

Chemistry of Sodium, Potassium, and Chlorine in Volcanic Gases on Io

Bruce Fegley, Jr.

Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri 63130-4899
E-mail: bfegley@levee.wustl.edu

and

Mikhail Yu. Zolotov

Department of Earth and Planetary Sciences, Washington University, St. Louis, Missouri 63130-4899

Received October 27, 1999; revised February 26, 2000

We used thermochemical equilibrium calculations in the O–S–Na–K–Cl–H system to model the speciation of volcanic gases emitted from high-temperature (1000–2000 K) silicate magmas on Io. The effects of temperature, pressure, and bulk composition of the gases are explored. The bulk compositions are based on atomic ratios observed in Io's plasma torus and extended atmosphere, and from chondritic abundances. The results show that chlorides of Na and K are the major Cl gases, NaCl, Na, and (NaCl)₂ are the major Na gases, and KCl, (KCl)₂, and K are the major K gases for systems with (Na + K)/Cl > 1. The abundances of Na, K, and Cl gases change dramatically at (Na + K)/Cl = 1. As the (Na + K)/Cl ratio decreases below unity, which is possible for lower temperature volcanic vents, the major Cl gases change to Cl₂, Cl, S₂Cl, and SCl₂. The results show that abundances of H-bearing gases are insignificant for plausible hydrogen abundances in Io. Higher temperatures and lower pressures increase the abundances of monatomic Na and K. Sodium, K, and Cl compounds condense as Na₂S (at higher temperatures and lower O/S ratios), Na₂SO₄ (at lower temperatures and higher O/S ratios), and NaCl and KCl. Under some conditions, Na₂SO₄ and Na₂S condense simultaneously. These condensates can form coatings on silicate ash particles in the vicinity of volcanic vents. Condensation temperatures decrease as pressure decreases, and condensation is not favored by low-pressure volcanic vents. Silicate magmas, especially alkaline ultrabasic magmas may be important sources of S, alkalis, and Cl on Io. Our predictions agree with spectral absorption features indicating that sodium sulfate and/or sodium sulfide may be present in red deposits on Io's surface. The two major sources of Na, K, and Cl in the plasma torus are sputtering from solid Na₂S/Na₂SO₄/chloride surface condensates and ionization of alkali chloride and monatomic alkali gases that could be present in volcanic plumes and Io's volcanic atmosphere. © 2000 Academic Press

Key Words: Io; volcanic gases; volcanic condensates; volcanism; alkalis; sodium; potassium; chlorine; sulfur; hydrogen; sodium sulfide; sodium sulfate; sodium chloride; potassium chloride.

INTRODUCTION

Intense volcanic activity on Jupiter's Moon Io supplies sulfur and oxygen, which are the two most abundant elements in the volcanic plumes, atmosphere, and plasma torus (Spencer and Schneider 1996). In addition, a significant part of Io's surface is covered by S- and O-bearing species: solid SO₂, possibly other sulfur oxides, and allotropes of elemental sulfur. Sodium and potassium, although less abundant than sulfur and oxygen, are also present in Io's extended atmosphere and plasma torus (Spencer and Schneider 1996). Recently, chlorine has been detected in the torus (Küppers and Schneider 2000).

Two major sources of S, O, Na, K, and Cl in the plasma torus have been suggested: the sputtering of materials on Io's surface, and gaseous molecules from volcanic plumes and the atmosphere. Sputtering of elements from surface materials is responsible for alkali atmospheres on the Moon and Mercury (Hunten *et al.* 1988, Killen and Ip 1999) and is probably an important process on Io as well (Chrissey *et al.* 1988, Wiens *et al.* 1997). On the other hand, powerful volcanic plumes up to several hundreds of kilometers high almost continuously supply material to Io's volcanic atmosphere and (following ionization and escape of gases) to the plasma torus as well. Both of these sources supply mostly volcanic material originating from gases emitted from magma, and from solid condensates, pyroclastic deposits, and solidified lava flows. It follows that the composition of Io's atmosphere and the torus can be used for the first order evaluation of the bulk composition of volcanic products (see Zolotov and Fegley 1998a,b, 1999).

Although alkalis and halogens have not been detected in volcanic plumes, in the atmosphere, or on Io's surface, a volcanic origin of these elements is likely. Hapke (1979) first discussed evaporation of Na from magmas to explain the occurrence of sodium in the torus. The extremely low amount of Si in the torus (Na *et al.* 1998) probably excludes any solid silicate source of

alkalis and Cl. In terrestrial volcanic gases, alkalis and chlorine are less abundant than sulfur and oxygen. However, their concentrations are not negligible (Bartels 1972, Crowe *et al.* 1987, Pennisi *et al.* 1988, Symonds *et al.* 1992, 1994). Chlorine (in the form of HCl) is the most abundant halogen emitted from terrestrial volcanoes, while sodium and potassium are the most abundant metals in degassing products of common silicate magmas (Symonds *et al.* 1994). These data are consistent with the high volatility of Na and K observed in laboratory studies of silicate melts (e.g., Corrigan and Gibb 1979, Rammensee and Fraser 1982, Markova *et al.* 1987) and heated meteorite samples (Tsuchiyama *et al.* 1981, Yakovlev *et al.* 1984). In addition to S- and O-bearing compounds, alkalis and chlorine are often observed in condensates from volcanic and fumarolic gases. Alkali chlorides (NaCl, KCl) are generally the most abundant condensates of the alkali elements (e.g., Tkachenko *et al.* 1999). It is thus possible that on Io intensive volcanic degassing of Na, K, and Cl (along with S and O) results in condensation of alkali chlorides and other compounds such as sodium sulfide (Na₂S) and sodium sulfate (Na₂SO₄) that are considered as plausible coloring agents on Io's surface (e.g., Nash 1993).

The purpose of this work is to evaluate quantitatively the speciation of Na-, K-, and Cl-bearing gases and condensed phases emitted from high-temperature volcanic gases on Io. The effects of temperature, pressure and bulk composition, including the effects of hydrogen, are considered. The calculations are a natural extension of our prior work on the chemistry and oxidation state of volcanic gases on Io (Zolotov and Fegley 1998a,b, 1999). Preliminary results are described by Fegley and Zolotov (1999) and Zolotov and Fegley (2000a). The results are discussed in terms of types of volcanic plumes, mineralogical composition and color of volcanic condensates, juvenile versus recycled sources of elements in host magmas, and volcanic contributions to the composition of Io's atmosphere and torus.

COMPUTATIONAL METHODS

We used ideal gas thermochemical equilibrium calculations to model chemistry of the alkalis and chlorine in volcanic gases on Io. This is the same approach as used in our prior modeling of volcanic gas chemistry on Io (Zolotov and Fegley 1998a,b, 1999). The basic assumption, which is illustrated in Fig. 1 of Zolotov and Fegley (1999), is that volcanic gases on Io reach chemical equilibrium inside the volcanic conduit where the high temperatures and pressures lead to characteristic chemical reaction times (t_{chem}) that are less than the characteristic cooling time during eruption (t_{erupt}). However, in the erupted volcanic plume, the low temperatures and pressures lead to the opposite situation (i.e., $t_{\text{chem}} > t_{\text{erupt}}$) and chemical equilibrium is no longer attained. In between these two regions, in the vicinity of the volcanic vent, t_{chem} and t_{erupt} become equal and quenching of the high-temperature chemical equilibria occurs during the supersonic eruptions. Zolotov and Fegley (1998a) presented thermochemical kinetic calculations showing that ionian vol-

canic gases are in chemical equilibrium until being quenched at the volcanic vent. Furthermore, a large body of data shows that terrestrial volcanic gases erupted at temperatures ≥ 900 K typically attain chemical equilibrium (Symonds *et al.* 1994).

Calculations were done over the same temperature (1000–2000 K) and pressure (10^{-8} – 10^2 bar) ranges as in our prior work. The temperature range spans the observed temperatures of hot spots on Io and the suggested temperature of the magma (e.g., McEwen *et al.* 1998). The pressures of Io's volcanic vents are unknown with the exception of Pele. We used observations of S, S₂, SO, and SO₂ at Pele (McGrath *et al.* 2000, Spencer *et al.* 2000) to calculate pressures of $10^{-4.7}$ to $10^{-5.4}$ bar in the vicinity of Pele's volcanic vent (Zolotov and Fegley 2000b). This is at the low end of the range we consider here, but different types of volcanic vents could have pressures within the range chosen. The pressures in the erupted volcanic plumes are much lower, but we are modeling chemistry inside the volcanic conduit, not in the erupted plume after expansion, cooling, and quenching of high-temperature chemistry have taken place. We use a nominal temperature of 1500 K and a nominal pressure of 1 bar in calculations that explore the effects of variable elemental ratios on volcanic gas chemistry. This was done because the elemental ratios derived from observations of the Io torus may not necessarily be identical to the elemental ratios in ionian volcanic gases. We also explore the effects of variable temperature and pressure on the chemistry of volcanic gases with fixed elemental abundances.

Our previous work considered volcanic gas chemistry of sulfur and oxygen gases and explored O/S atomic ratios ranging from about 10^{-7} (i.e., essentially pure sulfur vapor) to 3 (i.e., essentially pure SO₃) with a nominal O/S ratio of unity (Zolotov and Fegley 1998a,b, 1999). As discussed in detail in our prior papers, all the available data on the composition of Io's surface, extended atmosphere and plasma torus, and for the Loki plume (Pearl *et al.* 1979) indicate that volcanic gases on Io probably vary in composition from essentially pure sulfur vapor to almost pure SO₂. Volcanic gases with higher O/S ratios, which can be thought of as SO₂–O₂ mixtures or as SO₂–SO₃ mixtures, appear implausible but cannot be definitively ruled out. Here we consider O/S ratios ranging from 0.01 to 2.0 and following our prior work adopt a nominal O/S atomic ratio of unity, which roughly matches the composition of the plasma torus (Moos *et al.* 1991).

Although several sulfur-bearing molecules have been definitively observed in volcanic plumes on Io (Pearl *et al.* 1979, McGrath *et al.* 2000, Spencer *et al.* 2000), the elemental abundances of alkali and halogen elements in volcanic gases on Io are still unknown. Sodium, potassium, sulfur, and oxygen are present in neutral clouds and in the Io plasma torus, and chlorine was recently detected in the torus (Spencer and Schneider 1996, Küppers and Schneider 2000). We used compositional data for Io's extended atmosphere (including the neutral clouds) and plasma torus in combination with the chondritic abundances of S, Na, K, and Cl to constrain plausible values for the bulk sodium, potassium, and chlorine elemental abundances

TABLE I
Elemental Abundances Used in the Calculations

Atomic ratio	Nominal value	Adopted range	CI chondritic value ^a
O/S	1.00	0.01–2.00	17.2
Na/S	0.05	10 ⁻⁵ –0.20	0.13
Cl/S	0.04	0.01–0.20	0.01
K/S ^b	0.005	Varies with Na	0.00834
H/S ^c	10 ⁻²⁰	10 ⁻²⁰ –10 ⁻¹	11.9

^a Lodders and Fegley (1998).

^b The K abundance is calculated from the adopted Na/S ratio and the Na/K ratio of 10 from Brown (1998).

^c An arbitrarily low nominal value is adopted for the H/S ratio.

in volcanic gases on Io. The nominal elemental abundances and range of values used in our calculations are expressed as atomic ratios relative to sulfur and are listed in Table I. Our choices for the nominal elemental abundances are described below.

The Na/S ratio in the plasma torus is in the range of 0.01–0.10 (e.g., Vogt *et al.* 1979, Bagenal and Sullivan 1981, Spencer and Schneider 1996). Chondritic Na/S atomic ratios range from 0.13 in CI chondrites, which is also the solar abundance ratio, to 0.72 in the sulfur-poor CH chondrites. The mean Na/S ratios in carbonaceous (CI, CM, CO3, CV3), ordinary (H, L, LL), and enstatite (EH, EL) chondrites fall in between these two extremes and are 0.20, 0.44, and 0.22, respectively (Lodders and Fegley 1998). The temperatures for 50% condensation of Na and S in the solar nebula (at 10⁻⁴ bar total pressure) are 970 and 674 K, respectively (Lodders and Fegley 1998). Sodium is more refractory than sulfur, which is depleted relative to its solar abundance in most chondrites. The lower Na/S ratios in CI and CM chondrites are probably more appropriate for Io's original bulk composition which is predicted to have been similar to that of water-bearing carbonaceous chondrites (Prinn and Fegley 1981). However, the Na/S ratio in Io's lithosphere could now be higher because Na and S have probably partitioned to different extents between Io's silicates and its Fe–FeS core. We adopted 0.05 as the nominal Na/S atomic ratio in our calculations on the basis of Na/S ratios for the Io torus. We also used Na/S ratios ranging from 10⁻⁵ to 0.20 in the computations, which spans the CI chondritic Na/S ratio.

The Cl⁺ abundance in the plasma torus is 2 ± 0.5% relative to all ions (Küppers and Schneider 2000), giving a Cl/S ratio of about 0.04 for an O/S ratio of unity in the torus. The total chlorine density in the torus is between 1.5 and 5.5% of all ions (Küppers and Schneider 2000) and corresponds to Cl/S ratios ranging from 0.03 to 0.11. These Cl/S ratios are several times higher than chondritic Cl/S atomic ratios, which range from a low of 0.0063 in H chondrites to a high of 0.0144 in CM chondrites. The mean Cl/S ratios in carbonaceous (CI, CM, CO3, CV3), ordinary (H, L, LL), and enstatite (EH, EL) chondrites are 0.0120, 0.0087, and 0.0080, respectively. The CI chon-

dritic ratio, which is also the solar ratio, is 0.0117 (Lodders and Fegley 1998). The 50% condensation temperature for chlorine (at 10⁻⁴ bar total pressure) in the solar nebula is 863 K (Lodders and Fegley 1998), so Cl is slightly more refractory than sulfur. The jovian subnebula model of Prinn and Fegley (1981) predicts that Io should have accreted with the solar Cl/S ratio. Both Cl and S are incompatible volatile elements in silicate magmas so they could be present in volcanic gases at about the bulk Cl/S ratio in Io. The dominant chlorine and sulfur-bearing volatiles in volcanic gases on Earth are HCl and SO₂. The HCl/SO₂ molar ratio is about 0.01 in volcanic gases at Kilauea, which is a basaltic hot spot volcano (Symonds *et al.* 1994), and would be a first-order proxy for ionian volcanoes. As discussed later, the predicted chlorine chemistry of ionian volcanic gases depends on whether or not the (Na + K)/Cl ratio is less than, equal to, or greater than unity. We take a nominal Cl/S ratio of 0.04 in our calculations and also explore the effects of Cl/S ratios ranging from 0.01 to 0.20 on the chemistry of ionian volcanic gases.

Potassium is also observed in the Io plasma torus and neutral clouds but is less abundant than sodium (Spencer and Schneider 1996). Potassium and Na have about the same volatility in the solar nebula and have 50% condensation temperatures (at 10⁻⁴ bar total pressure) of 1000 and 970 K, respectively (Lodders and Fegley 1998). The mean K/Na atomic ratios in carbonaceous (CI, CM, CO3, CV3), ordinary (H, L, LL), and enstatite (EH, EL) chondrites are 0.058, 0.076, and 0.072, respectively. Brown (1998) has observed K and Na in Io's extended atmosphere and reports an average Na/K ratio of 10 ± 3. We did two sets of calculations using either his ratio or the CI chondritic Na/K atomic ratio of 15.5. There is no significant difference between the two sets of computations; here we report the results obtained using a Na/K ratio of 10.

Hydrogen (and water) are very depleted on Io. There are no definitive detections of any H-bearing species on Io although spectral features possibly due to water ice and H₂S ice have been reported (Spencer and Schneider 1996). It is unclear how much (or little) hydrogen Io contains. The CI and CM chondrites contain 1–2% by mass hydrogen, predominantly as water in hydrous minerals (Lodders and Fegley 1998). Earth has at least 0.028% by mass water (due to its hydrosphere) and may have a few times more than this if significant amounts of water reside in hydrous minerals in the terrestrial mantle. Ordinary chondrites contain about 10–100 parts per million by mass hydrogen in hydrous minerals and organic matter. On Venus, the mean sub-cloud water abundance of 30 parts per million by volume corresponds to a bulk water abundance of about one part per billion by mass (Lodders and Fegley 1998).

Even though Io is depleted in hydrogen (and water), we included hydrogen in some of our computations because it has important effects on the chemistry of volcanic gases (e.g., see the volcanic gas analyses tabulated by Symonds *et al.* (1994)). On Earth, steam is generally the dominant volatile in volcanic gases. Furthermore, H₂S is an important sulfur gas in some volcanoes.

TABLE II
Compounds Included in the Computations and the
Thermodynamic Data Sources Used^a

Cl, Cl₂, ClO, Cl₂O, O, O₂, O₃, S, S₂, S₃, S₄, S₅, S₆, S₇, S₈, S₈ (s, liq), SCl, SCl₂, S₂Cl, S₂Cl₂, SO, SO₂, SO₃, S₂O, SOCl₂, SO₂Cl₂, Na, Na (s, liq), Na₂, NaCl, NaCl (s, liq), (NaCl)₂, (NaCl)₃, Na₂SO₄, Na₂SO₄ (s, liq), NaH, NaO, Na₂O, NaOH, Na₂S (s, liq), K, K (s, liq), K₂, KNa, KO, K₂O, KOH, KS, K₂S (s, liq), KCl, (KCl)₂, KCl (s, liq), K₂SO₄, K₂SO₄ (s, liq), H₂, HCl, H₂O, OH, H₂S, HS

^a Thermodynamic data are taken from the NIST-JANAF Tables (Chase 1998) except data for the following compounds: S₂O, SOCl₂, and HS (Barin 1995); (NaCl)₃ and KNa (Gurvich *et al.* 1978); KS and K₂S (Pankratz *et al.* 1987). The data for S₂Cl₂ and SOCl₂ are tabulated to 1500 K and have been extrapolated to 2000 K in our calculations.

Finally, HCl and HF are the dominant halogen species in terrestrial volcanic gases. We used an arbitrarily low H/S atomic ratio of 10⁻²⁰ for our nominal hydrogen abundance in most calculations. The possible effects of hydrogen on ionian volcanic gas chemistry were studied in a set of computations using variable H/S atomic ratios ranging up to 0.1, which is certainly much higher than the bulk H/S ratio on Io. As discussed later, these computations show that hydrogen only affects ionian volcanic gas chemistry at these high H/S ratios.

About 70 solid, liquid, and gaseous compounds were included in our calculations. These compounds and the thermodynamic data sources used are given in Table II. The thermochemical equilibrium calculations were done using our existing computer codes, which operate using a mass balance, mass action algorithm (Fegley and Lodders 1994) and a Gibbs free energy minimization algorithm (Van Zeggeren and Storey 1970). The results from the two codes agree very well. In this paper we model the condensation chemistry of pure compounds and neglect any mutual solubility between alkalis (e.g., KCl solubility in NaCl). This was done because studies of condensates from terrestrial volcanic and fumarolic gases show separate crystals of halite (NaCl) and sylvite (KCl), instead of a solid solution of the two minerals (Bernard and Le Guern 1986). However, terrestrial natrocarbonatite magmas are typically solutions of several salts, so it is possible that multicomponent liquids will condense out of ionian volcanic gases instead of pure liquids. Mutual liquid solubility would widen the range of temperatures and pressures over which condensates are stable relative to the stability fields of the pure phases.

DISCUSSION OF THE COMPUTATIONAL RESULTS

We first discuss the effects of temperature and pressure on the chemistry of volcanic gases with the nominal elemental abundances given in Table I. Then we consider separately the effects of variable elemental abundances on the gas phase chemistry. Finally, we discuss the condensation chemistry of the volcanic gases.

Temperature Dependent Gas Phase Chemistry

Sulfur. Figure 1a illustrates the chemical equilibrium abundances of sulfur-bearing gases at 1 bar total pressure as a function of temperature from 1000 to 2000 K. In general, the results in Fig. 1a are very similar to our prior results for volcanic gas chemistry in the S–O system (Zolotov and Fegley 1998a,b, 1999). Sulfur dioxide (~65 vol%) and S₂ (~30 vol%) are the first and second most abundant sulfur gases over the entire temperature range considered and either SO (at higher *T*) or S₂O (at lower *T*) is the third most abundant gas. Other sulfur vapor allotropes, notably S₃ and S₄, become increasingly important with decreasing temperature, but they are less abundant than S₂O at *T* ≥ 1000 K.

Because Na and K are less abundant than sulfur, their chemistry does not significantly alter that of sulfur. The two major effects are that at high temperatures the four gases KS, Na₂SO₄, K₂SO₄, and K₂S collectively consume about 0.1% of the total sulfur abundance, and second that condensation of liquid Na₂S and liquid Na₂SO₄ removes about the same amount of sulfur from the gas. As we will show below, the effect of Na chemistry on that of sulfur becomes important only at a Na/S atomic ratio of 0.20, which is the upper end of our assumed range of Na/S ratios. However, this value is greater than the largest Na/S value of ~0.09 observed in the Io torus and is also greater than the CI chondritic Na/S atomic ratio of 0.13. Thus, sulfur chemistry in volcanic gases on Io is essentially the same as chemistry of the S–O system and the conclusions reached by us in our prior papers remain unchanged.

Sodium. Figure 1b presents the equilibrium abundances of sodium gases as a function of temperature. To the best of our knowledge, these are the first quantitative computations that predict the abundances of Na species in volcanic gases on Io although prior authors have speculated on the possible presence and form of Na in ionian volcanic gases. Sodium chloride (NaCl) is the dominant sodium gas over all temperatures considered. The second most abundant sodium-bearing gas is either monatomic Na (*T* > 1600 K) or (NaCl)₂ (*T* < 1600 K). The third most abundant gas switches from (NaCl)₂ (at higher temperatures) to Na, and then to (NaCl)₃ with decreasing temperature.

Condensation of liquid Na₂S occurs at ~1780 K. Liquid Na₂SO₄ forms instead of Na₂S at temperatures below ~1650 K. Sodium sulfate remains stable down to at least 1000 K. Condensation of liquid NaCl occurs at 1363 K and removes most of all sodium from the gas. The condensed liquids probably cool and solidify rapidly in the vicinity of volcanic vents, but the presence of some gaseous NaCl, Na₂SO₄, and KCl in plumes and local volcanic atmospheres is not excluded. The correlation of visible wavelength emissions due to neutral atomic Na with volcanic plumes and volcanic centers on Io (Geissler *et al.* 1999a) suggests that gaseous Na species are present in plumes and/or local volcanic atmospheres. However, the partitioning of Na (and K) between gas and condensates is not known at present.

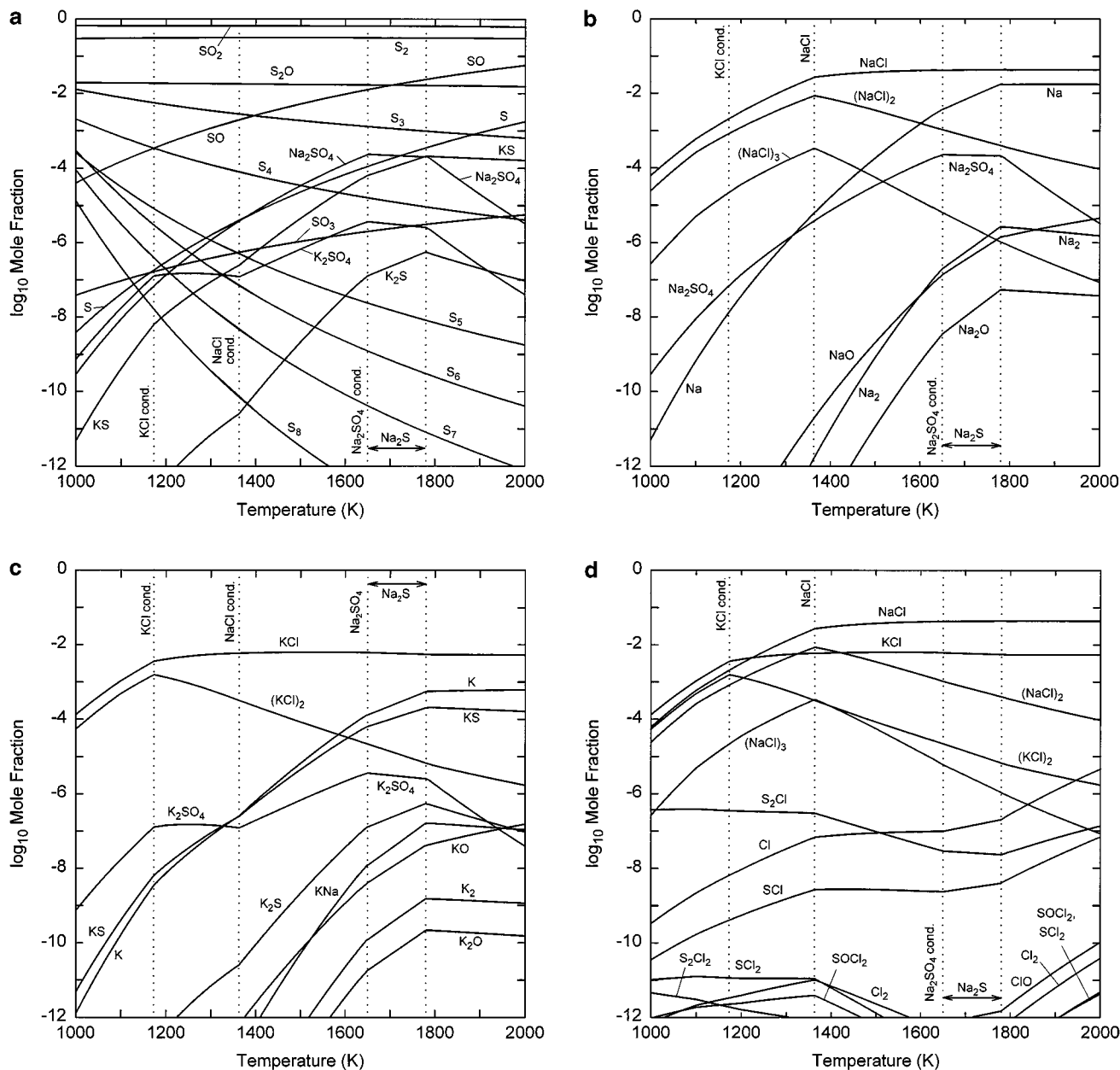


FIG. 1. Chemical equilibrium abundances of (a) sulfur, (b) sodium, (c) potassium, and (d) chlorine gases as a function of temperature at 1 bar total pressure and for the nominal elemental abundances given in Table I. In this and subsequent figures, the mole fraction (X) of a gas is defined as the partial pressure of the gas divided by the total pressure (i.e., $X_i = P_i/P_T$ for gas i). The vertical dotted lines show the condensation temperatures of liquid Na_2S (1780 K), liquid Na_2SO_4 (1650 K), liquid NaCl (1363 K), and liquid KCl (1173 K). The arrow labeled Na_2S shows the range of temperatures where liquid Na_2S is stable; it is replaced by liquid Na_2SO_4 at 1650 K, which remains stable to lower temperatures.

Potassium. Figure 1c displays potassium equilibrium chemistry, which is similar to that of sodium. If thermodynamic data were available, we might find that $(\text{KCl})_3$ contains about the same fraction of total gaseous potassium as $(\text{NaCl})_3$ does of total gaseous sodium at lower temperatures. One difference between sodium and potassium chemistry is that K is more volatile than Na and all of it remains in the gas until liquid KCl condenses at 1173 K. Another difference is that KS is the third most abundant potassium gas at high temperatures. However, in general, Na and

K have similar chemistry and chlorides are the major gases for the two elements over the 1000–2000 K range.

Chlorine. Figure 1d shows the equilibrium abundances of chlorine compounds. The two most abundant chlorine gases are generally NaCl and KCl , with the former being more abundant above ~ 1225 K. The dimeric species $(\text{NaCl})_2$, $(\text{KCl})_2$, and $(\text{NaCl})_3$ are the next most abundant chlorine gases. Monatomic Cl , S_2Cl_2 , and SCl are minor species under these conditions. Molecular chlorine, other sulfur chlorides, and sulfur

oxychlorides are of negligible importance. Because of the importance of the alkali chlorides, chlorine chemistry is affected indirectly by the condensation chemistry of the alkali elements.

Pressure Effects on the Gas Phase Chemistry

Sulfur. Figure 2a shows equilibrium abundances of sulfur gases as a function of variable total pressure at 1500 K. In general, the chemistry in this figure is the same as that for the S–O system and shown in Fig. 2 of Zolotov and Fegley (1998b). Sulfur dioxide and S_2 are the first and second most abundant sulfur gases, respectively, over almost the entire pressure range

considered. The abundances of S and SO increase and the abundance of S_2O decreases with decreasing pressure. The abundances of alkali-bearing sulfur gases never exceed 0.1% of the total sulfur abundance.

An interesting feature is the effect of total pressure on the condensation chemistry of the alkalis. With increasing pressure, the first condensate formed is liquid Na_2S , which appears at 0.06 bar and is stable up to ~ 0.15 bar where liquid Na_2SO_4 forms instead. Sodium sulfate remains stable up to the highest pressure considered, 100 bar. Liquid NaCl condenses at 3.9 bar and liquid KCl forms at 40 bar.

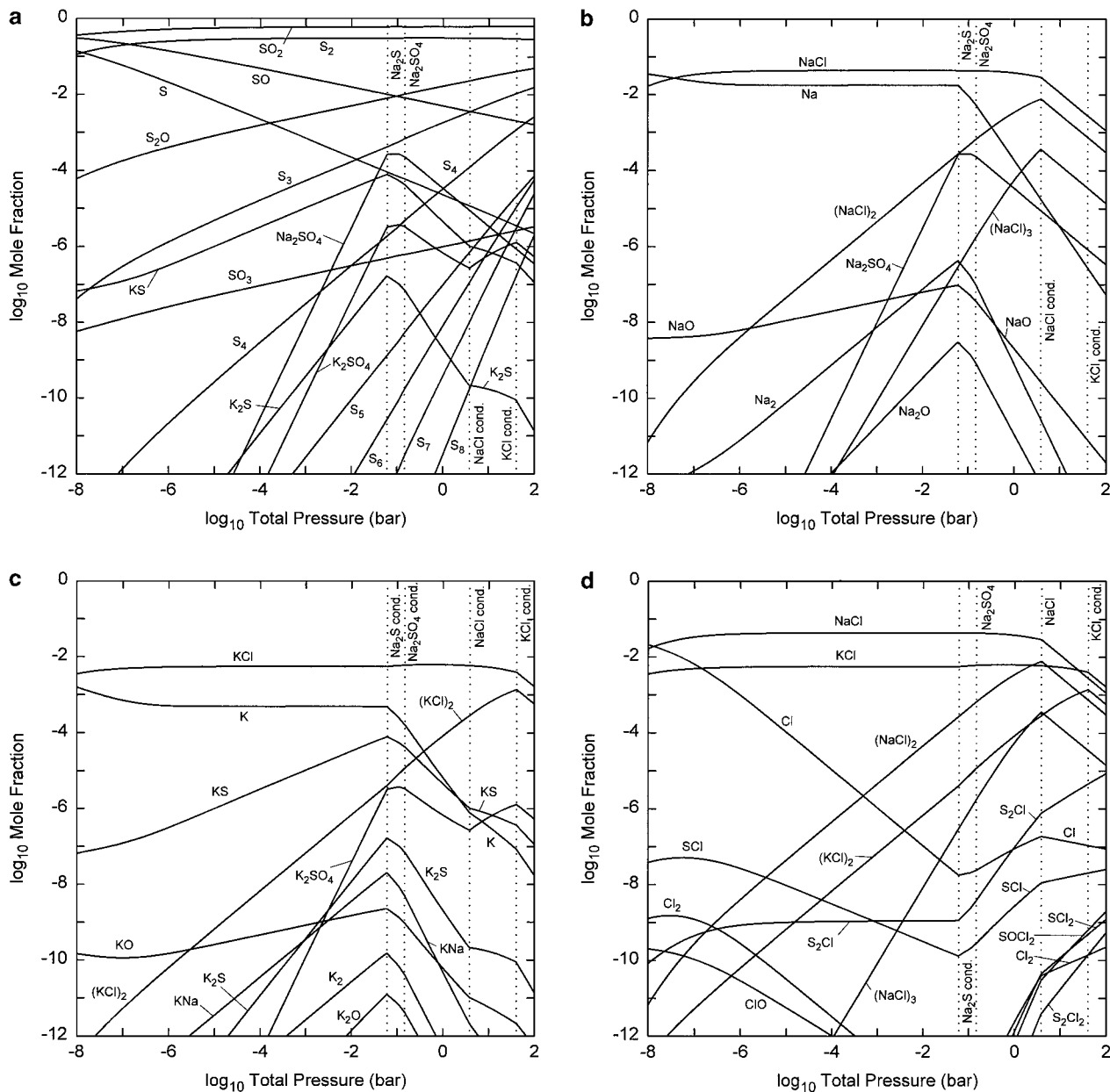


FIG. 2. Chemical equilibrium abundances of (a) sulfur, (b) sodium, (c) potassium, and (d) chlorine gases as a function of total pressure at 1500 K and nominal elemental abundances. The vertical dotted lines in this figure show the condensation pressures for liquid Na_2S ($10^{-1.22}$ bar), liquid Na_2SO_4 ($10^{-0.83}$ bar), liquid NaCl ($10^{0.59}$ bar), and liquid KCl ($10^{1.60}$ bar). Liquid Na_2S is stable from $10^{-1.22}$ to $10^{-0.83}$ bar, at which point liquid Na_2SO_4 condenses.

Sodium. Figure 2b shows the sodium gas chemistry as a function of total pressure. Monatomic Na is the dominant gas at pressures less than $10^{-7.4}$ bar and NaCl is the major gas at higher pressures. Sodium chemistry is fairly simple at low pressures, with NaCl and Na comprising essentially 100% of all gas phase sodium. The next most abundant gas, NaO, makes up less than one part per million of total sodium. However, with increasing pressure several molecular species become increasingly important, with the three most abundant gases (after Na and NaCl) being $(\text{NaCl})_2$, Na_2SO_4 , and $(\text{NaCl})_3$. The relative importance of these three species is a sensitive function of the total pressure, and $(\text{NaCl})_2$ and $(\text{NaCl})_3$ are the second and third most abundant Na gases at the highest pressures shown. The condensation chemistry of sodium was described above in the discussion of Fig. 2a.

Potassium. Figure 2c displays potassium chemistry as a function of total pressure. This is qualitatively similar to sodium chemistry in that KCl and monatomic K are the two major gases. At pressures greater than 0.06 bar, K rapidly drops in abundance until $(\text{KCl})_2$ becomes more abundant at about 0.48 bar total pressure. Potassium chemistry, like sodium chemistry, is fairly simple at low pressures and more complex at higher pressures where $(\text{KCl})_2$, K, and KS are either the second or third most abundant gases. Presumably if thermodynamic data were available, we would find that $(\text{KCl})_3$ is comparable in importance to $(\text{NaCl})_3$ at higher pressures. Finally, condensation of liquid KCl occurs at about 40 bar and depletes all K gases at higher pressures.

Chlorine. The pressure effects on chlorine chemistry are shown in Figure 2d. At low pressures of 10^{-7} to 10^{-8} bar, monatomic Cl is comparable in abundance to KCl and NaCl. However, these two species are the dominant chlorine gases over virtually the entire pressure range considered. With increasing pressure the Cl gas abundance decreases sharply and the abundances of the dimeric species $(\text{NaCl})_2$ and $(\text{KCl})_2$ and of $(\text{NaCl})_3$ increase dramatically. In general, abundances of the sulfur chlorides (except SCl) and oxychlorides also increase with increasing pressure but are commonly lower than those of the alkali chloride gases. Finally molecular chlorine and ClO are negligible at all pressures considered.

Effects of Variable Elemental Abundances on the Gas Phase Chemistry

The calculations discussed above were done using the nominal elemental abundances from Table I. However, because these abundances are uncertain, we also explored the effects of different Na, O, Cl, and H abundances on the resulting gas phase chemistry.

The Na/S ratio. Figures 3a–3d show the influence of the Na/S atomic ratio on chemistry of sulfur, sodium, potassium, and chlorine gases, respectively, at 1500 K and 1 bar total pressure. The O–S–Cl–H elemental ratios are held constant at their nominal values from Table I and the Na/K ratio is held constant at the nominal value of 10 in these computations.

Figure 3a shows that sulfur chemistry is essentially unaltered by the presence of sodium for Na/S ratios at and below the observed values in the Io torus. However, the abundances of SO_2 and S_2 converge as the Na/S ratio continues to increase beyond 0.09 and they become almost equal at $\text{Na/S} = 0.20$. There are also slight increases in the abundances of other sulfur vapor allotropes (S_3 – S_8) and slight decreases in the abundances of other oxidized sulfur gases (SO , SO_3) in this compositional range. This is due to condensation of liquid Na_2SO_4 (at $\text{Na/S} \sim 0.037$). Liquid K_2SO_4 does not condense until higher Na/S ratios beyond the range of this figure.

Sodium chemistry is shown in Fig. 3b. Sodium chloride is the major Na gas at all Na/S ratios considered. The second most abundant gas is $(\text{NaCl})_2$, followed by either $(\text{NaCl})_3$ or Na. All gas abundances remain approximately constant once liquid Na_2SO_4 condenses.

Figure 3c shows potassium chemistry, which is similar to sodium chemistry. The Na/K ratio is fixed at a value of 10 in these computations, so the total potassium abundance varies in concert with the sodium abundance. Potassium chloride remains the dominant gas over the compositional range considered, and $(\text{KCl})_2$ is always the second most abundant potassium gas. The condensation of liquid K_2SO_4 occurs at a higher Na/S ratio than those shown.

Chlorine chemistry is displayed in Fig. 3d and is fairly complex because the chemistry of chlorine is closely coupled to that of sulfur, sodium, and potassium. The nominal Cl/S ratio in our computations is 0.04, and the nominal Na/K ratio is 10, so a $(\text{Na} + \text{K})/\text{S}$ ratio of 0.04 gives equal abundances of Na + K and chlorine. For simplicity we will refer to the $(\text{Na} + \text{K})/\text{S}$ ratio as the alkali/S ratio because the abundances of the other (as yet undetected) alkali metals (Li, Rb, and Cs) on Io are probably much less than the Na and K abundances. If the actual alkali/S and Cl/S ratios in ionian volcanic gases are different than our nominal values, an alkali/Cl ratio of unity will occur at different values of the alkali/S and Cl/S ratios. However, our results show that an alkali/Cl ratio of unity is a boundary between one region at lower alkali/Cl ratios where elemental chlorine gases, sulfur chlorides, and oxychlorides are important species and a second region at higher alkali/Cl ratios where alkali chlorides are important species. Figure 3d shows that as the $(\text{Na} + \text{K})/\text{Cl}$ ratio decreases below unity Cl_2 becomes the major gas, and SCl_2 , S_2Cl , Cl, and SOCl_2 also become important gases. However, NaCl is the major chlorine gas for the range of Na/S ratios which are observed in the Io torus. As the Na/Cl ratio increases, KCl, $(\text{NaCl})_2$ and $(\text{KCl})_2$ become increasingly important, and sulfur chlorides, oxychlorides, and elemental Cl gases are of negligible importance.

The O/S ratio. Figures 4a–4d illustrate the effect of O/S atomic ratios ranging from 0.01 to 2.0 on the chemistry of sulfur, sodium, potassium, and chlorine compounds at 1500 K and 1 bar total pressure. The sulfur chemistry shown in Fig. 4a is similar to that displayed in Fig. 1 of Zolotov and Fegley (1998a,b) which are for 1400 K and 10^{-4} or 10 bar, respectively.

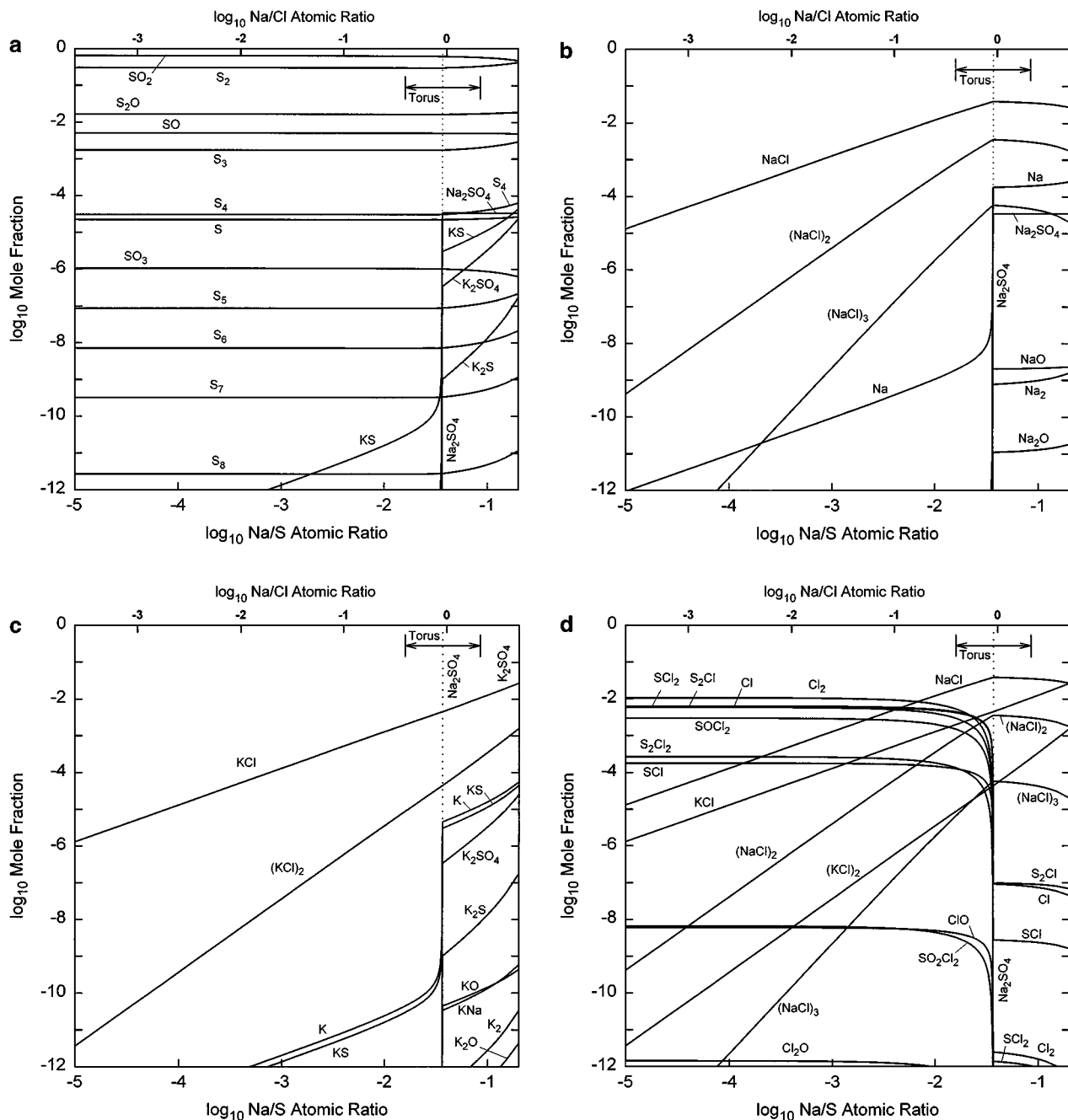


FIG. 3. Chemical equilibrium abundances of (a) sulfur, (b) sodium, (c) potassium, and (d) chlorine gases as a function of the Na/S atomic ratio at 1500 K and 1 bar total pressure. The corresponding Na/Cl atomic ratio is also shown. The Na/K ratio = 10 and nominal values from Table I are used for the O, Cl, and H abundances. The vertical dotted line shows where liquid Na_2SO_4 becomes stable ($\text{Na}/\text{S} = 0.0366$). Sodium sulfide does not form and liquid K_2SO_4 forms only at higher Na/S ratios beyond the range of the graph. The arrow labeled “torus” shows the range of Na/S ratios observed in the Io torus.

The major features of sulfur chemistry in ionian volcanic gases, which we have described previously, are essentially unaltered by the presence of Na, Cl, and K.

Sulfur dioxide remains the major sulfur gas at O/S ratios greater than ~ 0.7 and S_2 is the major sulfur gas at lower O/S ratios. The S_2O abundance is relatively insensitive to the O/S ratio over almost the entire range considered until $\text{O}/\text{S} \sim 2$, when it drops sharply. At this temperature and pressure, either liquid

Na_2S or liquid Na_2SO_4 coexists with the gas. The abundances of all sulfur vapor allotropes (S_2 – S_8), KS, and K_2S are insensitive to O/S ratios less than ~ 0.4 , where liquid Na_2S is present, but the abundances of Na_2SO_4 and K_2SO_4 vary steeply in this region. However, the alkali sulfate gases have constant abundances at O/S ratios greater than ~ 0.4 , where Na_2SO_4 forms and remains stable at higher O/S ratios. Figure 4a stops at $\text{O}/\text{S} = 2.0$ (i.e., “pure” SO_2), but sulfur chemistry at higher O/S ratios is shown

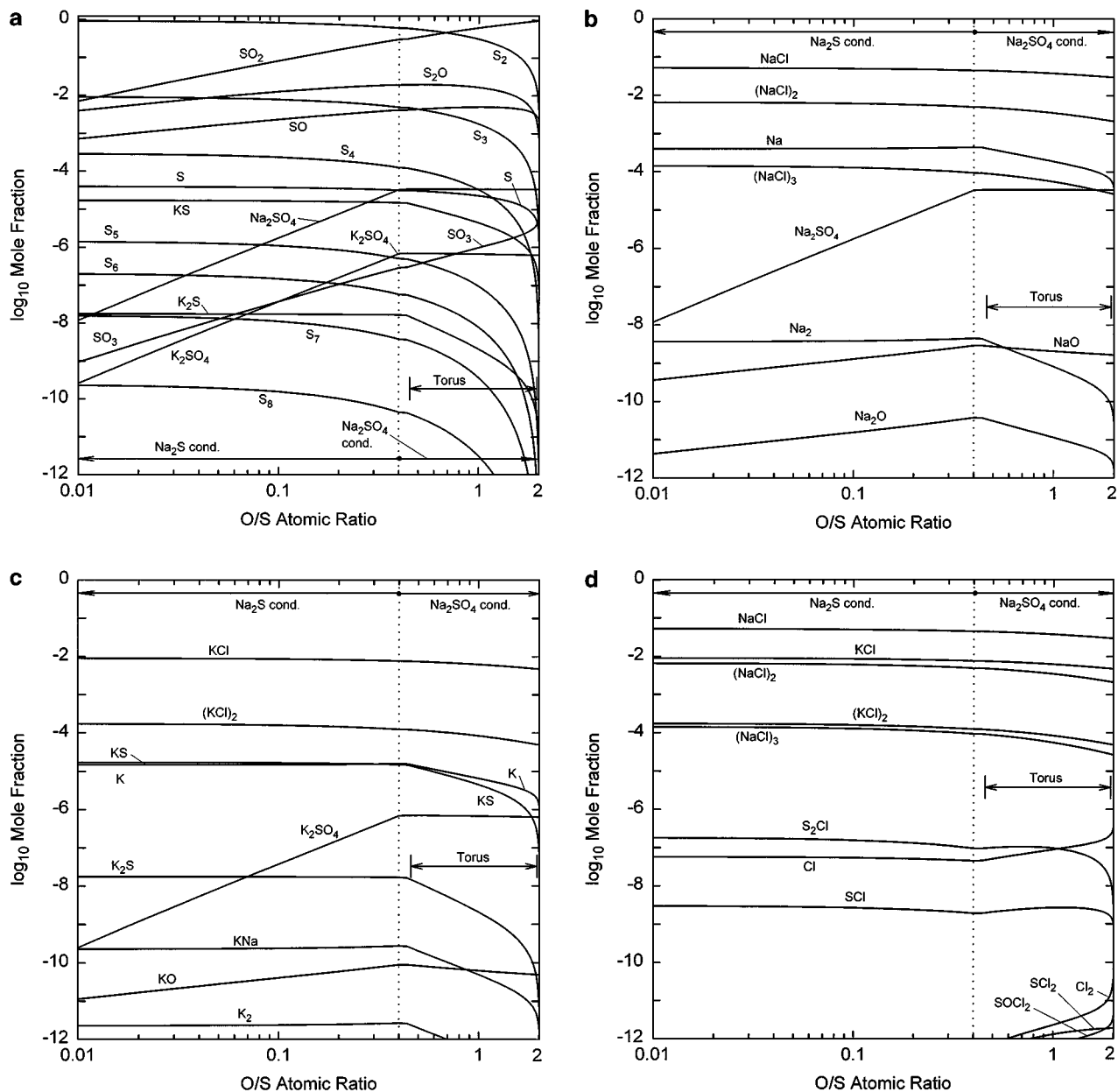


FIG. 4. Chemical equilibrium abundances of (a) sulfur, (b) sodium, (c) potassium, and (d) chlorine gases as a function of the O/S atomic ratio at 1500 K and 1 bar total pressure. The nominal values from Table I are used for the Na, Cl, K, and H abundances. The vertical dotted line on this figure shows the point ($O/S = 0.42 \pm 0.02$) where liquid Na_2S , which is stable at lower O/S ratios, is replaced by liquid Na_2SO_4 , which remains stable to higher O/S ratios.

in Fig. 1 of Zolotov and Fegley (1998a,b). Volcanic gases with O/S ratios in this range are SO_2 – O_2 mixtures with several hundred parts per million by volume (ppmv) SO_3 , several tens of parts per million by volume monatomic O, and ~ 10 ppmv SO.

Figure 4b displays sodium chemistry as a function of the O/S ratio. Sodium chloride is the major gas over the entire range considered. The next most abundant gases are $(\text{NaCl})_2$ and Na. Depending on the O/S ratio, either $(\text{NaCl})_3$ or Na_2SO_4 is the fourth most abundant gas. The abundances of most sodium gases are relatively insensitive to the O/S ratio over most of the range shown. As O/S ratios close to 2 are approached, the

abundances of Na, Na_2 , and Na_2O drop sharply while the abundances of the three Na chlorides and Na_2SO_4 remain relatively constant.

Potassium chemistry is shown in Fig. 4c. Again, this is similar to sodium chemistry in that KCl is the dominant gas and $(\text{KCl})_2$ is second in abundance. Potassium monosulfide and monatomic K are the third and fourth most abundant gases, respectively. The O/S ratio has relatively little effect on potassium gases until values close to 2 are approached where almost all species drop sharply, except KCl, $(\text{KCl})_2$, and K_2SO_4 , which remain almost constant.

Figure 4d shows chlorine chemistry. This is dominated by the alkali chlorides, which are the five most abundant Cl-bearing gases. Chlorine chemistry is not affected by variations in the O/S ratio, except close to SO_2 stoichiometry where monatomic Cl and Cl_2 begin to increase sharply and S_2Cl and SCl decrease sharply. The abundances of the alkali chlorides decrease slightly as $\text{O/S} = 2$ is approached.

The Cl/S ratio. Figures 5a–5d illustrate the effect of Cl/S atomic ratios ranging from 0.01 to 0.20 on the chemistry of

sulfur, sodium, potassium, and chlorine compounds at 1500 K and 1 bar total pressure.

Figure 5a shows that the five most abundant sulfur gases (SO_2 , S_2 , S_2O , SO , and S_3) at this temperature and pressure are unaffected as the Cl/S ratio increases from 0.01 to 0.20. The less abundant sulfur-bearing gases are also virtually unaffected except for sodium and potassium species. Liquid Na_2SO_4 is stable at Cl/S ratios less than and equal to 0.055. The abundances of Na_2SO_4 , K_2SO_4 , KS , and K_2S change sharply at $\text{Cl/S} = 0.055$ and, except for Na_2SO_4 , which remains constant, increase as

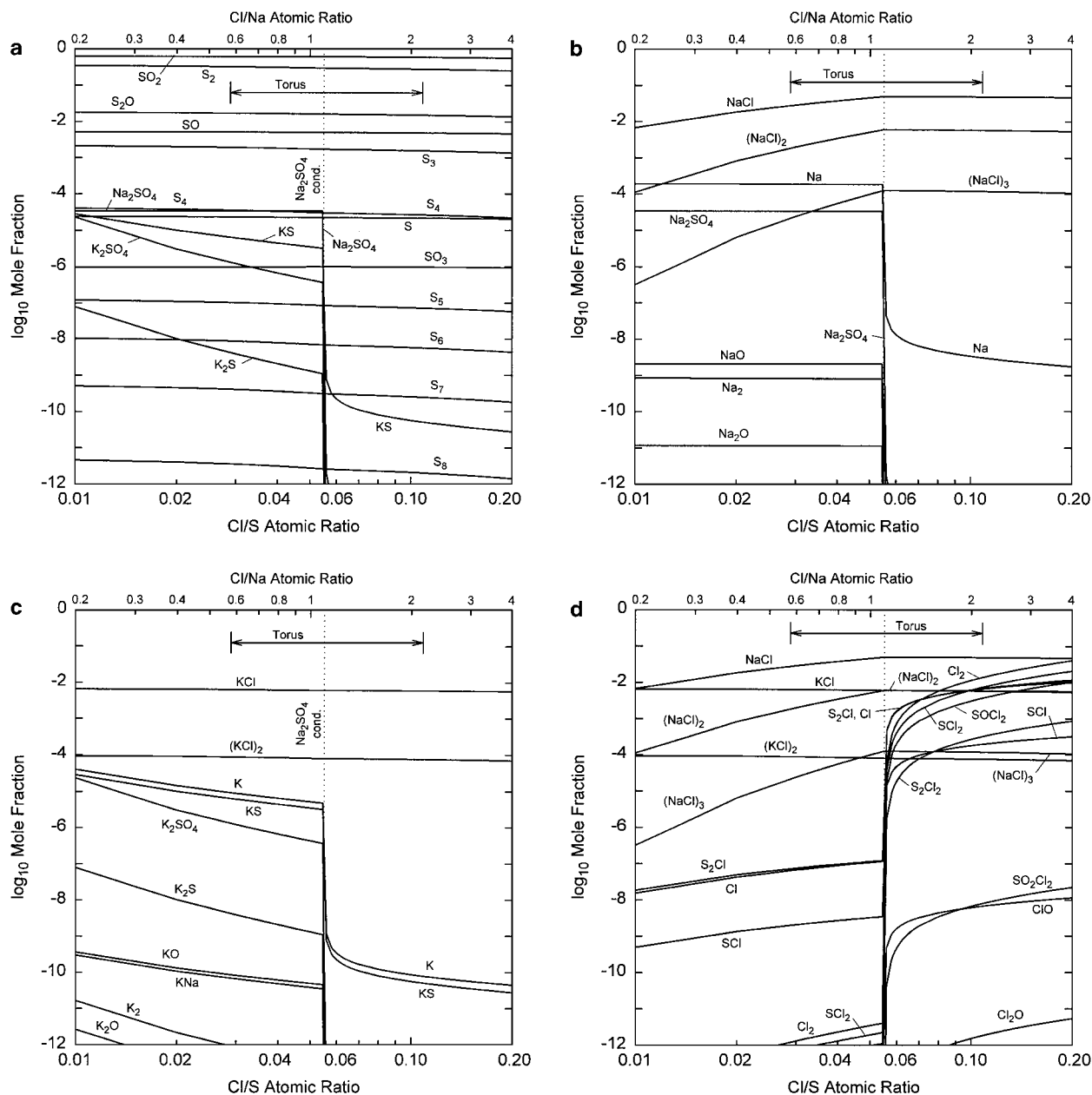


FIG. 5. Chemical equilibrium abundances of (a) sulfur, (b) sodium, (c) potassium, and (d) chlorine gases as a function of the Cl/S atomic ratio at 1500 K and 1 bar total pressure. The nominal values from Table I are used for the O, Na, K, and H abundances. The vertical dotted line on this figure shows where Na_2SO_4 , which is stable at Cl/S ratios of 0.055 and below, forms. The arrow labeled “torus” in this figure shows the range of Cl/S ratios (0.029–0.106) for the Io torus from Küppers and Schneider (2000).

the Cl/S ratio decreases below this value. As seen in this and subsequent figures, the Cl/S ratio of 0.055 is a critical point where dramatic shifts occur in the gas phase chemistry of Na, K, and Cl. This Cl/S ratio is almost, but not exactly, equal to a Cl/Na ratio of one. However, as discussed earlier for Fig. 3d, the alkali/Cl ratio is the critical parameter for chemistry of Na, K, and Cl. Thus, a Cl/S ratio of 0.055 corresponds to a Cl/(Na + K) ratio of unity. If the Na/K ratio were different than 10, the critical Cl/S ratio would have a different value corresponding to $\text{Cl}/(\text{Na} + \text{K}) = 1$.

Sodium chemistry is shown in Fig. 5b. The Cl abundance does not affect the two major Na-bearing gases over a wide range of Cl/S ratios. At very low values ($\text{Cl}/\text{S} \sim 0.012$) below the range of Cl/S ratios appropriate for the Io torus, Na becomes the second most abundant sodium gas. The third most abundant gas shifts from Na to $(\text{NaCl})_3$ as the Cl/S ratio increases; this change occurs within the range of Cl/S ratios compatible with the observations of Cl^+ in the torus. The abundances of several gases (Na, Na_2SO_4 , NaO, Na_2 , and Na_2O) decrease sharply as the Cl/S ratio increases to 0.055, and only Na has a mole fraction greater than 10^{-12} at Cl/S ratios greater than 0.055.

Figure 5c shows analogous behavior for potassium. The two major gases remain KCl and $(\text{KCl})_2$. The abundances of most of the other potassium species show sharp changes at $\text{Cl}/\text{S} = 0.055$. Monatomic K and KS remain the third and fourth most abundant K-bearing gases at higher Cl/S ratios, but their abundances are markedly decreased from those at Cl/S ratios equal to and less than 0.055.

Chlorine chemistry is displayed in Fig. 5d. At Cl/S ratios less than 0.055, chlorine chemistry is dominated by Na and K chlorides and all other Cl-bearing gases are trace species. A dramatic shift occurs at a Cl/S ratio of 0.055 where Cl_2 , Cl, and several sulfur chlorides become much more abundant. However, NaCl remains the major chlorine gas up to a Cl/S ratio of 0.20.

The H/S ratio. Figure 6 summarizes how the presence of hydrogen alters the chemistry of ionian volcanic gases at 1500 K and 1 bar total pressure. The H/S ratio was varied over a wide range to show trends in the abundances of H-bearing compounds and for comparison with the upper limits for H_2O , H_2S , and HCl determined for the Loki plume by the Voyager 1 IRIS experiment (Pearl *et al.* 1979). In terms of mole fractions, the averaged upper limits are 0.023, 0.35, and 0.010 for H_2O , H_2S , and HCl, respectively.

At H/S ratios less than $\sim 10^{-6.5}$, the major hydrogen gases in order of decreasing importance are HS, HCl, NaOH, and KOH. As the hydrogen abundance continues to increase, H_2O becomes more important until it becomes the major hydrogen bearing gas at an H/S ratio of $\sim 10^{-5}$. The abundances of H_2S and H_2 increase more sharply than do the abundances of HS, HCl, NaOH, and KOH and the former two gases become the second and third most abundant hydrogen species at H/S ratios above ~ 0.003 . The abundances of NaOH and NaH, which is a trace species, increase with the hydrogen abundance. Sodium chemistry is unaffected otherwise. Potassium chemistry is simi-

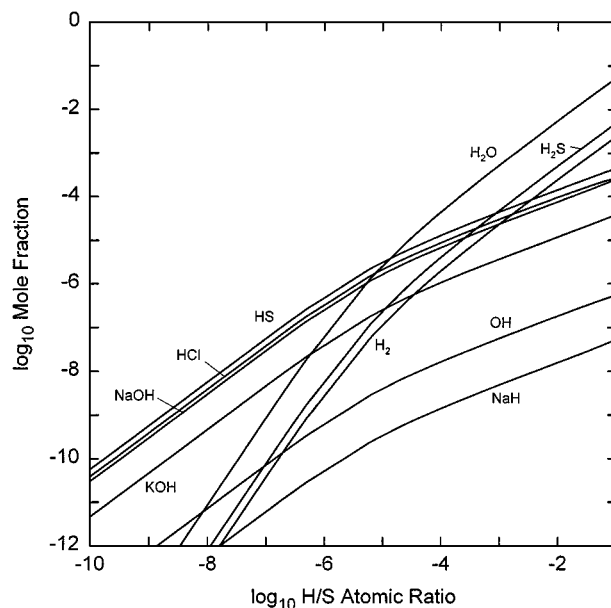


FIG. 6. Chemical equilibrium abundances of hydrogen-bearing species as a function of the H/S atomic ratio at 1500 K and 1 bar total pressure. The nominal values from Table I are used for the O, S, Na, Cl, and K abundances.

lar to sodium chemistry, although KOH becomes the third most abundant potassium gas at H/S ratios above ~ 0.003 .

The major change to chlorine chemistry is that HCl becomes more important as the hydrogen abundance increases. Hydrogen chloride is the major chlorine gas emitted from terrestrial volcanoes. However, Io is probably much drier than Earth, so HCl should be much less important for volcanic gas chemistry there. The three most abundant chlorine gases at all H/S ratios considered are NaCl, KCl, and $(\text{NaCl})_2$ in this order. The KCl dimer is the fourth most abundant Cl-bearing gas at H/S ratios less than ~ 0.01 , but the HCl abundance exceeds the $(\text{KCl})_2$ abundance at higher H/S ratios.

Figure 6 illustrates that very high H/S ratios are needed before the predicted H_2O , H_2S , and HCl abundances exceed the Voyager upper limits on these species. However, even at $\text{H}/\text{S} \sim 0.1$, the largest ratio considered, less than 1% of all sulfur is present as H_2S . At this H/S ratio H_2S is only as important as SO and remains less abundant than SO_2 , S_2 , and S_2O . It is implausible that ionian volcanic gases have H/S ratios ~ 0.1 and the Voyager upper limits are thus not very good constraints on the amount of hydrogen that may be outgassed from Io today.

Condensation Chemistry

Figure 7 shows how the condensation chemistry of sodium and potassium compounds varies with total pressure for the nominal elemental abundances listed in Table I. Perhaps the most important effect is that increasing pressure leads to condensation at higher temperatures. Sodium sulfide is always the high-temperature condensate at this bulk composition. Sodium sulfide melts at 1445 ± 10 K (Chase 1998), so liquid Na_2S condenses at

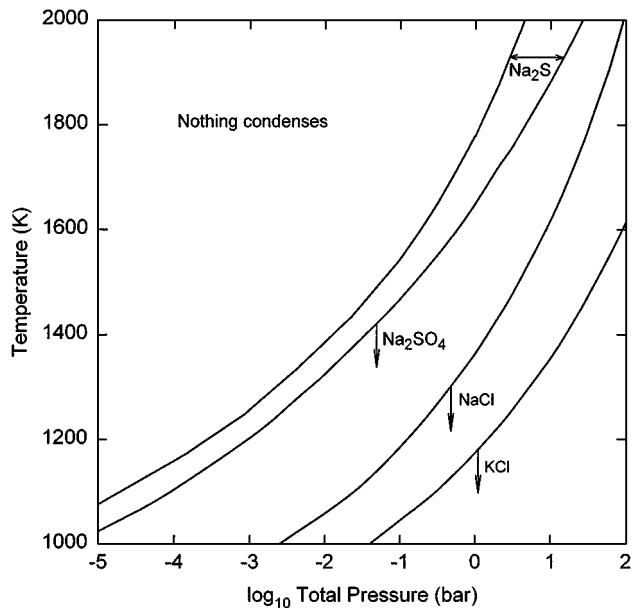


FIG. 7. Condensation temperatures of Na_2S , Na_2SO_4 , NaCl , and KCl as a function of the total pressure for the nominal elemental abundances given in Table I. No condensates are stable at high temperatures and low pressures (top left region of the graph).

higher pressures. Depending on the total pressure, Na_2S is stable for tens of degrees to a few hundred degrees higher than Na_2SO_4 . Sodium sulfate melts at 1157 K and condenses as a liquid over almost the entire pressure range shown. Sodium chloride condenses several hundred degrees below Na_2SO_4 and coexists with it. The lowest temperature condensate in this temperature range is KCl . Sodium chloride melts at 1074 K and KCl melts at 1044 K so these two compounds condense as solid halite and sylvite, respectively, over part of the pressure range shown.

The condensation sequence is somewhat altered at different O/S ratios and this is illustrated in Fig. 8. Sodium sulfide remains the high-temperature condensate over a wide range of O/S ratios, but the Na_2SO_4 condensation temperature increases steeply as O/S increases and it becomes the highest-temperature condensate at O/S ratios near 1.5. At O/S ratios less than ~ 0.15 , a new field appears where Na_2S and Na_2SO_4 coexist for a range of temperatures. This field increases in size as both the O/S ratio and temperature decrease. In contrast to the complex behavior exhibited by sodium sulfide and sulfate, the NaCl and KCl condensation temperatures are insensitive to the O/S ratio and only decrease slightly as the O/S ratio increases.

The composition of the predicted volcanic condensates is shown in Fig. 9 as a function of temperature at 1 bar total pressure. Three different O/S ratios of 1.5, 1.0, and 0.1 are shown. At O/S = 1.5, Na_2SO_4 condenses and no Na_2S forms, while in the latter two cases Na_2S is the only condensate forming at high temperatures, with sodium sulfate, NaCl , and KCl coexisting at lower temperatures. Sodium sulfide also coexists with sodium sulfate for a limited temperature range in the case of the more reducing gas. This is also evident from Fig. 8.

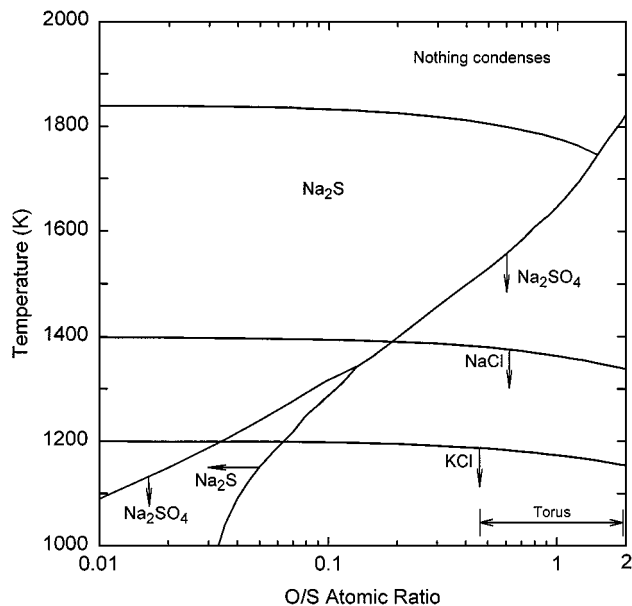


FIG. 8. Condensation temperatures of Na_2S , Na_2SO_4 , NaCl , and KCl as a function of the O/S atomic ratio at 1 bar total pressure. The nominal values from Table I are used for the S, Na, K, and Cl elemental abundances. The arrow labeled “torus” shows the range of O/S atomic ratios in the Io torus.

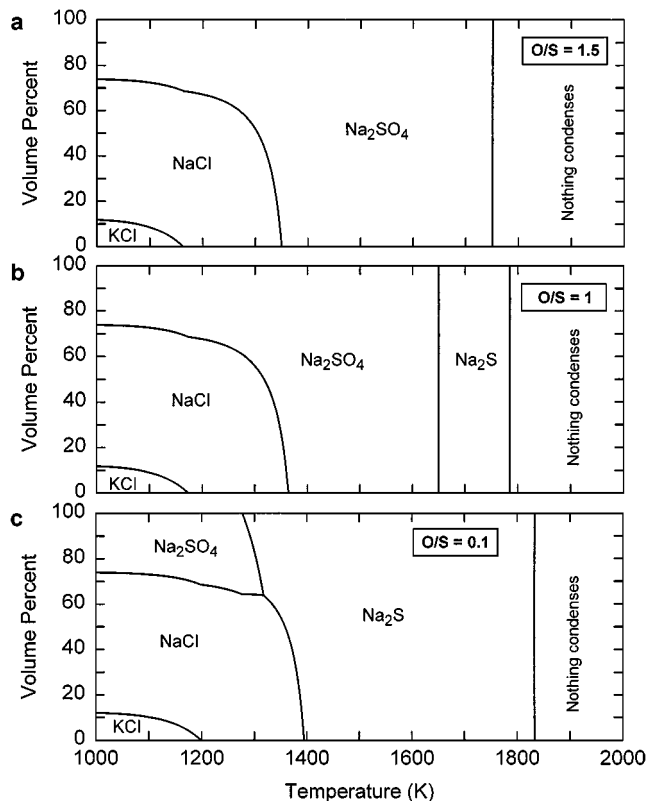


FIG. 9. Composition in volume percent of volcanic condensates as a function of temperature at 1 bar total pressure and three different O/S ratios of 0.1, 1.0, and 1.5. The ratios, relative to sulfur, of other elements are the same as in the nominal model listed in Table I.

APPLICATIONS TO IO

Volcanic Degassing of Alkalis and Chlorine on Io

Several different factors influence the volcanic degassing of alkalis and chlorine on Io: the predominance of sulfur in magmatic gases, the anhydrous character of the magmas, the unusually high temperatures of at least some volcanic vents, and the low ambient pressure at Io's surface. The predominance of sulfur in magmatic gases on Io favors the formation of sodium sulfate and sulfide and condensation of these phases. The anhydrous nature of the magmas can enhance the amount of Cl in the gas phase because the Cl concentration in terrestrial magmatic gases is anticorrelated with the amount of water in the magmas (Webster *et al.* 1999). The low water content of ionian magmas probably does not directly affect the degassing of alkalis (e.g., Sanders *et al.* 1981) because in silicate melts alkalis are associated with oxygen and also with chlorine in alkaline magmas. However, the dryness of magma source regions probably increases liquidus temperatures. In turn, the higher liquidus temperatures increase the amount of degassed volatiles because vapor pressures increase exponentially with increasing temperature.

Both the high temperatures of ionian magmas and their adiabatic decompression at Io's low-pressure near-surface environment (Kieffer 1982) should favor extraction of volatiles into the gas phase. Laboratory measurements of sodium and potassium concentrations in basaltic melts that have been heated for different periods of time (Corrigan and Gibb 1979, Donaldson 1979) and laboratory measurements of sodium and potassium vapor pressures above mafic and ultrabasic melts (Yakovlev *et al.* 1984, Markova *et al.* 1987), alkali feldspar melts (Rammensee and Fraser 1982), and heated chondritic meteorites (Tsuchiyama *et al.* 1981, Ruzicka *et al.* 1998) show that these two elements are volatile and easily lost to the vapor at high temperatures. Theoretical calculations of the sodium and potassium vapor pressure above chondritic silicate melts (Fegley and Cameron 1987) also show the high volatility of Na and K.

Generally speaking, the bulk composition of volcanic gases can vary with temperature, pressure, and composition of ionian magmas. Higher temperature and/or lower pressure increase the vaporization of S, Na, K, and Cl from magmas. However, the effects are different for each element. For example, the maximum amount of some more volatile but less abundant elements such as Cl that can be degassed may be limited by their relatively low concentrations in the magma. Although terrestrial volcanic gases and experimental data indicate similar volatilities of Na and K from silicate melts (e.g., Crowe *et al.* 1987, Markova *et al.* 1987), some experimental data demonstrate that K becomes more volatile than Na at very high (>2000 K) temperatures (Walter and Giutronich 1967). Degassing is also affected by the oxidation state of magma, as we discussed for sulfur in Zolotov and Fegley (1999). The volatility of Na and K increases as the oxidation state of the magma decreases (Tsuchiyama *et al.* 1981, Symonds *et al.* 1992) and as the amount of sulfur in the magma increases (Sanders *et al.* 1981). In addition, the volatil-

ity of Na compared to K increases, as magma becomes more reduced (Yakovlev and Kosolapov 1980). Finally, as discussed later, magmatic interactions with volatile-rich deposits formed volcanically or by other processes, may also be a source of alkalis, chlorine, and sulfur in volcanic gases.

Alkalis. Our results show that NaCl, Na, and (NaCl)₂ are the major sodium species expected in volcanic gases on Io. The Na/S and O/S ratios are of secondary importance for determining the major sodium gas. Diatomic sodium vapor, sodium oxide gases, and Na₂SO₄ gas are less abundant than either Na or NaCl. There are no thermodynamic data for sodium sulfide gases (e.g., the Na analogs to KS and K₂S) and these two gases were not included in our computations. However, by analogy with potassium chemistry we do not expect either NaS or Na₂S to be the dominant sodium species in ionian volcanic gases, although they may be present at minor or trace levels.

Although sodium sulfate and/or sodium sulfide are not major constituents of the volcanic gases, these two compounds are the most abundant high-temperature condensates. They can form together or separately depending on temperature, oxidation state, and pressure of the volcanic gas (Figs. 7–9). The calculated stability of condensed Na₂S at low O/S ratios is consistent with the formation of alkali sulfides in experimental modeling of sulfur–magma interactions on Io done by Johnson and Burnett (1990). The formation of Na₂SO₄ at more oxidizing conditions is in agreement with experimental data for interaction of Na-silicates with SO₂–O₂ gas mixtures (Johnson and Burnett 1993). The stability fields for condensed Na₂SO₄ and Na₂S are also consistent with results obtained by Burnett (1995) in his independent theoretical study of the interaction of silicate magmas with S-bearing deposits in the crust of Io. In addition, oxygen fugacity values for the sodium sulfate–sulfide buffer (Na₂SO₄ = Na₂S + 2O₂) coincide with the redox conditions for relatively reduced (i.e., sulfur-rich, O/S ~0.01 to 0.1) ionian volcanic gas (see Fig. 5 in Zolotov and Fegley 1999). All these investigations indicate a competition of sodium sulfate and sulfide in igneous processes on Io.

The major potassium gases emitted from ionian volcanoes will be KCl, (KCl)₂, and monatomic K. Potassium chloride vapor is the dominant potassium gas over the 1000–2000 K temperature range (see Fig. 1c). This conclusion holds over the range of total pressures and elemental abundances explored in our calculations. To summarize, most of the gaseous sodium and potassium volcanically outgassed on Io are in NaCl, Na, (NaCl)₂, KCl, (KCl)₂, and K and the two most abundant high-temperature condensates are Na₂SO₄ and Na₂S.

Chlorine. Sodium and potassium chlorides are the most abundant chlorine gases in our calculations under virtually all temperatures and pressures for the nominal elemental abundances in Table I. The (Na + K)/Cl ratio (i.e., the alkali/Cl ratio) is the most important factor that determines the nature of outgassed chlorine compounds. As shown in Fig. 3d, chlorine chemistry begins to change when the alkali/Cl ratio becomes unity.

Atomic and molecular chlorine and several sulfur chlorides (notably S_2Cl and SCl_2) become important Cl gases at alkali/Cl ratios less than unity. The measurements of Na, K, and Cl in the Io torus give an alkali/Cl ratio of about unity, but at present it is unclear if this ratio is actually >1 or is 1 or <1 .

Cosmochemical arguments discussed earlier suggest that the bulk alkali/Cl ratio on Io is greater than one. Furthermore, in common silicate magmas, sodium (with abundances of 0.1–6 wt%) is usually several times more abundant than chlorine (with abundances of 0.1–0.3 wt%) (Naumov *et al.* 1996). Nevertheless, chlorine has a much higher volatility and predominates over sodium in terrestrial volcanic gases (Crowe *et al.* 1987, Symonds *et al.* 1992, 1994). This raises two important questions: What are the likely alkali/Cl ratios in volcanic vents on Io? Does sodium dominate over chlorine in Io's torus? We suggest several answers to these questions.

Chlorine and its compounds are more volatile but less abundant than sodium and its compounds. As the magma temperature increases, the degassing of chlorine is ultimately limited by its abundance in the magma, eventually leading to an increase in the alkali/Cl ratio in the outgassed volatiles. We thus expect three qualitatively different types of volcanic vents having different alkali/Cl ratios on Io.

High-temperature vents, such as those inferred from Galileo spacecraft observations to have maximum temperatures up to 2000 K (e.g., McEwen *et al.* 1998) could have alkali/Cl ratios greater than unity. The reduced character and high sulfur content in those magmas should also favor degassing of sodium and potassium. The alkali chlorides may be the major chlorine gases, while sodium and potassium may be in part in atomic form. Degassing from high-temperature magmas could be the major source of volatiles on Io and would be consistent with torus alkali/Cl ratios greater than unity. Conversely low-temperature vents and fumaroles could have alkali/Cl ratios less than unity, as we see in terrestrial volcanic gases. However, in contrast to Earth, where HCl is the major Cl-gas, molecular chlorine and sulfur chlorides (S_2Cl , SCl_2) can be important chlorine gases from low-temperature vents on Io because it is so dry. Finally, volcanic vents with intermediate temperatures can be transitional in nature with alkali/Cl ratios ~ 1 and may emit a complex mixture of alkali chlorides, sulfur chlorides, sulfur oxychlorides, and atomic and molecular chlorine.

Regardless of the temperature of the magma, alkali/Cl ratios ~ 1 would be observed if NaCl- and KCl-rich deposits (that could be evaporitic, hydrothermal, or volcanic in origin as discussed below) are contaminated by upwelling magmas. The latter case (i.e., alkali/Cl ~ 1 in outgassed volatiles) has broad importance for the chemistry and photochemistry of Io's atmosphere and surface. In this regard we note that although the torus alkali/Cl ratio is apparently greater than unity, the amount of Cl in the torus could be underestimated because only Cl^+ is observed. Additional chlorine may be present as other species (e.g., neutral Cl, Cl^- , Cl^{2+} , etc.) and Cl^+ may represent only a fraction of the total Cl abundance in the torus. This point is also made by Küppers and Schneider (2000), who discuss constraints on the

Cl^{2+}/Cl^+ ratio, but we are unaware of any constraints on Cl and Cl^- in the torus.

Finally, observations of terrestrial volcanic gases and sublimates and thermodynamic modeling of terrestrial (e.g., Symonds *et al.* 1992, 1994) and lunar (Fegley 1991, Fegley and Swindle 1993) volcanic gases show that chlorine is responsible for degassing and transport of many metallic elements (e.g., Fe, Cu, Zn) as chloride gases such as $FeCl_2$, $CuCl$, $ZnCl_2$. These studies also show that the abundance of metal chloride gases increases as the hydrogen (i.e., the water) abundance drops. Thus, degassing and fractionation of metals as chloride gases may be an important process on Io.

Sources of Alkalis and Chlorine in Ionian Volcanic Gases

Analogies with terrestrial petrology suggest that alkalis and chlorine should be present in silicate magmas on Io, and extremely high temperatures (like those inferred for several volcanic vents on Io) would favor vaporization of alkalis and Cl from these melts. However, it is also possible that Na, K, and Cl are emitted from melts that are enriched in these elements. On Earth, the most abundant magmas enriched in alkalis and chlorine are also silica-rich (e.g., granitic and rhyolitic magmas). Keszthelyi and McEwen (1997) proposed such magmas in their computer modeling of igneous differentiation on Io. However, the temperatures of silicic magmas, which are usually <1300 K, are not consistent with the highest observed temperatures for hot spots on Io. In addition, Galileo Solid State Imaging (SSI) data for dark material on Io's surface display a shallow spectral absorption feature at $0.9 \mu m$ that is consistent with basic or ultrabasic (i.e., silica-depleted) rather than silica-rich magmas (Geissler *et al.* 1999b). This interpretation agrees with the high magma temperatures (up to 2000 K) of at least several volcanic hot spots (e.g., McEwen *et al.* 1998). Degassing from ultrabasic alkaline magmas, which was proposed by Zolotov and Fegley (1999), would provide a reasonable explanation for both the high-temperature hot spots and the presence of alkalis and chlorine in the torus. The solubility of chlorine in magmas increases with the abundances of Na and K (e.g., Carroll and Webster 1994, Webster 1997, Kravchuk *et al.* 1998), and it follows that alkaline magmas would be an important source of chlorine on Io.

Zolotov and Fegley (1999) also argued that alkaline ultrabasic magmas would be effective carriers of sulfur on Io. Volcanic ultrabasic alkaline rocks (e.g., meimechites) and related plutonic rocks are not abundant on Earth and have ages less than 2.7×10^9 years. It has been argued that these rocks formed only when the terrestrial upper mantle became oxidized significantly and contaminated by subducted material enriched in alkalis and other incompatible elements (Kogarko 1997). It is possible that the oxidizing nature of Io's mantle (Zolotov and Fegley 1999, 2000b) and/or remelting of ancient volcanic products submerged into the base of Io's lithosphere by intense volcanic resurfacing would provide conditions favorable for generation of melts rich in alkalis. The ultrabasic Mg-rich character of magmas could be caused by a high degree of melting of mantle peridotites,

which can be depleted rocks such as harzburgites (Kogarko and Ryabchikov 2000), followed by mixing of these Mg-rich melts with alkali-rich lithospheric magmas. In addition, igneous or sedimentary rocks enriched in alkalis may be assimilated partially by upwelling high-temperature ultrabasic melts throughout the lithosphere and recycled in subsequent eruptions. This model for the formation of ultrabasic alkaline magmas is more consistent with the tremendous igneous activity of Io than the model of a low-degree melting of undepleted mantle, which does not involve lithospheric material. Note that these two alternative sources of ultrabasic alkaline magmas, the base of the lithosphere or the underlying mantle, have also been discussed by Arndt *et al.* (1995) to explain the origin of terrestrial meimechites. However, meimechites have K/Na ratios higher than unity and they cannot be direct analogs to ionian ultrabasic alkaline magmas.

Compounds of sulfur, sodium, potassium, and chlorine may be enriched at and near Io's surface as a result of Io's extensive volcanic activity. If so, then interactions of new magmas with these deposits (e.g., in magma chambers and/or channels) could lead to recycling of these elements. In addition, this recycling could involve nonvolcanic deposits possibly formed as a result of ancient aqueous processes. If Io were accreted from hydrous minerals formed in the jovian subnebula (Prinn and Fegley 1981), the uppermost parts of Io could have been enriched in alkalis and chlorine during hydrothermal alteration. One possibility is that water (fluid or gas)–rock interaction followed by hydrogen escape and oxidation of Io's mantle and crust (cf. Zolotov and Fegley 1999) and tidally driven magmatic activity led to formation of oxidized and anhydrous layers enriched in alkalis, sulfur, and chlorine. This suggestion is consistent with an earlier model of possible hydrothermal deposits that has been proposed to explain the color of Io's surface (Fanale *et al.* 1974, 1977). Furthermore, Nash and Fanale (1977) and Kargel (1993) have also discussed an aqueous origin of sulfur and alkali deposits on Io. The recent discovery of chlorine in the torus by Küppers and Schneider (2000) is interesting because sulfur, sodium and chlorine are the major solutes in Earth's ocean and are the major constituents of terrestrial evaporites. Although evaporite deposits formed during an early stage of Io's geologic evolution would have been heavily reprocessed (Kargel *et al.* 1999) in igneous processes, crustal rocks could be enriched in typical evaporite elements: Na, K, Cl, and S. Such an enrichment is an intriguing possibility that might give insights for the composition of an ocean inside Europa.

Observational Constraints on the Composition of Volcanic Condensates

A significant part of Io's surface is covered by volcanic pyroclastic material or volcanic condensates (Spencer and Schneider 1996, Spencer *et al.* 1997, Geissler *et al.* 1999b). About one-third of the surface is covered by red material, which is especially prominent around the Pele volcano (Geissler *et al.* 1999b). In addition to elemental sulfur and sulfur oxides (Spencer and

Schneider 1996, Spencer *et al.* 1997), sodium sulfate and sodium and potassium sulfides have been proposed by Fanale *et al.* (1979), Nash and Nelson (1979), and Nash (1988, 1993) to account for the spectral reflectance of Io in the 0.2- to 5.0- μm region and the color of the red deposits. Howell *et al.* (1989) reported spectroscopic upper limits of 25% for Na_2SO_4 on Io's surface. Although Ospina *et al.* (1992) have reported a tentative identification of Na_2SO_4 on the surface, their data have not been confirmed by independent observations. Spencer *et al.* (1997) concluded that we still have no spectral evidence for sodium-bearing compounds on the surface. The Galileo SSI data do not change this conclusion; they neither support nor rule out the presence of sodium sulfides and sulfates (Geissler *et al.* 1999b). If the Na/S ratio in volcanic gases does not exceed 10%, as measured in the torus, Na_2SO_4 and Na_2S could probably not be distinguished with currently available spectral data. However, high-spatial-resolution Galileo NIMS data from the Io close fly-bys in 1999 and 2000 could be used to search for and identify Na_2SO_4 and Na_2S . Halite (NaCl) and sylvite (KCl) are also predicted volcanic condensates. However, the percentages of NaCl and KCl in condensates are limited by the low abundances of Cl and K, which are a few percent or less of the sulfur abundance. Thus it may be difficult to detect condensed alkali chlorides spectroscopically.

Alkali chlorides and sodium sulfate/sulfide can form coatings on silicate ash particles in the vicinity of volcanic vents. Outside the vents (in plumes or on the surface), various sulfur-bearing condensates can form (e.g., SO_2 , S_2O , S_n allotropes). These S-bearing condensates condense at lower temperatures than and can mask the Na-, K-, and Cl-bearing condensates. Therefore S-bearing condensates are probably primarily responsible for the color of Io's surface.

White condensates are attributed to SO_2 frost and yellow to red deposits are probably due to various sulfur allotropes such as S_3 and S_4 , which can form by UV photolysis of S_2 vapor (Spencer *et al.* 1997, 2000, Moses *et al.* 2000). In addition, color variations in sulfur deposits may be caused by trace element and/or sodium sulfide impurities (Kargel *et al.* 1999).

Compositional differentiation of particles and/or gases in volcanic plumes can lead to the observed concentric zoning around some volcanoes (Lopes-Gautier *et al.* 2000). Kargel *et al.* (1999) pointed out that terrestrial volcanic vents commonly exhibit zoned sublimates. It is possible that some concentric zones around Io's volcanoes are enriched in the condensates we predict to be stable.

Chemistry of Volcanic Plumes and Local Volcanic Atmospheres

As discussed earlier in this paper, the supersonic adiabatic expansion of gases in ionian volcanic plumes (Kieffer 1982) should result in immediate quenching of high-temperature chemistry in the vicinity of the volcanic vents. Thus, although we are not explicitly modeling chemistry in volcanic plumes, our calculations of volcanic gas equilibria at high temperatures provide a guide to the compositions of the plumes and the short-lived

volcanic atmospheres around them. Differences in the temperature, pressure, and bulk compositions of volcanic gases should be reflected in the compositions of volcanic plumes and the local volcanic atmospheres. For example, high-temperature, high-pressure, and sulfur-rich volcanoes can produce SO_2 - S_2 plumes and local atmospheres that contain significant amounts of atomic Na and a moderate amount of gaseous alkali chlorides. Low-temperature, low-pressure, and more oxidized volcanoes could generate SO_2 -dominated atmospheres containing smaller amounts of Na, K, and Cl mostly in the form of gaseous alkali chlorides. If abundances of S, O, Na, K, and Cl species in plumes and/or the local volcanic atmospheres can be determined instrumentally (e.g., by infrared or mass spectroscopy), it should be possible to constrain the temperature, pressure, and bulk compositions for different volcanic vents on Io (Zolotov and Fegley 2000a, b). In this regard, we note that a number of species including SO_2 , OCS, CO, CO_2 , HCl, and CuCl have been detected and that temperatures have been estimated in terrestrial volcanic gases using spectroscopic methods (e.g., Murata 1960, Mori and Notsu 1997).

SUMMARY AND FUTURE WORK

Thermochemical equilibrium calculations were used to model the speciation of S, O, Na, K, Cl, and H in volcanic gases on Io and how this varies with temperature, pressure, and bulk elemental composition. The results show that Na and K chlorides are the major Cl-bearing gases, that monatomic NaCl, Na, and $(\text{NaCl})_2$ are the major Na-bearing gases, and that KCl, $(\text{KCl})_2$, and monatomic K are the major K-bearing gases. Hydrogen-bearing gases are not expected and only become important at implausibly large H/S ratios (i.e., hydrogen elemental abundances). These results are valid over a wide range of temperatures, pressures, and bulk compositions.

However, the nature of the major Cl-bearing gases depends on whether or not the $(\text{Na} + \text{K})/\text{Cl}$ (i.e., the alkali/Cl) atomic ratio is less than, equal to, or greater than one. The observed alkali/Cl ratio in the Io torus is about unity, but it is not certain if this ratio is less than, equal to, or greater than one. High-temperature volcanic vents are expected to have alkali/Cl ratios greater than unity. In this case sodium and potassium chlorides are the major Cl gases and all other Cl gases have negligible importance. If the alkali/Cl ratio were < 1 , which is possible for lower temperature volcanic vents, Cl_2 , Cl, S_2Cl , and SCl_2 and other sulfur chlorides and sulfur oxychlorides become increasingly important. Volcanic vents with alkali/Cl ratios equal to one should emit a complex mixture of alkali chlorides, Cl_2 , Cl, sulfur chlorides, and sulfur oxychlorides. Photochemical modeling of volcanic atmospheres corresponding to these three cases is currently under way (Moses *et al.* 2000).

Sodium sulfide and sodium sulfate are predicted to condense at and around volcanic vents on Io's surface. Sodium sulfide generally condenses at higher temperatures and more reduced conditions than does sodium sulfate. Sodium and potassium chlo-

rides condense at lower temperatures. All of these condensates may form coatings on silicate ash particles. The predicted volcanic condensates agree with prior experimental, observational, and theoretical work proposing that sodium sulfide, sulfate, and alkali chlorides are present on Io's surface. Some of these condensates have been suggested to form the red deposits seen on Io.

Our results predict two sources of alkalis and Cl in the plasma torus: sputtering from solid Na_2S , Na_2SO_4 , NaCl, and KCl surface condensates and ionization of alkali chloride gases and monatomic alkali gases that could be present in volcanic plumes and Io's volcanic atmosphere.

Finally, several different types of observations are needed to improve our knowledge of Io's geochemistry, the composition of volcanic gases, and the sources of elements observed in the torus. Gases in volcanic plumes can be analyzed spectroscopically as done by Voyager (Pearl *et al.* 1979) and for volcanic gases on Earth (Murata 1960, Mori and Notsu 1997). Volcanic entry probes equipped with temperature and pressure sensors and miniature mass spectrometers can measure the temperature, pressure, and chemical composition of gases emitted from different volcanic vents. Geochemical analyses of volcanic condensates and lava flows can be made using a combination of spectroscopic methods (e.g., for icy condensates) and *in situ* elemental analyses (e.g., for halides, oxides, silicates, elemental sulfur, sulfides, and sulfates). A number of miniaturized instruments such as X-ray fluorescence (XRF), alpha-particle, and gamma-ray spectrometers have been developed for such analyses of rocky material. Less advanced versions of several of these instruments have been used successfully on the surfaces of the Moon, Mars, and Venus (740 K, 96 bar). In the latter case elemental analyses have been done in ~ 60 min in a hostile environment, suggesting that similar performance can be obtained on Io's surface.

ACKNOWLEDGMENTS

This work was supported by NASA Planetary Atmospheres Program Grant NAG5-6366. We thank R. Osborne for help with editing, Jeff Kargel, and an anonymous referee for their reviews.

REFERENCES

- Arndt, N. T., K. Lehnert, and Y. Vasilev 1995. Meimechites: highly magnesian lithosphere-contaminated alkaline magmas from deep subcontinental mantle. *Lithos* **34**, 41–59.
- Bagenal, F., and J. D. Sullivan 1981. Direct plasma measurements in the Io torus and inner magnetosphere of Jupiter. *J. Geophys. Res.* **86A**, 8447–8466.
- Barin, I. 1995. *Thermochemical Data of Pure Substances*, 3rd ed. VCH, Weinheim.
- Bartels, O. G. 1972. Estimate of volcanic contributions to the atmosphere and volcanic gases and sublimates as the source of the radioisotopes beryllium-10, sulfur-35, phosphorus-32, and sodium-22. *Health Phys.* **22**, 387–392.
- Bernard, A., and F. Le Guern 1986. Condensation of volatile elements in high-temperature gases of Mount St. Helens. *J. Volcanol. Geotherm. Res.* **28**, 91–105.
- Brown, M. E. 1998. Potassium in Europa's atmosphere. *Icarus*, submitted.

- Burnett, D. S. 1995. Competition between Na_2SO_4 and Na sulfide in the upper crust of Io. *J. Geophys. Res.* **100**, 21265–21270.
- Carroll, M. R., and J. D. Webster 1994. Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. In *Volatiles in Magmas* (M. R. Carroll and J. R. Holloway, Eds.), pp. 231–279. Mineralogical Society America, Washington, DC.
- Chase, M. W. 1998. *NIST-JANAF Thermochemical Tables*, 4th ed. *J. Phys. Chem. Ref. Data*, Monograph 9.
- Chrisey, D. B., R. E. Johnson, J. W. Boring, and J. A. Phipps 1988. Ejection of sodium sulfide by the sputtering of the surface of Io. *Icarus* **75**, 233–244.
- Corrigan, G., and F. G. F. Gibb 1979. The loss of Fe and Na from a basaltic melt during experiments using the wire-loop method. *Mineral. Mag.* **43**, 121–126.
- Crowe, B. M., D. L. Finnegan, W. H. Zoller, and W. V. Boynton 1987. Trace element geochemistry of volcanic gases and particles from 1983–1984 eruptive episodes of Kilauea Volcano. *J. Geophys. Res.* **92**, 13708–13714.
- Donaldson, C. H. 1979. Composition changes in a basalt melt contained in a wire loop of platinum-rhodium ($\text{Pt}_{80}\text{Rh}_{20}$): Effects of temperature, time, and oxygen fugacity. *Mineral. Mag.* **43**, 115–119.
- Fanale, F. P., R. H. Brown, D. P. Cruikshank, and R. N. Clark 1979. Significance of adsorption features in Io's IR reflectance spectrum. *Nature* **280**, 761–763.
- Fanale, F. P., T. V. Johnson, and D. L. Matson 1974. Io: A surface evaporate deposit? *Science* **186**, 922–925.
- Fanale, F. P., T. V. Johnson, and D. L. Matson 1977. Io's surface composition: Observational constraints and theoretical considerations. *Geophys. Res. Lett.* **4**, 303–306.
- Fegley, B., Jr. 1991. Thermodynamic models of the chemistry of lunar volcanic gases. *Geophys. Res. Lett.* **18**, 2073–2076.
- Fegley, B., Jr., and A. G. W. Cameron 1987. A vaporization model for iron/silicate fractionation in the Mercury protoplanet. *Earth Planet. Sci. Lett.* **82**, 207–222.
- Fegley, B., Jr., and K. Lodders 1994. Chemical models of the deep atmospheres of Jupiter and Saturn. *Icarus* **110**, 117–154.
- Fegley, B., Jr., and T. D. Swindle 1993. Lunar volatiles: Implications for lunar resource utilization. In *Resources of Near-Earth Space* (J. S. Lewis, M. S. Matthews, and M. L. Guerrieri, Eds.), pp. 367–426. Univ. of Arizona Press, Tucson.
- Fegley, B., Jr., and M. Yu. Zolotov 1999. Degassing and condensation of Na-, K-, and Cl-bearing compounds emitted from high-temperature lava on Io. *EOS Trans. AGU* **80**, F625.
- Geissler, P. E., A. S. McEwen, W. Ip, M. J. S. Belton, T. V. Johnson, W. H. Smyth, and A. P. Ingersoll 1999a. Galileo imaging of atmospheric emissions from Io. *Science* **285**, 870–874.
- Geissler, P. E., A. S. McEwen, L. Keszthelyi, R. Lopes-Gautier, J. Granahan, and D. P. Simonelli 1999b. Global color variations on Io. *Icarus* **140**, 265–282.
- Gurvich, L. V., et al. 1978–1982. *Thermodynamic Properties of Individual Substances*, 2nd ed. Nauka, Moscow. [in Russian]
- Hapke, B. 1979. Io's surface and environs: A magmatic-volatile model. *Geophys. Res. Lett.* **6**, 799–802.
- Howell, R. R., D. B. Nash, T. R. Geballe, and D. P. Cruikshank 1989. High-resolution infrared spectroscopy of Io and possible surface materials. *Icarus* **78**, 27–37.
- Hunten, D. M., T. H. Morgan, and D. E. Shemansky 1988. The Mercury atmosphere. In *Mercury* (F. Vilas, C. R. Chapman, and M. S. Matthews, Eds.), pp. 562–612. Univ. of Arizona Press, Tucson.
- Johnson, M. L., and D. S. Burnett 1990. Igneous origin for the Na in the cloud of Io. *Geophys. Res. Lett.* **17**, 981–984.
- Johnson, M. L., and D. S. Burnett 1993. SO_2 -rock interaction on Io: Reaction under highly oxidizing conditions. *J. Geophys. Res.* **98**, 1223–1230.
- Kargel, J. S. 1993. Crustal structure and igneous processes in a chondritic Io. *Lunar Planet. Sci. XXIV*, 751–752.
- Kargel, J. S., P. Delmelle, and D. B. Nash 1999. Volcanogenic sulfur on Earth and Io: Composition and spectroscopy. *Icarus* **142**, 249–280.
- Keszthelyi, L., and A. McEwen 1997. Magmatic differentiation of Io. *Icarus* **130**, 437–448.
- Kieffer, S. 1982. Dynamics and thermodynamics of volcanic eruptions: Implications for the plumes on Io. In *Satellites of Jupiter* (D. Morrison, Ed.), pp. 647–723. Univ. of Arizona Press, Tucson.
- Killen, R. M., and W. H. Ip 1999. The surface-bounded atmospheres of Mercury and Moon. *Rev. Geophys.* **37**, 361–406.
- Kogarko, L. N. 1997. Alkaline magmatism and the evolution of the oxidation potential of the Earth's mantle. *Geochem. Intl.* **34**, 343–347.
- Kogarko, L. N., and I. D. Ryabchikov 2000. Geochemical evidence for meimechite magma generation in the subcontinental lithosphere of polar Siberia. *J. Asian Earth Sci.* **18**, 195–203.
- Kravchuk, I. F., S. D. Malinin, and A. B. Slutsky 1998. Chlorine in fluid-magmatic systems: Experimental data. *Mineral. Mag.* **62**, 811–812.
- Küppers, M., and N. M. Schneider 2000. Discovery of chlorine in the Io plasma torus. *Geophys. Res. Lett.* **27**, 513–517.
- Lodders, K., and B. Fegley, Jr. 1998. *The Planetary Scientist's Companion*. Oxford Univ. Press, New York.
- Lopes-Gautier, R., S. Doute, W. D. Smythe, L. W. Kamp, R. W. Carlson, and 11 colleagues 2000. A close-up look at Io from Galileo's near-infrared mapping spectrometer. *Science* **288**, 1201–1204.
- Markova, O. M., O. I. Yakovlev, G. A. Semenov, and A. N. Belov 1987. The vaporization of natural melts in a Knudsen cell. *Geochem. Intl.* **24**, 36–45.
- McEwen, A. S., L. Keszthelyi, J. R. Spencer, G. Schubert, D. L. Matson, R. Lopes-Gautier, and 9 colleagues 1998. High-temperature silicate volcanism on Jupiter's moon Io. *Science* **281**, 87–90.
- McGrath, M. A., M. J. S. Belton, J. R. Spencer, and P. Sartoretti 2000. Spatially resolved spectroscopy of Io's Pele plume and SO_2 atmosphere. *Icarus* **146**, 476–493.
- Moos, H. W., P. D. Feldman, S. T. Durrance, W. P. Blair, C. W. Bowers, A. F. Daviden, W. W. V. Dixon, H. C. Ferguson, R. C. Henry, R. A. Kimble, G. A. Kriss, J. W. Kruk, K. S. Long, and O. Vancura 1991. Determination of ionic abundances in the Io torus using the Hopkins Ultraviolet Telescope. *Astrophys. J.* **382**, L105–108.
- Mori, T., and K. Notsu 1997. Remote CO , COS , CO_2 , SO_2 , HCl detection and temperature estimation of volcanic gas. *Geophys. Res. Lett.* **24**, 2047–2050.
- Moses, J. I., M. Yu. Zolotov, and B. Fegley, Jr. 2000. Photochemistry near an active volcanic plume on Io. *EOS Trans. AGU* **81**, S290.
- Murata, K. J. 1960. Occurrence of CuCl emission in volcanic flames. *Am. J. Sci.* **258**, 769–772.
- Na, C. Y., L. M. Trafton, E. S. Barker, and S. A. Stern 1998. A search for new species in Io's extended atmosphere. *Icarus* **131**, 449–452.
- Nash, D. B. 1988. Infrared reflectance spectra of sodium sulfide (Na_2S) with contaminant disodium carbonate: Effects of adsorbed water vapor and carbon dioxide and relation to studies of Io. *Icarus* **74**, 365–368.
- Nash, D. B. 1993. A case for Na_2S on Io's surface: Sulfide volcanism? In *Io: An International Conference*, pp. 75–76. San Juan Capistrano Research Institute, San Juan Capistrano, CA.
- Nash, D. B., and E. P. Fanale 1977. Io's surface composition based on reflectance spectra of sulfur-salt mixtures and proton-irradiation experiments. *Icarus* **31**, 40–80.
- Nash, D. B., and R. M. Nelson 1979. Spectral evidence for sublimates and adsorbates on Io. *Nature* **280**, 763–766.
- Naumov, V. B., V. I. Kovalenko, O. M. Ivanitskiy, and N. I. Savel'yeva 1998. Concentration of chlorine in magmatic melts (based on inclusions in minerals). *Geochem. Intl.* **33**(2), 144–155.
- Opsina, M. J., R. R. Khanna, and J. C. Pearl 1992. Laboratory IR identifications of possible surface compounds on Io. *Bull. Am. Astron. Soc.* **24**, 943.

- Pankratz, L. B., A. D. Mah, and S. W. Watson 1987. *Thermodynamic Properties of Sulfides*. U.S. Bureau of Mines Bulletin 689. U.S. Government Printing Office, Washington, D.C.
- Pearl, J. C., R. Hanel, V. Kunde, W. Maguire, D. Fox, S. Gupta, C. Ponnamperna, and F. Raulin 1979. Identification of gaseous SO₂ and new limits for other gases on Io. *Nature* **280**, 755–758.
- Pennisi, M., M. F. Le Cloarec, G. Lambert, and J. C. Le Roulley 1988. Fractionation of metals in volcanic emissions. *Earth Planet. Sci. Lett.* **88**, 284–288.
- Prinn, R. G., and M. B. Fegley, Jr. 1981. Kinetic inhibition of CO and N₂ reduction in circumplanetary nebulae: Implications for satellite composition. *Astrophys. J.* **249**, 308–317.
- Rammensee, W., and D. G. Fraser 1982. Determination of activities in silicate melts by Knudsen cell mass spectrometry. *Geochim. Cosmochim. Acta* **46**, 2269–2278.
- Ruzicka, A., G. A. Snyder, and L. A. Taylor 1998. Mega-chondrules and large, igneous-textured clasts in Julesberg (L3) and other ordinary chondrites: Vapor-fractionation, shock-melting, and chondrule formation. *Geochim. Cosm. Acta* **62**, 1419–1442.
- Sanders, D. M., M. E., Wilke, S. Hurwitz, and W. K. Haller 1981. Role of water vapor and sulfur compounds in sodium vaporization during glass melting. *J. Am. Ceram. Soc.* **64**, 399–404.
- Spencer, J. R., and N. M. Schneider 1996. Io on the eve of the Galileo Mission. *Annu. Rev. Earth Planet. Sci.* **24**, 125–190.
- Spencer, J. R., K. L. Jessup, M. A. McGrath, G. E. Ballester, and R. Yelle 2000. Discovery of gaseous S₂ in Io's Pele plume. *Science* **288**, 1208–1210.
- Spencer, J. R., A. S. McEwen, M. A. McGrath, P. Sartoretti, D. B. Nash, K. S. Noll, and D. Gilmore 1997. Volcanic resurfacing of Io: Post-repair HST imaging. *Icarus* **127**, 221–237.
- Summers, M. E., and D. F. Strobel 1996. Photochemistry and vertical transport in Io's atmosphere and ionosphere. *Icarus* **120**, 290–316.
- Symonds, R. B., M. H. Reed, and W. I. Rose 1992. Origin, speciation, and fluxes of trace-element gases at Augustine volcano, Alaska: Insights into magma degassing and fumarolic processes. *Geochim. Cosm. Acta* **56**, 633–657.
- Symonds, R. B., W. I. Rose, G. J. S. Bluth, and T. M. Gerlach 1994. Volcanic-gas studies: Methods, results, and applications. In *Volatiles in Magmas* (M. R. Carroll and J. R. Holloway, Eds.), pp. 1–66. Mineralogical Society America, Washington, D.C.
- Tkachenko, S. I., R. P. Porter, M. A. Korzhinskii, M. D. Van-Berden, K. I. Shmulovich, and G. S. Shteinberg 1999. Mineral- and ore-forming process in high-temperature fumarolic gases of Kudryavyy volcano, Iturup Island, Kuril archipelago. *Geochem. Intl.* **37**, 355–365.
- Tsuchiyama, A., N. Hiroko, and K. Ikuo 1981. Vaporization of sodium from silicate melt spheres and its application to the formation of chondrules. *Geochim. Cosm. Acta* **45**, 1357–1359.
- Van Zeggeren, F., and S. H. Storey 1970. *The Computation of Chemical Equilibria*. Cambridge Univ. Press, Cambridge.
- Vogt, R. E., W. R. Cook, A. C. Cumings, T. L. Garrard, N. Gehrens, and 6 colleagues 1979. Voyager 1: Energetic ions and electrons in the jovian magnetosphere. *Science* **204**, 1003–1007.
- Walter, L. S., and J. E. Cintronich 1967. Vapor fractionation of silicate melts at high temperatures and atmospheric pressures. *Solar Energy* **11**, 163–169.
- Webster, J. D. 1997. Chlorine solubility in felsic melts and the role of chlorine in magmatic degassing. *J. Petrol.* **38**, 1793–1807.
- Webster, J. D., R. J. Kinzler, and E. A. Mathez 1999. Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. *Geochim. Cosmochim. Acta* **63**, 729–738.
- Wiens, R. C., D. S. Burnett, W. F. Calaway, C. S. Hansen, K. R. Lykke, and M. J. Pellin 1997. Sputtering products of sodium sulfate: Implications for Io's surface and for sodium-bearing molecules in the Io torus. *Icarus* **128**, 386–397.
- Yakovlev, O. I., and A. I. Kosolapov 1980. Effect of the oxygen partial pressure on evaporation from rock melts. *Geochem. Intl.* **17**(1), 115–119.
- Yakovlev, O. I., O. M. Markova, G. A. Semenov, and A. N. Belov 1984. Results of an experiment on vaporization of the Krymka chondrite. *Meteoritika* **43**, 125–133. [in Russian]
- Zolotov, M. Yu., and B. Fegley, Jr. 1998a. Volcanic production of sulfur monoxide (SO) on Io. *Icarus* **132**, 431–434.
- Zolotov, M. Yu., and B. Fegley, Jr. 1998b. Volcanic origin of disulfur monoxide (S₂O) on Io. *Icarus* **133**, 293–297.
- Zolotov, M. Yu., and B. Fegley, Jr. 1999. Oxidation state of volcanic gases and the interior of Io. *Icarus* **141**, 40–52.
- Zolotov, M. Yu., and B. Fegley, Jr. 2000a. Volcanic degassing of hydrogen compounds on Io. *Lunar Planet. Sci. XXXI*, abstract 1186.
- Zolotov, M. Yu., and B. Fegley, Jr. 2000b. Eruption conditions of Pele volcano on Io inferred from chemistry of its volcanic plume. *Geophys. Res. Lett.* **27**, 2789–2792.