VOLCANIC ORIGIN OF ALKALI HALIDES ON IO. L. Schaefer and B. Fegley, Jr., Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washingtion University, St. Louis, MO 63130-4899. Email: laura_s@levee.wustl.edu, bfegley@levee.wustl.edu.

Introduction: The recent observation of NaCl (gas) on Io [1] confirms our earlier prediction that NaCl is produced volcanically [2]. Here we extend our calculations by modeling thermochemical equilibrium of O, S, Li, Na, K, Rb, Cs, F, Cl, Br, and I as a function of temperature and pressure in a Pele-like volcanic gas with O/S/Na/Cl/K = 1.518/1/0.05/0.04/0.005 and CI chondritic ratios of the other (as yet unobserved) alkalis and halogens. For reference, the nominal temperature and pressure for Pele is 1760±210 K and 0.01 bars based on Galileo data and modeling [3,4].

Computations: Calculations were done from 1000-2200 K and 10^{-6}-10^{+1} bars using the CONDOR code described by [5].

Results: The figures below show the major species of Li, Na, K, Rb, Cs, F, Cl, Br, and I in the gas. The figures show the gaseous abundances at 1760 K, the nominal temperature for Pele [3], as a function of pressure. The two vertical dashed lines bracket the pressures calculated for Pele in [4].

Sodium and Potassium: As calculated in [2], the major species of Na and K are the chloride and the monatomic gas (see Fig. 1(a)). The chloride is the most abundant gas for each element at high pressures. As pressure drops, the abundance of the chloride decreases whereas the abundance of the monatomic gas increases. The third most abundant gas for each element is the fluoride. The abundance of NaF is essentially independent of pressure. The abundance of KF increases slightly with decreasing pressure. In the Pele pressure range, NaCl (g) makes up ~81% of total sodium, Na (g) ~16%, and NaF(g) ~3%. Potassium chloride constitutes ~91% of total potassium, K (g) ~5%, and KF (g) ~4%.

Lithium: The most abundant gas of lithium is LiCl (g), followed by LiF (g) (Fig. 1(a)). With decreasing pressure, the abundance of LiCl (g) drops, whereas the abundance of LiF (g) increases, so that below 10^{-6} bars LiF (g) is the more abundant. The third most abundant gas is monatomic Li (g) (Fig. 1(b)), which is 1.5-2.5 orders of magnitude less abundant than the halides. The abundance of monatomic Li (g) decreases with increasing pressure. The fourth most abundant gas is LiBr (g) (Fig. 1(b)), which has an approximately constant abundance from 10^{+1} to 10^{-3} bars. The abundance then decreases more than an order of magnitude between 10^{-3} to 10^{-6} bars. In the Pele pressure range, monatomic Li (g) makes up ~0.2% of the total lithium, LiCl (g) ~66.7%, and LiF (g) ~33%.

Rubidium: The most abundant rubidium gases are shown in Fig. 1(b). RbCl (g) is dominant with an approximately constant abundance. Next in order of abundance are Rb (g) and RbF (g), which have very similar abundances from 10^{0} to 10^{-4} bars. As pressure decreases, however, monatomic Rb (g) becomes more abundant as the halide gases dissociate. With decreasing pressure, Rb^+ (g) also becomes more abundant. At high pressures, RbF (g) is more abundant than monatomic Rb (g). For Pele pressures, RbCl (g) is ~92% of total rubidium, and RbF (g) and monatomic Rb (g) are ~4% each.

Cesium: The most abundant species of cesium are shown in Fig. 1(c). Cesium chloride is the most abundant cesium gas. The next most abundant species varies with pressure. At extremely low pressures of 10^{-5} to 10^{-6} bars, Cs^+ (g) is the second most abundant species. The abundance of Cs^+ (g) decreases steeply with increasing pressure. Above 10^{-5} bars, the second most abundant species is CsF (g), followed by monatomic Cs (g). The positive ion is more abundant than monatomic Cs (g) below ~$10^{-3.5}$ bars. Above this pressure, the abundance of Cs (g) is approximately constant with pressure, until high pressures when the abundance decreases steeply. The abundances of the halide gases are also approximately constant with pressure over wide ranges. In the Pele region, CsCl (g) consumes ~90% of total cesium, CsF (g) ~9% and monatomic Cs (g) ~1%.

Chlorine: Almost all chlorine is consumed by the alkali halides, especially by NaCl (g) and KCl (g). The next most abundant alkali chloride gas is LiCl (g), which is ~2 orders of magnitude less abundant than KCl (g). As pressure decreases, the abundance of monatomic Cl (g) increases markedly as the alkali chlorides, NaCl (g) in particular, dissociate into atoms. Figure 1(a) illustrates the strong correlation between the increasing abundances of Na (g), Cl (g), and the decreasing abundance of NaCl (g). As the abundance of Cl (g) increases, so does the abundance of Cl^- (g), but the ion is over two orders of magnitude less abundant. Inside the Pele range, NaCl (g) consumes ~89% of total chlorine, and KCl (g) consumes ~11%.

Fluorine: As with chlorine, the two most abundant species are NaF (g) and KF (g). Whereas the abundances of all of the alkali chlorides decrease with decreasing pressure, only NaF (g) decreases in abundance. All of the other alkali fluoride monomers (KF, LiF, RbF, LiF) increase slightly at very low pressures. Consequently, monatomic F (g) is much less abundant than monatomic Cl (g). At most pressures the third most abundant fluoride gas is LiF (g). Under Pele pressure conditions, NaF (g) consumes ~88% of total fluorine, KF (g) ~11%, and LiF (g) ~1%.

Bromine: Figure 1(b) shows the most abundant bromine species. For pressures greater than 10^{-4} bars, the major Br gases are NaBr (g) and KBr (g), which have approximately constant abundances with increasing pressure. At lower pressures, the alkali bromide abundances decrease with decreasing pressure. Monatomic bromine increases with decreasing pressure, and levels off. The third most abundant gas for pressures less than ~10^{-3} bars is Br^- (g). Above this pressure, the third most abundant gas is LiBr (g), followed closely by RbBr (g). Inside the Pele pressure region, NaBr (g) consumes ~87% of total bromine, KBr (g) ~12% and monatomic Br (g) ~1%.

Iodine: Figure 1(c) shows the major iodine species. As with chlorine and bromine, the major species at high pressures for iodine is NaI (g), which decreases in abundance as pressures drops. Comparing the different halogens, we can see a trend in the pressures at which the conversion from monatomic gas to sodium halide occurs. The cross-over pressure increases going down the halogen group from Cl to Br to I. The cross-over pressure for iodine is ~10^{-2} bars, which falls in the pressure range calculated for Pele [4]. At this point, the next most abundant gases are KI (g), I^- (g), RbI (g), and LiI (g). The alkali iodides steadily decrease in abundance below this pressure and are fairly constant in abundance above this pressure. The negative ion peaks in abundance at the cross-over point and decreases in abundance to both higher and lower pressure. In the Pele region, NaI (g) consumes ~56% of total iodine, monatomic I (g) ~35%, and KI (g) ~9%.

Summary: We calculate the equilibrium distribution of the minor alkali and halogen elements in a volcanic gas at the temperature and pressure for the Pele vent [3,4]. We predict that the major species of the alkalis at these conditions are the chlorides, fluorides and monatomic gases. The major species of the halides are the sodium and potassium halides and the monatomic gases.

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Figure 1: Major gaseous species of the alkalis and halides at the nominal Pele temperature 1760 K. (a) Na, K, Cl, F, Li, (b)Br, Rb, Li, (c) I, Cs.