the solution. Hence, one may treat ternary mixtures in this system as pseudobinary mixtures, with little sacrifice in accuracy, by combining MgSO₄ + NiSO₄ on a molar basis into a single component. Therefore, the chondrite salt vein compositions reported by Fredriksson and Kerridge (1988), which strictly must be described with no less than four major components (H₂O and sulfates of Mg, Ni, and Na), can be reduced to three components. Examined in more detail, the Ni/Mg ratios of solid solutions are always greater than in the coexisting liquid, so Ni can be considered a compatible element.

**Synthesis.** The physical chemistry of carbonaceous chondrite-equilibrated sulfate brines may be roughly approximated in the system H₂O-MgSO₄ (Fig. 2a), and more accurately in the ternary system H₂O-MgSO₄-Na₂SO₄ (Fig. 3a). Minor sulfate components (sulfates of Ni, Mn, and K) usually would not have major effects on the liquid's physical properties and major phase equilibria. However, it is possible to make a rough accounting for these components as long as their concentrations are low. With little loss in accuracy one may sum K₂SO₄ and Na₂SO₄ into a single component and MgSO₄, NiSO₄, and MnSO₄ into another component. However, as terrestrial experience shows very well, complex igneous fractionations can cause initially minor components to become major ones in strongly differentiated materials. In this event, quaternary and higher-order chemical systems may be required for a more accurate accounting.
CaSO₄ and the carbonates of Ca, Mg, and Fe are sparingly soluble under a broad range of environmental conditions. While these salts are important constituents of carbonaceous chondrites, they were formed by largely in situ processes of solution and precipitation, and would not have constituted an important fraction of the ionic load in chondritic hypersaline brines.

The chondritic ratio of Cl/S ~ 0.01, sharply limiting the potential volumes of low-temperature chloride brines. Taking Ganymede as an example, eutectic melting at ~52°C in the system MgCl₂–CaCl₂–H₂O, involving all the chlorine present, could yield 0.22 mass percent of eutectic brine, equivalent to 0.37 vol% of Ganymede (assuming Ganymede contains 60% by mass of chondritic rock containing 698 ppm Cl). Although this is not a large quantity, it is capable of forming a crust 3 km thick if completely extruded. If nothing else is capable of melting, perhaps because convective adiabats are cooler than the melting points of aqueous sulfates, then chloride brine volcanism could dominate surface geology and composition.

One reviewer suggested that low-temperature petrologic evolution of ice-bearing systems containing both chlorides and sulfates could be very complex. Alternatively, as another reviewer suggested, chlorine could remain immobilized in stable, nearly insoluble phases such as chlorapatite and sodalite until temperatures in the range of hundreds of degrees Celsius are attained. In the latter case, late-stage eruptions of hydrothermal chloride brines may occur during dehydration of phyllosilicates.

4. DENSITIES AND VISCOSITIES OF BRINES

**Densities.** Published sources give the densities of aqueous salt solutions as functions of composition and temperature (CRC Handbook of chemistry and Physics, Fabuss et al. 1966, Korosi and Fabuss 1968, Chen et al. 1980). The data collectively cover concentrations up to the aqueous salt eutectics, and extend over a wide range of temperatures above 293 K. Figure 4 gives the densities of planetologically important aqueous salts as functions of concentration for 293 K and 1 bar. These data can be extrapolated and interpolated over data gaps to obtain the eutectic liquid densities at the eutectic temperatures. The eutectic liquid in the system H₂O–MgSO₄ (17 wt% MgSO₄) at the eutectic temperature (~3.9°C) has a density of about 1.186 g cm⁻³.

The densities of frozen eutectic mixtures of ice and salts are also of planetological interest, particularly in the systems involving H₂O, MgSO₄, and Na₂SO₄. The densities of most solid sulfate phases of interest have been published (CRC Handbook), but the density of MgSO₄·12H₂O has not. A preliminary measurement of this density, 1.51 ± 0.01 g cm⁻³, was presented orally by Hogenboom et al. (1991). The densities of solid magnesium and sodium sulfates are shown graphically as a function of water content in Fig. 5: to the level of precision presented in this diagram these densities are not significantly temperature-dependent.

Figure 6 summarizes the densities of selected liquids and solids of cryovolcanic interest. All liquids in Fig. 6 are buoyant with respect to rock–ice mixtures, thus encouraging early aqueous volcanism.

A frozen eutectic mixture of 47% ice and 53% MgSO₄·12H₂O has a density of about 1.126 g cm⁻³, about 5% lower than the density of the coexisting liquid. A frozen eutectic mixture in the system H₂O–MgSO₄–Na₂SO₄ has a density ~1.133 g cm⁻³. Thus, the solid floats on the liquid, presenting the same buoyancy “problem” as occurs for water and ice. Once a thick volcanic crust forms subsequent volcanism is inhibited by the negative buoyancy of the late-arriving liquids relative to that of the solid crust (Croft 1985). Adapting the suggestion of Croft et al. (1988) for ammonia–water magmatism, early
1.2.1.0.11.0.2

377

384

1.2

1.0

85% MgCl₂–H₂O–Br

388

MgCl₂–H₂O–Br

388

MgCl₂–H₂O

390

MgCl₂–H₂O

390

NH₃·2H₂O

392

Ammonia–water liquids

392

Frozen MgSO₄–H₂O eutectic

392

Water

392

NH₃·2H₂O

392

Ice I

395

**FIG. 6.** Densities of selected solids and liquids of volcanological interest. After Kargel (1990).

Viscosities. The viscosity of magma is encountered in every problem of magma migration and lava flowage. Kargel et al. (1991), in an experimental study of ammonia–water liquids and crystal–liquid slurries, highlighted the important effects of partial crystallization on rheology. The relative differences in lava rheologies are well indicated by comparisons of liquid viscosities at their respective freezing points in the crystal-free state. These data should not be directly utilized in rheological modeling of lava flows since they do not take into account the important effects of partial crystallization. Rather, these data are useful for determining geologically familiar rheological analogs (e.g., silicate lavas). The undaunted physical modeler might choose to utilize these data after applying an empirical factor accounting for crystallization (Greenberg et al. 1991, Schenk 1990), or by employing an empirical function relating the relative viscosity and degree of crystallinity (Kargel et al. 1991).

Available viscosity data with appropriate extrapolations are shown in Fig. 7 for aqueous magnesium sulfate. The eutectic H₂O–MgSO₄ liquid has a viscosity ~ 0.06 P. The eutectic liquid in the system H₂O–MgSO₄–Na₂SO₄ has a viscosity ~0.10 P. Aqueous eutectic NaCl, MgCl₂,

...
CaCl₂ and NaCl indicate viscosities of, respectively, 0.05, 0.2, and 0.4 P. Multicomponent aqueous chlorides may have somewhat higher viscosities, but probably not over 1 P. The viscosities of silicate liquids at their respective freezing points are summarized in Fig. 8. Aqueous substances represent eutectic compositions, the viscosities of which are from Kargel et al. (1991) and sources referenced in the text. The viscosities of silicate liquids are based on published viscometry of natural and synthetic silicate liquids (Shaw 1969, Urbain et al. 1982, McBirney and Murase 1984, Murase et al. 1985, Tauber and Arndt 1986, Ryerson et al. 1986, Hummel and Arndt 1985, Scarfe et al. 1983). The melting points of silicates are based on experimental phase equilibria (dry) from Cox et al. 1979 and Morse 1985. The quantity (MgO + FeO)/SiO₂, in weight percent, is a measure of the degree of differentiation of silicate liquids. Strongly silica-undersaturated alkaline liquids do not lie on the curve.

5. APPLICATIONS

5.1. Structural Models

Construction. This section examines possible internal chemical structures resulting from the differentiation of a series of generic satellites and asteroids in the system H₂O-MgSO₄-NaSO₄, plus inert rock (Fig. 3a). The supply and transfer of heat is not considered, but rather is assumed to be sufficient to induce complete differentiation. The deep internal pressures in large asteroids, in icy satellites the size of Tethys, and in the icy crust of Europa are on the order of a kilobar. This is a sufficiently low pressure that Fig. 3a and satellite structural models based on Fig. 3a, even though strictly valid for 1 atm, are probably suitable approximations. However, the interior pressures in Ganymede and other large icy satellites attain up to 50 kbars, and qualitatively important effects on phase equilibria are expected. Even so, the models presented here are useful in advertising the probable importance of salts, particularly sulfates, in the low-temperature differentiation and geologic evolution of these large objects. But high-pressure phase equilibria in relevant systems are sorely needed for more accurate modeling and reliable insights into the histories of the larger objects (Hogenboom et al. 1991 and in preparation).

Structural models in Fig. 9 were constructed for five initial rock fractions varying from 1.0 (pure chondritic rock) to 0.4 by mass. The percentage of sulfates in the rock component was calculated using the average S abundance in Orgueil, 6.25 mass% (Anders and Grevesse 1989), and the average fraction of this S occurring as sulfates, 0.40 (Fredriksson and Kerridge 1988, Table 1); these two values yield the fraction of sulfate sulfur (S²⁻) in Orgueil: 2.50% by mass. This amount of oxidized S was apportioned among the elements Ca, Mg, and Na in the ratios measured by Fredriksson and Kerridge (1988, Table 2), with the minor approximation that NiSO₄ and MnSO₄ in Orgueil were summed along with MgSO₄, and K₂SO₄ was summed with Na₂SO₄. The mass fractions of sulfates in the chondritic rock component, calculated on an anhydrous basis, are MgSO₄ 6.05%, Na₂SO₄ 2.07%, and CaSO₄ 1.79%. Only the first two components are highly water-
soluble, giving a total of 8.12% highly soluble salts. The calculated mass percentages of hydrated salts are epsomite \((\text{MgSO}_4 \cdot 7\text{H}_2\text{O})\) 8.80%, bloedite \((\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O})\) 4.87%, and gypsum \((\text{CaSO}_4 \cdot 2\text{H}_2\text{O})\) 2.27%. The quantity of water associated with the two highly soluble phases, epsomite and bloedite, sums to 5.55%.

The exact meaning of “rock : ice ratio” is unclear when dealing with systems containing hydrated silicates and salts. Furthermore, the quantity of rock differs before and after leaching. A more precise term is needed,

\[ R_i = \frac{m_{t,i}}{(m_{t,i} + m_w)}, \]

where \(R_i\) is the initial mass fraction of chondritic rock (including salts and water of hydration), \(m_{t,i}\) is the initial mass of chondritic rock, and \(m_w\) is the mass of water added to the chondritic rock. The total fraction of water in an ice–chondrite mixture is greater than 1 \(- R_i\) since the rock itself contains water. \(R_i\) would correspond to the true rock fraction only if chondritic rock and ice are mixed without reequilibration or differentiation. Reequilibration without differentiation actually would yield more rock and less ice than indicated by \(R_i\) since epsomite and bloedite would take up water as they transformed to mirabilite and magnesium sulfate dodecahydrate. Low-temperature differentiation and leaching of soluble salts from the rock would result in less rock than \(R_i\). The final mass fraction of rock, \(R_f\), after differentiation is

\[ R_f = (1 - 0.1367)R_i = 0.8633 R_i, \]

Melting and crystallization sequences can be followed in Fig. 3a after calculating the fractions of \(\text{H}_2\text{O}, \text{MgSO}_4,\) and \(\text{Na}_2\text{SO}_4\). Fig. 2a (system \(\text{H}_2\text{O}–\text{MgSO}_4\)) considerably assists the interpretation of petrologic evolution in the ternary system (Fig. 3a). The amount of water in each model satellite is calculated as the amount of water of hydration of epsomite and bloedite in the initial rock (5.55% of initial rock mass) plus the amount of added water. Phyllosilicate water is assumed to be stably bound to the rock. The amounts of the ternary components are ressumed to 100%. Chondrite–water mixtures are shown in Fig. 3a as the straight line running from the composition of Orgueil to the water apex.

Differentiation was assumed to progress by continuous fractional melting, resulting in a perfectly gravitationally stably stratified structure. Figure 9 shows the internal structures of the five differentiated model objects. The idealized evolution of each model is briefly described below.

**Model A.** Figure 9a, with \(R_i = 1.0\), shows the differentiated structure of an object initially composed of pure chondritic rock with no added water. Epsomite and bloedite melt incongruently, yielding the peritectic liquid \(P_2\) (Fig. 3a), containing over 30% \(\text{MgSO}_4\) and 4% \(\text{Na}_2\text{SO}_4\). Liquid \(P_2\) is less dense than the rocky residue, so the liquid is readily erupted, forming a volcanic crust. Each successive volcanic flow would have an identical composition until either epsomite or bloedite is exhausted in the object’s interior. \(P_2\) flows could solidify by fractional crystallization (where crystals gravitationally settle and segregate from the liquid almost as rapidly as they form) or by equilibrium crystallization (where crystals remain in contact and continuously reequilibrate with the cooling liquid). Solidification of most silicate flows approximates equilibrium crystallization. If liquid \(P_2\) volcanic flows cool analogously, the final homogenous crystalline mixture would be composed of 84% \(\text{MgSO}_4 \cdot 12\text{H}_2\text{O}\) + 11% \(\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}\) + 5% ice. However, as discussed in Section 4, the low viscosity of the hypersaline \(P_2\) brine might favor fractional crystallization. In this case each flow would consist of several layers of different compositions; the top and last layer to solidify would have the composition of ternary eutectic \(E\).

In the next stage of melting, the residue left by formation of liquid \(P_2\) melts incongruently at peritectic \(P_3\) (Fig. 3a). Liquid \(P_3\), not shown in Fig. 3a (but consult the binary approximation in Fig. 2a), is denser than the volcanic crust of composition \(P_2\), and probably would be unable to ascend to the surface. Rather, liquid \(P_3\) would pool near or intrude the base of the crust, eventually forming the upper mantle layer of the asteroid.

The residue left from the second stage of melting then suffers a third stage of incongruent melting, yielding a small amount of liquid and a final solid residue composed of anhydrous sulfates. This stage of melting also yields a liquid substantially denser than the upper mantle, thus resulting in the formation of a lower mantle layer. The anhydrous sulfates probably would remain in the rocky core until water was released from the dehydration of gypsum and phyllosilicates.

The average density of this object after differentiation is 2.69 g cm\(^{-3}\), representing \(-2.8\%\) volume expansion over the undifferentiated initial chondrite. Much of this expansion takes place after formation of the peritectic \(P_3\) crust. Since all liquids generated subsequently would tend to intrude beneath this early-formed crust, one expects extensional strains of \(-1\%\), sufficient to cause significant crustal rifting.

**Model B.** Figure 9b shows the structure of a satellite with \(R_i = 0.7\). This object contains enough water that epsomite and bloedite contained in the initial chondritic rock would react with added water to form magnesium sulfate dodecahydrate and mirabilite, leaving excess water to form ice. This mixture first melts at the ternary eutectic \(E\) resulting in the formation of a thick volcanic layer (later to become the upper mantle). If each successive volcanic flow cooled by equilibrium crystalliza-
FIG. 9. Structural models of differentiated objects having various initial rock fractions ranging from 1.0 to 0.4. Left-hand column of each diagram gives the structures. The middle column gives the mineralogies of each layer (MS12, MgSO_4 · 12H_2O, NS10, Na_2SO_4 · 10H_2O: ROCK, the composition of Orgueil minus leachable Mg and Na sulfates and these phases' apportionments of hydrated water). The right-hand column gives the densities of each frozen layer.

tion this layer would be composed of 50% ice + 44% MgSO_4 · 12H_2O + 6% Na_2SO_4 · 10H_2O; its density is 1.133 g cm^{-3} (at 1 atm pressure).

Fractional eutectic melting and extraction of liquid E (in Fig. 3a) from the interior would drive the solid residue toward the binary join H_2O–Na_2SO_4. The subsequent evolution of this residue, composed of ice and mirabilite (plus rock), is best visualized in the binary H_2O–Na_2SO_4 phase diagram (Fig. 2b). A second stage of melting could occur at the binary eutectic, producing a liquid containing 4% Na_2SO_4 and no MgSO_4. This liquid has a density of about 1.05 g cm^{-3}, substantially less than the density of the frozen ternary eutectic layer (1.13 g cm^{-3}). Therefore, this binary liquid could easily ascend to the surface, forming a crust composed of 91% ice + 9% mirabilite, and leaving a residue in the rocky core composed of mirabilite. Mirabilite may then melt incongruently at 32.5°C, forming an anhydrous residue of thenardite and a liquid containing 34% Na_2SO_4. The dense binary peritectic liquid would intrude at the base of the mantle, forming a frozen lower
mantle composed of 76% mirabilite + 24% ice. The average density of this satellite is 1.76 g cm\(^{-3}\).

**Model C.** The initial rock fraction, \( R_i = 0.6689 \), has been chosen so that ternary eutectic melting leaves a residue of ice and mirabilite in precisely the ratio of the binary eutectic; thus, ternary eutectic melting is followed by binary eutectic melting in the system H\(_2\)O–Na\(_2\)SO\(_4\), without leaving a residue of either salt or ice. \( R_i \) is also very similar to Ganymede’s; Mueller and McKinnon (1988) calculated \( R_i = 0.64 \) to 0.65 when the rock was assumed to have a CI chondrite composition and Ganymede was assumed to be differentiated. The differentiation of this object is qualitatively the same as in model B except that there is no mirabilite residue and, thus, no Na\(_2\)SO\(_4\)-rich lower mantle layers. The average density of this satellite is 1.68 g cm\(^{-3}\).

**Model D.** This model is again similar to models B and C except that water ice is left in the residual rocky core after mirabilite is exhausted during the binary phase of melting in the system H\(_2\)O–Na\(_2\)SO\(_4\). The excess water ice melts at 273 K, yielding pure water with a density less than the ternary eutectic mantle, but greater than the density of the binary sodium sulfate-rich layer; hence, water may tend to intrude between these two salt-rich layers. However, when it freezes, water ice is less dense than the overlying layer composed of ice and mirabilite, so the intruding ice may tend to work its way to the surface over time. In any case, the assumption that the final differentiated structures are gravitationally stable stratified means that the final structure indeed exhibits an ice crust. Exactly what really would happen is not obvious. Ice might ascend slowly in small diapirs, rather like terrestrial salt domes, or overturn could be catastrophic. Alternatively, this water could dissolve substantial quantities of salt, becoming gravitationally stable at depth or mixing with the crust or mantle.

The average density of this object is 1.54 g cm\(^{-3}\). With \( R_i = 0.6 \), this mixture is similar to Callisto’s composition as calculated by Mueller and McKinnon (1988) (although obviously the structure calculated here is different from that calculated by Mueller and McKinnon).

**Model E.** This is qualitatively the same as model D, but the amount of water is greater, resulting in a thicker ice crust. The average density is 1.26 g cm\(^{-3}\), similar to the least dense, iciest satellites in the Solar System.

**Importance of Na\#.** Na is defined as Na\(_2\)SO\(_4\)/\((\text{Na}_2\text{SO}_4 + \text{MgSO}_4)\). The models in Fig. 9 assume that the initial rock has the composition of Orgueil, with Na\# = 0.255. However, Na\# differs among various chondrites, and even varies considerably within Orgueil itself, so Na\# should really be considered a free parameter.

The models in Fig. 9 have Na\# = 0.255, compared to Na\# = 0.15 for the ternary eutectic liquid. Any line drawn from eutectic E through any of the ice-bearing mixtures (models B, C, D, and E) necessarily intersects the joint H\(_2\)O–Na\(_2\)SO\(_4\) (see Fig. 3a). Simply, but significantly, this means that ternary eutectic melting of any mixture of ice and Orgueil-like rock will leave a residue containing H\(_2\)O and Na\(_2\)SO\(_4\), and not retaining MgSO\(_4\). Hence, MgSO\(_4\) is always the first component to be exhausted in models B through E in Fig. 9, with the consequence that the differentiated structures always have a mirabilite–ice binary eutectic layer overlying a ternary MgSO\(_4\)-rich layer.

If, however, Na\# < 0.15 in the initial rock component then the ternary eutectic liquid has Na\# greater than the initial rock; then ternary eutectic melting would leave a residue composed of H\(_2\)O and MgSO\(_4\) and depleted in Na\(_2\)SO\(_4\). Therefore, the petrologic evolution of objects having Na\# < 0.15, and their resulting differentiated structures and geologic histories, would be very different from those depicted in Fig. 9.

**Fate and significance of minor components.** Figure 9 does not consider the possible petrologic roles of minor soluble and abundant but weakly soluble components. Consideration of petrologically evolved silicate planets such as the Earth and Moon, where minor mantle components often become major crustal constituents, is sufficient reason to briefly consider minor salts in the evolution of icy satellites and asteroids.

Phase equilibria shown in Fig. 3 indicate that Ni is compatible while Mn and K can be considered incompatible with respect to Mg-rich sulfates. Therefore, early-generated liquids will be Ni-poor and K- and Mn-rich compared to the initial salts, thus enriching the solid residuum in Ni and depleting it in K and Mn. Continued melting will yield liquids progressively more enriched in Ni and depleted in K and Mn. Complex evolutionary scenarios could involve remelting prior melts. This could yield liquids so enriched in K and Mn that they become major components, and could grossly deplete Ni. It is not known whether any icy satellites or asteroids have such complicated geological histories, but a brief look at Europa and Ganymede suffices to allow this possibility. Magmatic redistribution of \(^{40}\text{K}\)-carrying salts such as K\(_2\)SO\(_4\) could be an important factor affecting the subsequent thermal structures and evolution of differentiated asteroids and icy satellites.

K and Rb salts could eventually be useful in automated, *in situ* isotopic dating of cryovolcanic flows (Kargel 1989). K and Rb salts have yielded correct ages for terrestrial evaporites, although groundwater flow and subtle heating often disturbs parent–daughter systems (Brookins et al. 1980, 1985). The frequent problems encountered in dating terrestrial evaporites would not be expected in deep-frozen cryovolcanic flows.

CaSO\(_4\) is expected to be a minor component under all
circumstances because of its low solubility. Its abundance, though low, is very sensitive to the abundances of major salts and to the mode of petrogenesis of the liquid. For instance, the abundance of CaSO₄ is very different in waters formed by melting ice (in the presence of gypsum), by dehydrating gypsum, or by dehydrating phyllosilicates (in the presence of anhydrite).

In sum, minor salts could be very useful in chemical and isotopic probing of the evolution and internal structures of icy satellites and asteroids, provided that in situ analyses become feasible.

**High-temperature dehydration.** The models in Fig. 9 consider only low-temperature melting events, ignoring the potential of gypsum and phyllosilicates to contribute water to the crust and mantle through comparatively high-temperature dehydration. Indeed, the residual rock cores shown in Fig. 9 still contain about 14.6% water of hydration. This water could be released beginning near 40°C with the dehydration of gypsum (Posnjak 1938), and continuing in steps to 500°C with the dehydration of clays. If low-temperature leaching does not release chlorine, then it would surely be liberated during the dehydration of phyllosilicates. A brief consideration of elemental and water abundances suggests that these hydrothermal fluids would contain an average of ~1% chloride salts. Anhydrous sulfates left from prior melting events would also dissolve in the fluid.

**Implications of a possible high-temperature origin of sulfates.** Oxidation of reduced sulfur to form the sulfates observed in carbonaceous chondrites requires, of course, a source of oxygen. This source remains a topic of continuing speculation. Oxidizing agents may have included HOH formed by ultraviolet hydrolysis reactions in protoplanetary atmospheres, or O₂ generated in satellite and asteroid interiors by γ and β hydrolysis of water (J.S. Lewis, private communication). These mechanisms may yield sulfate by reactions at low temperatures. The fact that terrestrial oxidation of sulfides such as pyrite occurs rapidly in sedimentary environments clearly indicates that, given a suitably oxidizing aqueous environment, low-temperature kinetics are no hindrance to efficient sulfate formation. However, M. Zolensky (private communication) suggests that a comparatively high-temperature (>100°C) event may have been responsible for oxidation and aqueous alteration in CI chondrites.

This high-temperature scenario could have important implications for this work. High temperatures might not permit large amounts of water to be retained: ice could melt and the water might be extruded before sulfur oxidations occur, or, if temperatures never exceed the melting point of ice, sulfates might never be formed. Either way, aqueous sulfate magmatism as described in this work might not occur. On the other hand, high-temperature formation of sulfates might be followed by higher-temperature dehydration of phyllosilicates; such an event might yield hypersaline sulfate brines, but brine magmatism would follow a radically different scenario than outlined in the models above. Alternatively, pressures >24 kbars in the deep interiors of large icy satellites might allow sulfate-forming reactions in high-pressure ice-bearing assemblages. As an additional or alternative phenomenon, impact shock heating may result in local high-temperature conditions favoring formation of sulfates, while colder regolith more distant from the impact site could retain ice and perhaps cold-trap ice melted by the impact. Sulfate-and ice-rich compositions could also be produced by heterogeneous accretion of separate ice-rich and sulfate-rich planetesimals. These complex scenarios are presented as a reminder that sulfate magmatism is neither bound to follow simple scenarios, nor is sulfate brine magmatism the inevitable consequence of melting cosmic ice-rock mixtures.

### 5.2 Carbonaceous Chondrites


It is frequently noted that aqueous alteration and chemical precipitation in the chondrites apparently occurred largely in situ, and that redistribution of soluble matter was restricted to the scales of individual salt veinlets and nodules (mm–cm scales). Large-scale redistribution would certainly have caused bulk samples of these meteorites to deviate strongly from chondritic (solar) composition, which is not observed (significant but small departures are observed, on small spatial scales). This means that the salt veins are probably not igneous dikes or cryovolcanic conduits in the usual sense in that relatively little transfer of aqueous brine took place along these fractures. Figure 9a, a model representation of a generic differentiated chondritic asteroid, does not represent the evolution of the carbonaceous chondrites, which are essentially undifferentiated.

Ice may have been involved in the genesis of some
Chondrite brines and salts (Grimm and McSween 1989, Jones et al. 1988). This is an important issue toward which the compositions of sulfates contribute considerable insight. The origin of sulfate ion has been linked to the oxidation of reduced sulfur (Lewis 1967, Lewis and Krouse 1969), since native S and sulfates (among other alteration products) are observed with reaction relationships with corroded sulfides, especially pyrrhotite (Bostrom and Fredriksson 1964, Bass 1970).

Richardson (1978) inferred that three successive generations of salt veins precipitated in several different CI chondrites, these generations being dominated first by Ca–Mg–Fe–carbonates, then by Ca–sulfate (gypsum), and last by Mg–Ni–Na–sulfate. This sequence is in order of increasing degree of oxidation and increasing solubility in water. The collective set of observations, including petrographic relations discussed by many other workers suggests that the CI chondrites were derived from an asteroidal impact regolith. The aqueous environment of the salt veins evolved from relatively acidic, moderately reducing, low salinity conditions during precipitation of carbonates, to basic, oxidizing, hypersaline conditions during precipitation of Mg-rich sulfates. The increase in salinity may have involved one or more of three factors: progressive silicate alteration by the brine, or either evaporative or freezing concentration of salts. However, the third series of salt veins described by Richardson (1978) can also be explained by a very late event involving dehydration and recrystallization of sulfates due to solar heating after the meteoroid entered an Earth-crossing orbit, or even after landing on Earth.

Saturation in magnesium sulfate requires a hypersaline brine equal to or more saline than the H₃O–MgSO₄ eutectic (17% MgSO₄), roughly five times saltier than sea water. It is productive to examine published meteorite sulfate compositions in the context of aqueous sulfate equilibria.

**Chondrite sulfates: The Ni problem.** Several salt veins from two different meteorites contain large but widely variable amounts of NiSO₄, while other veins in the same meteorites contain almost none (Fredriksson and Kerridge 1988), implying gross macroscopic chemical disequilibrium. As shown in Fig. 3e and discussed in Part 3, the partitioning behavior of Mg and Ni between liquids and solids in the aqueous Mg–Ni–sulfate system is of order unity, and complete solid solution exists between the two sulfate end-members. Thus, severe fractionation of Ni from Mg to the degree observed cannot be accomplished by normal igneous processes. But the fact that severe fractionation did occur is all the more remarkable since aqueous processes are believed to have occurred largely in situ, with little opportunity for multistaged igneous fractionation. Two explanations for this are offered below, the first one involving the pH of the solution, the second involving progressive oxidation.

Large variations in the abundance of NiSO₄ could occur if the solution pH shifted between slightly acidic values where Ni could have existed as dissolved NiSO₄, and slightly basic values where Ni existed stably as Ni(OH)₂ or some other nearly insoluble solid. For Ni activities ~0.01 the critical pH for this equilibrium is ~6.5 (Brookins 1988). This is sufficiently basic that Fe should reside in stable solid oxides or hydroxides, consistent with the lack of a major FeSO₄ component in chondrite salt veins. It is also sufficiently acidic that Mg would remain as soluble MgSO₄ rather than solid Mg(OH)₂. Solution pH could rise above 6.5, triggering precipitation of Ni(OH)₂, by progressive hydrolysis of silicates or by freezing or evaporative concentration of minor alkali sulfates in an initially acidic solution. Subsequent magnesium sulfate precipitates would be sharply depleted in Ni. Alternatively, or additionally, the extremely variable Ni abundances in chondrite sulfates could be related to a trend of progressive oxidation that can be inferred on independent grounds. Partial oxidation of (Fe, Ni)S results in the residual sulfide becoming more Ni-rich than it was initially, since NiS is oxidized with greater difficulty than FeS. Late-stage oxidation of Ni-rich sulfides would produce Ni-rich sulfate veins.

**Mg–Na sulfate compositions of chondrite veins.** The ternary compositions of chondrite sulfates provide useful constraints on the origin of the veins. As discussed in Part 3, phase equilibria among highly soluble salts in C1 and C2 chondrites can be described accurately in the three-component system H₂O–MgSO₄–Na₂SO₄ (Fig. 3a) if minor components are summed with chemically similar major ones. Very importantly, recall that we do not reliably know the original amount of hydrated water in these salts. The ternary compositions of these salts provide reliable information only on their Na/Mg ratios. It is useful to define an expression for this ratio: Na# = ["Na₂SO₄" : ("Na₂SO₄" + "MgSO₄")], where "MgSO₄" includes NiSO₄ and MnSO₄ calculated as the molar equivalent mass of MgSO₄, and "Na₂SO₄" includes K₂SO₄ calculated as the molar equivalent mass of Na₂SO₄.

Analyses of four individual sulfate veins and two bulk soluble extracts of sulfates from two meteorites have been reported in the literature (Bostrom and Fredriksson 1964, Fredriksson and Kerridge 1988). More recent analyses of sulfates from 10 carbonaceous chondrites yielded semiquantitative estimates of sodium and magnesium sulfate contents (Burgess et al. 1991), but the analytical techniques utilized were very crude and the breakdown of total sulfates into metal sulfate components was by rather indirect and uncertain inference. Thus, the data of Burgess et al. do not significantly assist in this particular exercise.

Two bulk soluble extracts of Orgueil sulfates give...
Na# = 0.255 and 0.083, clearly indicating that this meteorite is grossly heterogeneous with respect to its sulfate vein compositions. Expressed as molar fractions these numbers are, respectively, 0.226 and 0.071. Despite first appearances, this heterogeneity does not indicate fluid transport and salt/fluid fractionation on the spatial scale of Orgueil (decimeters). This is because each portion of Orgueil contains both veins and matrix, and what is present in the local veins is absent in the matrix so that each bulk sample of Orgueil (including veins and matrix) remains more or less solar in composition.

Four individual vein analyses give Na#'s of 0.338 (Orgueil vein #7), 0.336 (Orgueil vein #6), 0.335 (Ivuna vein #20), and 0.143 (Ivuna vein #19) (from Fredriksson and Kerridge 1988). In molar fractions these numbers are, respectively, 0.302, 0.301, 0.300, and 0.124. Of these vein analyses, three (from two different meteorites) are virtually identical in Na#, although Ni/Mg varies considerably. The other vein is similar to any of three eutectics, including the eutectic in equilibrium with ice, mirabilite, and epsomite (Fig. 3a).

The three clustered Na#'s do not correspond to any known eutectic liquid in the aqueous Mg–Na sulfate system, nor do they correspond to any of the mixed Mg–Na sulfates known to occur. Fredriksson and Kerridge (1988) suggested a compositional similarity to nickel bloedite (MgSO₄ · Na₂SO₄ · 4H₂O), but the stoichiometry is incorrect for this or any other known sulfate. If bloedite is a major mineral then a consistent fraction of epsomite or another pure magnesium sulfate must be intermixed in these veins. The clustering of these three sulfates seems real, however. Since it is unlikely that three veins from two meteorites just happen to have the same composition, this clustering argues for the existence either of a previously unknown mixed salt with the approximate stoichiometry (Mg, Ni)₂Na₂(SO₄)₃ · xH₂O, or of a previously unknown eutectic occurring near this composition. Kinetic factors may have been responsible for precipitation of an unknown metastable mixed Mg–Na–sulfate compound (which may subsequently have reverted to bloedite and epsomite). Alternatively, it is possible that the pressure variable is responsible; perhaps at the modest pressures deep in the interiors of chondrite parent bodies an unknown high-pressure mixed sulfate precipitates with the stoichiometry inferred above, or perhaps high pressures result in a different invariant melting composition corresponding to the clustered vein compositions. The Ivuna #19 sulfate composition, corresponding closely to known eutectics, may represent melting or precipitation at lower pressures where phase equilibria are similar to the 1-atm case. In any event, an experimental study of polybaric phase relations in this system would be a valued endeavor, as would the acquisition of additional high-quality chondrite sulfate compositions. Unless the method of Burgess et al. (1991) can be significantly improved this author does not recommend the heating–oxidation technique.

Chemical data reported by Fredriksson and Kerridge (1988) indicate that in one Mg–Na–Ni sulfate vein, apparently the vein Ivuna #19, Na and Ni are concentrated together on one side of the vein. Such zoning probably indicates chemical evolution of the brine from which this vein precipitated; hence, the liquid composition was not precisely that of a eutectic, at least not at the time the vein precipitated (the parent solution could be a high-pressure eutectic, however). Figure 3e tells us that any sulfates precipitated early would tend to have slightly higher Ni contents than the liquid, and precipitation would force the liquid to migrate in the direction of Ni depletion. The early liquidus phase assemblage was both Na- and Ni-rich. Candidate sodic phases are mirabilite and bloedite. However, even the most sodic portions of this vein contain more Mg than either of these phases, so the brine must have been precipitating along a eutectic involving coprecipitation of a magnesium sulfate in addition to a sodic phase. In the region of Fig. 3e there are few choices. Given also the Na# of this vein, 0.143, it seems quite probable that the early evolution of this brine involved cooling and precipitation along the eutectic between mirabilite and epsomite. If cooling continued these solid phases would react with the residual liquid at the peritectic, forming magnesium sulfate dodecahydrate; perhaps eventually the liquid would attain the eutectic involving precipitation of water ice. This evolution would result in just the sort of chemical trends observed, since Na and Ni would be depleted in the late-forming crystal assemblage. It also indicates that the brine was not in equilibrium with ice when the highly sodic portion of the vein was precipitated. This conclusion is consistent with the calculations of Zolensky et al. (1989), who concluded that CI (C1) chondrites were probably altered from CM (C2) or CV3 (C3) chondrite material at temperatures ~50 to 150°C, while CM (C2) chondrites were altered near 0°C.

5.3. Europa

Europa has one of the youngest, smoothest, brightest, and geologically most active surfaces in the Solar System (Smith et al. 1979). Europa's average albedo, 0.7 (Buratti and Veverka 1983), is exceeded in the Solar System only by the surfaces of Enceladus and Triton, both of which also have had geologically dynamic histories. Water ice reflectivity and absorption features in the visible and near infrared spectrum of Europa require water ice to be the dominant component of the visible surface (Clark 1980, Clark et al. 1986). Other, more subtle spectral features and albedo variations, however, indicate minor impurities including sulfur dioxide (Ockert et al. 1987). Europa ap-
parently suffered global volcanic resurfacing comparatively recently. Indeed, Squyres et al. (1983) suggested that active and very widespread resurfacing may be occurring by frost deposition associated with water volcanism. Europa's mean density, 3.04 g cm$^{-3}$, is intermediate between the densities of aqueously differentiated C1 chondrites (2.69 g cm$^{-3}$; model A, above) and Io (3.53 g cm$^{-3}$) and is just slightly greater than the density of C2 chondrites. Squyres et al (1983) suggested that Europa contains a dense, mainly anhydrous rocky core and a water ice crust ~100 km thick formed by dehydration of hydrous silicates.

Model A (Fig. 9a), though strictly applicable for the aqueous differentiation of C1 chondrites, qualitatively suggests a different structure and evolutionary history than modeled by Squyres et al. (1983). Europa originally may have resembled C2 chondrites, roughly approximated here as a mixture of one part C1 and two parts C3 chondrites supplying 6% water (Squyres et al. 1983). Thus, Europa contained one-third as much water, but also one-third as much salt as C1 chondrites. Differentiation may be approximated within the ternary system H$_{2}$O–MgSO$_{4}$–Na$_{2}$SO$_{4}$ (Fig. 3a). The initial stages of igneous evolution should be identical to that described in model A, except that the volumes of each differentiated layer would be one-third that shown in model A.

Europa shows clear indications of a prolonged and continuing igneous evolution, which must require a more complex scenario than outlined in model A. Indeed, Europa is nearly as large as Earth's Moon, where extensive igneous silicate differentiation occurred. It seems inescapable that radiogenic heating plus tidal deformational heating would have elevated internal temperatures in Europa to the point where gypsum and hydrous silicates would have dehydrated (Lewis 1971, Squyres et al. 1983). Thus, the remainder of Europa's water associated with hydrated silicates should also be in its crust. After this later addition of water, Europa's crust, ~110 km thick, would constitute ~8.8% of the satellite's mass (6.0% H$_{2}$O; 2.0% MgSO$_{4}$; 0.69% Na$_{2}$SO$_{4}$; minor sulfates of K, Mn, and Ni; 0.09% chlorides—probably mainly MgCl$_{2}$; 0.01% CaSO$_{4}$; and negligible Ca–Mg carbonates assuming slightly acidic to basic pH). Resuming the three major components to 100%, the bulk composition of Europa's crust would be H$_{2}$O 69%, MgSO$_{4}$ 23%, and Na$_{2}$SO$_{4}$ 8%.

Continued heating of Europa's crust by tidal dissipation would result in further differentiation of the crust. The road to complete differentiation would have been very complex, but once complete, Europa's crust would be composed of a thin lower crust ~15 km thick composed of anhydrous magnesium and sodium sulfates, and a thick (~95 km) ternary eutectic upper crust composed of ~50% water ice, 44% MgSO$_{4}$·12H$_{2}$O, and 6% Na$_{2}$SO$_{4}$·10H$_{2}$O. Any further heat input would result in repetitive congruent melting of the eutectic crustal layer. While trace and minor components could fractionate during repeated melting, the major components would maintain the same eutectic composition in the liquid phase and solid residues, irrespective of the extent of melting. The eutectic liquid is more dense than its coexisting solid assemblage, so eruptive activity would tend to be inhibited. Instead, the liquid would pool between the overlying frozen eutectic saline crust and the anhydrous lower crust, forming magma chambers or a saline magma ocean.

Complete freezing of lower crustal brine would be more difficult than in the salt-free case since solutes would depress the freezing points. While sulfates would mostly freeze out between 260 and 269 K, the aqueous eutectic chloride fraction of the brine would not completely freeze until about 221 K (for 1 atm; pressures of ~1 kilobar 95 km deep would depress the freezing point of the chloride solution to about 212 K). This could greatly reduce the rigidity of the upper crust, thus allowing prodigious rates of tidal dissipative heating and vigorous geologic activity to be maintained into the present epoch (Cassen et al. 1980, Squyres et al. 1983).

Crystallization of brines in the lower crust would result in volume expansion and possibly tensile fracturing of the upper crust. Lower crustal brines could be forcibly extruded under pressure during progressive freezing. Fractional crystallization seems likely, given the low viscosity of the brine and the high density differences between the brine and all solid phases. Complex vertical mineralogical zonation of the crystallizing magma could occur. Remelting of these layers would produce liquids of many compositions, some less dense and others more dense than the overlying ternary eutectic crust. Extrusive activity would selectively involve the least dense, least saline brines, e.g., aqueous sodium sulfate eutectic liquid formed by melting ice plus mirabilite.

Brine eruptions, whether or not resembling the model outlined above, should have left physical evidence on the Europan surface. The low relief of Europa's volcanic plains (compared, say, to Triton's) is consistent with the low viscosities of brines (Kargel et al. 1991). It is somewhat surprising that spectral evidence of salts has not been reported, as it seems difficult to avoid melting any part of Europa, at any stage in its evolution, without involving substantial quantities of salts. However, water evaporated from erupted brines would tend to recondense widely on the cold surface of Europa (Squyres et al. 1983) and might tend to hide the spectral signature of the expected magnesium and/or sodium sulfates and other salts. The ultraporous microstructure of Europa's surface as inferred from photometry (Domingue et al. 1991) is consistent with such frost deposition. Furthermore, cryovolcanic salts would be hydrated and mixed with water ice, so the strong spectral signature of intimately mixed ice...
and chemically bound water may mask the spectral signature of salts.

5.3. Ganymede

Geology and composition. Ganymede's average density, 1.93 g cm$^{-3}$, is much lower than those of Io (3.55) and Europa (3.01) (Schubert et al. 1986). Ganymede's density falls between the densities of compressed (nonporous) C1 chondrites (2.6–2.8), and compressed water ice (ranging from 0.92 to 1.4 for various relevant polymorphs), indicating that Ganymede, like the other icy satellites, contains substantial fractions of both rock and ice (Lupo and Lewis 1979, Schubert et al. 1986, Mueller and McKinnon 1988). This simple but important fact supports well-based theoretical predictions that ice should be an abundant low-temperature condensate in the outer Solar System and specifically in Ganymede (Lewis 1971, 1972). Telescopic observations confirm that ice is the major constituent of Ganymede's surface, although there is also an important rocky component (e.g., Clark et al. 1986).

The estimation of the ice and rock fractions in icy satellites has been an important objective of many workers. Schubert et al. (1986) and Mueller and McKinnon (1988) clearly showed that without tighter constraints on the composition of the rock and on Ganymede's state of differentiation, one cannot derive a unique rock fraction. This important parameter may be as low as 0.49 to as high as 0.65. However, the geology of Ganymede's surface requires at least some degree of internal differentiation. Extensive if not complete differentiation seems probable. Modeling the case of extensive differentiation, Mueller and McKinnon (1988) calculated rock fractions ranging from 0.54 to 0.59 depending on the type of rock composing Ganymede's core. However, the authors pointed out that regardless of the core's present composition it very likely evolved from an initial rock component resembling C1 chondrites. If the rock fraction is expressed in terms of the initial fraction of C1 chondrite rock, a differentiated Ganymede would have contained 44 to 65% of its mass as rock, the remainder being ice. The latter set of rock fractions, 0.64 to 0.65, corresponds to $R_c$ in the models shown in Fig. 9. The quoted range of 0.54 to 0.59 would roughly correspond to $R_i$, the final rock fraction after soluble salt extraction; however, this correspondence is not exact, since the models of Mueller and McKinnon (1988) leave the anhydrous salts in the rock while extracting only their water content.

Pre-Voyager theoretical models showed the likelihood that Ganymede would be differentiated (Consolmagno and Lewis 1978). This prediction is confirmed even in low-resolution full-disc images showing bright and dark terrains on Ganymede's surface. Higher resolution images reveal terrains with considerably varied crater densities and intensely fractured and volcanically flooded terrains, indicating a complex history of differentiation (Smith et al. 1979, Head et al. 1981, Woronow et al. 1982, Squyres 1982, Parmentier et al. 1982, Casachia and Strom 1984, Croft 1985 and 1986, McKinnon and Parmentier 1986, Schenk and McKinnon 1987, Croft and Goudreau 1987, Golombek and Banerdt 1986, Allison and Clifford 1987, Murchie and Head 1988, Mueller and McKinnon 1988, Tittemore 1990). Bright terrain typically intrudes older dark terrain (Parmentier et al. 1982, Squyres 1982), and usually the light terrain is heavily deformed by one or more sets of extensional and probably also transtensional tectonic features (Murchie and Head 1988).

Volcanism and extensional tectonism are closely interrelated on Ganymede as they are on Earth. Fracture zones are frequently the sources, and tectonic depressions are commonly the containment basins for erupted plains-forming liquids (Head et al. 1981, Parmentier et al. 1982, Allison and Clifford 1987). In many areas tectonic grooving was followed by cryovolcanic flooding, in turn sometimes followed by reactivation of grooving and reflooding. Thus, near the end of a period of heavy impacting, Ganymede seems to have suffered late episodes of intense tectonic and cryovolcanic surface modification (Woronow et al. 1982).

An absence of obvious flow margins in the best Voyager images of Ganymede's smooth plains indicates that flow thicknesses must be <100 m. Hence, the erupted liquids possessed low viscosities and yield strengths relative to much thicker flows on the satellites of Uranus and Neptune. After considering the 1/7g surface gravity, the erupted substances may have been rheologically comparable to any substance as "thin" as or "thinner" than andesite (Kargel 1990). Of course, silicate lavas are disallowed in Ganymede's situation, so rheologically compatible and compositionally likely substances would include water, salt brines, or ammonia–water liquids, the latter only as long as there are low contents of additional components and suspended crystals (Kargel et al. 1991). Since substantial quantities of ammonia are unlikely to have condensed in the relatively warm Jovian nebula, water or salt brines are more likely than ammonia–water liquid.

The freezing-point depression caused by salts also may assist in melting in a satellite that may convectively regulate its internal temperatures below the melting point of pure ice. Magnesium sulfate alone would only lower the melting point by 4 K, but certain other salts, particularly the chlorides, are more effective freezing point depressants. Once volcanism initiates the fraction of rock in the solid residual core increases, causing the viscosity of the core to increase, resulting in higher convective temperatures or even a complete failure of
the convective mechanism, thereby promoting further melting.

**Internal structure of a differentiated salty Ganymede.** Figures 9C and 9D bracket Ganymede's composition. Of course, these models do not consider the important effects of elevated pressures in Ganymede's interior, nor of qualitatively different scenarios involving possible fractional crystallization of magma oceans. Despite this outrageous neglect, it seems probable that Ganymede would have some type of compositionally layered structure; based on these models the structure would include a MgSO\(_4\)-rich mantle ~500 to 600 km thick, containing ~15-20% by mass MgSO\(_4\) and Na\(_2\)SO\(_4\), plus minor quantities of other salts. This layer would be overlain by less salt-rich icy upper mantle and crustal layers an additional several hundred kilometers thick.

Pressures near the core/mantle boundary would be ~12–13 kbars, so the mantle and crust also would be layered with respect to ice polymorphs, including phases up to ice VI near the base of the mantle. The effects of pressures on sulfate phase stability are uncertain, although sparse and conflicting experimental data suggest a phase change in epsomite near ~5 kbars and perhaps another at pressures over ~10 kbars (Bridgman 1948a,b, Livshits et al. 1963). Mantle and crustal compositions reflect phase equilibria during partial melting which would have occurred under pressures ranging as high as 50 kbars near the center of Ganymede. Such high pressures would certainly impact subsolidus and solid–liquid phase equilibria in ways that are difficult to predict. Therefore, Fig. 9 is not at all a reliable guide to Ganymede's interior structure, but is a valid indication of the probable importance of salts in Ganymede's and other icy satellite's histories and interior structures.

Taking Figs. 9c and 9d literally, Ganymede's surface would be composed of volcanic flows of water or sodium sulfate–water solutions. However, in reality it would be difficult to extrude these liquids through the magnesium sulfate-rich mantle without substantial contamination by magnesium sulfate. Also, if Ganymede's Na\# < 0.15 then sodium sulfate would be exhausted before magnesium sulfate, causing a different petrologic evolution of late-stage liquids. Coupled with the unknown pressure-related effects on phase equilibria, it is not yet possible to predict with any certainty what Ganymede's surface composition should be. Even so, it seems a priori highly probable that salts, particularly magnesium and/or sodium sulfates, would be significant components.

6. SUMMARY

Brine volcanism may explain resurfacing observed on some icy satellites, particularly Europa and Ganymede, and is expected to have been important in the evolution of chondritic asteroids. Carbonaceous chondrite mineralogies, cosmic elemental abundances, and salt solubilities suggest that MgSO\(_4\) and Na\(_2\)SO\(_4\) are the most important solutes. Internal chemical structural models of icy satellites and asteroids suggest a wide range of possible evolutionary scenarios, some involving the formation of thick salt-rich crusts and mantles.

Salt–water eutectic brines have densities lower than typical ice–rock mixtures, and therefore can be extruded onto the surfaces of icy satellites during early stages of differentiation. The ternary MgSO\(_4\)-Na\(_2\)SO\(_4\)-H\(_2\)O eutectic liquid has a density of ~1.19 g cm\(^{-3}\), compared to 1.13 g cm\(^{-3}\) for the equivalent frozen eutectic mixture; therefore, a solid eutectic crust would float on its own liquid. MgSO\(_4\)-rich aqueous volcanism would become increasingly difficult as a eutectic-composition crust became thicker. Early eutectic volcanism may generally yield to later plutonism or even formation of stable brine magma oceans. Late-stage water or Na\(_2\)SO\(_4\)-H\(_2\)O eutectic volcanism would be favored, since these liquids are less dense than the MgSO\(_4\)-rich eutectic crust. Such late-stage water-rich volcanism could occur if ice and mirabilite are left in excess amounts in the core after exhaustion of magnesium sulfate.

Hypersaline brines have much lower viscosities than familiar silicate lavas, although they are more viscous than pure water. Aqueous sulfate flows may produce extensive flows on the order of a meter thick, constructing vast volcanic plains of low relief such as observed on Ganymede and Europa. Chloride brines are generally more viscous than sulfate brines. Under low-g conditions on icy satellites and asteroids chloride brines would probably behave fluid dynamically much as basalt behaves on Earth, producing characteristic flow thicknesses of ~2–20 m. Chemical as well as geomorphic evidence should exist on the surfaces of objects affected by brine volcanism, and might be discernable in observations planned for Galileo.

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