

Volatile trace-element transport in high-temperature gases from Kudriavy volcano (Iturup, Kurile Islands, Russia)

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Abstract—Gases, condensates, sublimates and silica-tube deposits were sampled at Kudriavy volcano in 1995 within the temperature range from 160 to 920 °C. The main trace elements transported in the gas phase at 920 °C are Pb, Mo, Bi, Sn, In, As, Se and Te as well as elements partly derived from the wall rock (e.g., Mg, Si, Al). Dominant transporting species as calculated in a heterogeneous closed-system cooling model are chloride complexes (e.g., $\text{CuCl}_{(g)}$, $\text{TiCl}_{4(g)}$, $\text{FeCl}_{2(g)}$). However the Mo-group elements are transported as oxoacids whereas the Sn-group elements and the highly volatile elements of group V and VI of the periodic table are transported dominantly as the sulfide complexes. Bromide and iodide also play an important role in complexing trace elements at temperatures below 600 °C. An open-system equilibrium model where condensed phases are fractionated from the coexisting gas is introduced to simulate the deposition of natural sublimates and is directly compared to a silica-tube sublimation experiment. While the thermochemical models reflect the zonality of sublimates in the tube and some aspects of the sublimate mineral assemblages found in nature, they fail to reproduce the observed temperature distribution. It is concluded that the thermochemical equilibrium models used so far in the investigation of high-temperature volcanic gases do not sufficiently reproduce the volatility of a number of trace elements (e.g., Cu, Zn, Cd and In), because of the lack of consideration of solid solutions in sublimate formation as well as inadequate (and/or unavailable) thermochemical data and the possibility that the underlying equilibrium assumption is only partly correct.

1. INTRODUCTION

Volcanic gases contribute significantly to the general flux of partly hazardous and toxic substances such as heavy-metal volatiles and aerosols to the troposphere (e.g., Nriagu, 1989; Williams et al., 1992). Furthermore, the composition of volcanic gases provides some insight into the chemical output of degassing magmas into hydrothermal convection cells in the earth's crust. This contribution of heat and chemical components to hydrothermal systems plays a fundamental role in the formation of hydrothermal ore deposits.

Despite the importance of elemental transport by volcanic gases, available data on their composition are limited to not more than about a dozen different volcanoes. A compilation of eight condensates is given by Symonds et al. (1992). Additional data are available from Kilauea volcano (Crowe et al., 1987), Satsuma-Iwojima (Hedenquist et al., 1994), Kudriavy (Taran et al., 1995) and Vulcano (Aeolian Islands) (Wahrenberger et al., 2001). An exceptional long-term data set has been obtained from the Showa-Shinzan dome of Usu volcano (Symonds et al., 1996).

The interpretation and theoretical simulation of trace-element transport in the volcanic gas phase is inhibited by a variety of factors. Apart from the practical problems of sampling high-temperature gases on an active volcano, the measured condensate composi-

tion should be accepted as being the result of a variety of processes involving magmatic degassing, gas-rock reactions and in the case of medium- to low-temperature gases, the admixture with hydrothermal fluids.

Equilibrium thermodynamic calculations have been applied to these problems (e.g., Symonds and Reed, 1993; Quisefit et al., 1989) and provide insight into the chemistry of volatile transport and speciation for a variety of elements as well as some estimate of the contribution of reactions of the gas with adjacent wall-rock to the measured condensate composition. Thermodynamic modeling has also been used to predict the deposition of sublimates and wall-rock alteration minerals. Such calculations have been carried out on gases from Mt. St. Helens (Symonds and Reed, 1993), Mt. St. Augustine (Symonds et al., 1992; Getahun et al., 1996), Momotombo (Quisefit et al., 1989) and Merapi (Symonds et al., 1987). However, only the latter two studies draw on consistent data sets where gas compositions and condensates have been obtained nearly simultaneously on the same vent.

The applicability of such computational approaches relies on four basic assumptions comprising the accuracy of the input compositions, the accuracy and completeness of the thermochemical data used in the calculation, the assumption of ideality for all phases considered and, the attainment of equilibrium

among all phases involved. As yet, in view of the above-mentioned difficulties, the results of such calculations have not been demonstrated to be in agreement with respect to actual observations (e.g., Getahun et al., 1996).

The purpose of this paper is to provide further insight into the applicability of such thermochemical equilibrium calculations to simulate trace-element transport in volcanic gases by comparing the calculated results to the actual observed sublimate mineralogy and chemistry. This study provides a basis upon which to evaluate and improve the underlying assumptions. The study presented here discusses the transport, speciation and deposition of trace elements in sublimates from a high-temperature gas of Kudriavy volcano. It draws on a consistent data set of gases and condensates obtained simultaneously and on the same vents in September 1995. Two different computational approaches are used for the transport simula-

tion which involve both closed- and open-system cooling. The results are then compared to the measured elemental distribution and phase composition observed in a sublimation tube.

2. GEOLOGICAL SETTING

Kudriavy volcano (996 m elevation) is situated in Medvezhya caldera in the north of the island of Iturup (Kuriles), approximately 300 km to the northeast of Hokkaido (Figure 1). The eruptive products are basaltic to andesitic (Ehrlich, 1986; Avdeiko et al., 1992) with the last eruption having occurred in May/June 1883. Simkin and Siebert (1994) reported on a phreatic eruption in 1956, but the resulting eruptive products are apparently missing at the summit. Today's activity is restricted to quiescent degassing within the immediate crater area and to one hot spring at the foot of the neighboring Menshoi'Brat basaltic cone.

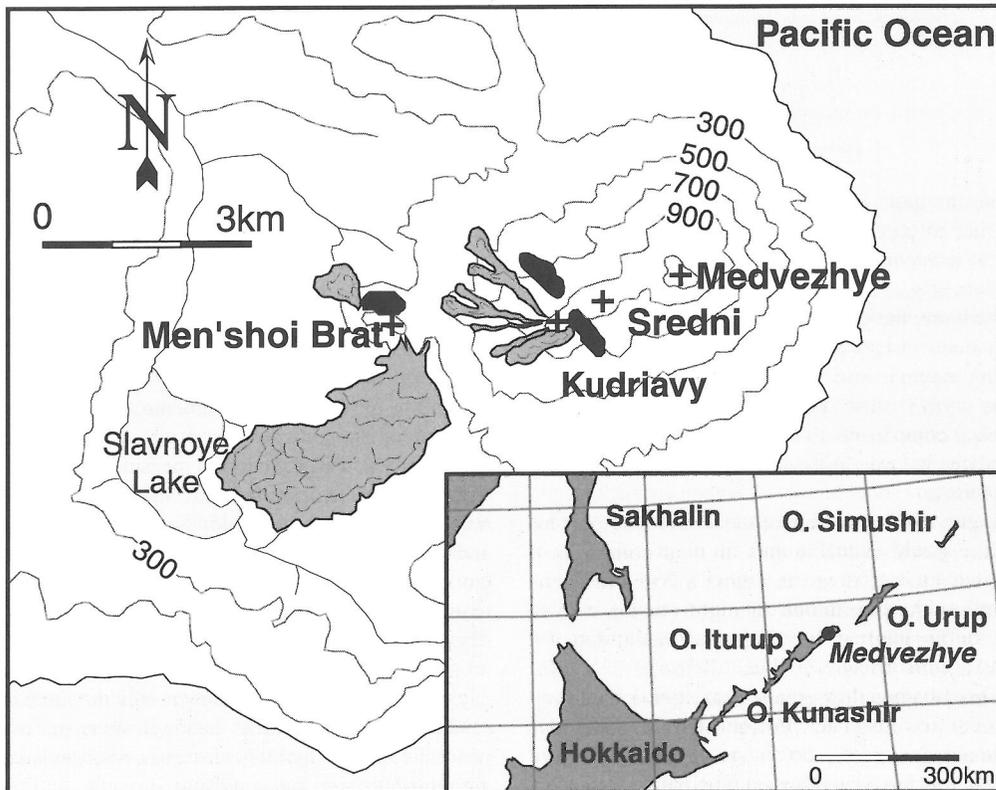


Figure 1: Geographic setting of Kudriavy volcano in Medvezhye caldera. The three major volcanic centers of the caldera Medvezhye, Sredni and Kudriavy lie along a roughly E-W trending line with a younger feature (Men'shoi Brats) to the West. The relative age to these centers is unknown (Erllich, 1986). Contour intervals are in meters above sea level. Dark gray shaded areas show major lava flows, black areas are andesitic domes.

Kudriavy volcano is of particular interest because of the high temperatures (up to 920 °C) and flow rates of up to 80 ms⁻¹ of the fumarole discharges. Active deposition of rhenium sulfide occurs (Korzhinsky et al., 1994) in association with a number of other sublimate phases including indium-containing compounds. Of interest, is the occurrence of native metals and other compounds which deposit in sublimation tubes inserted into the high-temperature fumaroles for various periods of time (Korzhinsky et al., 1995, 1996; Tkachenko et al., 1999; Shmulovich and Churakov, 1998). The chemistry and isotopic composition of gases collected between 1990 and 1992 have been discussed by Taran et al. (1995). Total SO₂ emission from Kudriavy in August/September 1995 was estimated to be 75 ± 50 td⁻¹ on the basis of COSPEC measurements (Williams et al., 1995).

3. ANALYTICAL METHODS

Gases were sampled using quartz-glass tubing and absorption bottles (Giggenbach, 1975) and subsequently analyzed using the methods (with minor modifications) outlined by Giggenbach and Goguel (1981). Coolant for condensate sampling was an ammonium nitrate/water mixture as well as pure water. Condensates were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) after dispersion of the sample in an ultrasonic bath and subsequent dilution with high-purity water.

Sublimation tubes (silica glass) were inserted directly into the same vent from which condensates and gas samples were collected (sample K95/2). The tubes were left in the fumaroles for three days and the temperature gradients were measured along the tube axis (396 to 874 °C). Upon arrival in the laboratory, the tube was cut into 5-cm long sectors. Half of each sector was then subjected to analysis by scanning electron microscopy and energy dispersive X-ray analysis using a JEOL 6400 SEM equipped with a Noran Voyager II EDAX system. The sublimates on the remaining part of the sector were dissolved in warm aqua regia, boiled to near dryness and diluted by 1M HCl (Merck "suprapur"). Blanks were prepared by applying the same procedures to an unused silica-glass tube. The solutions were subsequently analyzed by ICP-MS. The temperature distribution of phase composition and chemistry in the tube was thus obtained.

It should be mentioned that the sublimates in the tube were not deposited in perfect axial symmetry and care was taken to analyze material representative of each sector. In addition, the temperatures on the inside tube wall and along the central axis of the tube varied by 30 – 50 °C, depending on the flow velocity. The profile measured along the tube axis is therefore

taken as representative of the maximum temperature in the tube. The samples were exposed to air after collection and during transport/storage.

The detection limits for the ICP-MS analysis of silica-tube deposits are worse than that for the condensates. Therefore, not all elements analyzed in the condensate were detected in the sublimation tube deposits. This is caused by the higher blank/background concentrations due to low-level contamination by the acid digestion reagents as well as by the necessarily high dilution factors. Naturally deposited solid sublimate phases collected from active, high-temperature fumaroles were identified using SEM-EDAX in combination with a variety of different X-ray diffraction methods.

4. NUMERICAL PROCEDURES

Trace elements in volcanic gases can be transported in a number of different modes such as,

- (i) a true gaseous complex (e.g., SiF₄(g)), (Francis et al., 1996),
- (ii) a liquid or solid aerosol suspended in the gas flow (e.g., CuCl(s)), (Amman et al., 1993; Varekamp et al., 1986) and
- (iii) as particulate matter produced by abrasion and chemical attack or reaction of the wall-rock or sampling device by the gas (Symonds et al., 1992).

To model this multiphase composition, only heterogeneous equilibria involving solid, liquid (melt) and gaseous components were considered throughout this study. The minimum temperature of all calculations was set to 300 °C. The condensation temperature of hydrated sulfuric acid from Kudriavy gases is calculated to be below 250 °C at 1 bar, in agreement with evaluations of Symonds et al. (1992) in the case of St. Augustine gases. All phases are considered to behave ideally and in the case of gaseous components, to mix ideally. Solid solutions have been neglected. Calculations were restricted to a total pressure of 1 bar.

The thermochemical evaluations were carried out using the CSIRO/SGTE Thermodata program package (Turnbull and Wadsley, 1986). The code is based on the Gibbs free energy minimization procedure of Eriksson (1975). Thermodynamic data for the 519 gaseous inorganic and 404 condensed (solid and liquid) species were compiled from the JANAF tables (Chase et al., 1985) and other sources (Stull et al., 1969; Barin and Knacke, 1973; Barin et al., 1977; Knacke et al., 1991; Robie and Hemingway, 1995). Where necessary, heat capacity functions (e.g. Maier-Kelly) have been used to extrapolate beyond the temperature range for which the data were available as was the case for hematite, CaMoO_{4(c)} (powellite) and CaWO_{4(c)} (scheelite).

Solids and liquids are treated merely as one condensed state designated by the suffix, "(c)", throughout this study. Calculations were carried out in 9 to 12 element systems. The common basis for all thermodynamic systems considered comprises the eight elements C, O, H, S, Cl, Br, F and I. Reference states are the pure elements and substances at 298.15 K and 1 bar. All results of this study are limited by the characteristics of the numerical and computational techniques used, bearing in mind that the thermochemical data carry inherent uncertainties and the compilation from various sources may lead to inconsistencies, although care was taken to ensure internal consistency with respect to different reference states by correcting data to the same convention as necessary. The smallest concentration calculated was 10^{-38} mol mol⁻¹ and the terms "stable" and "unstable" used in the following discussions therefore refer to a concentration higher or lower than this number, respectively. Symonds and Reed (1993) have commented on the effect of inconsistencies in the use of the database GASTHERM and estimate the resulting error to be less than the error caused by the uncertainties in ΔG°_f (± 0.5 log units in terms of volatility and ± 50 °C for deposition temperatures in heterogeneous closed system cooling). As the database of this study partly draws on the same data sources as GASTHERM, a similar estimated uncertainty applies to this study.

The aim of thermodynamic equilibrium modeling of the high-temperature Kudriavy gases was to provide insight into the volatile, trace-element speciation as well as to the nature of the condensed phases with which they are in equilibrium. In addition, the thermodynamic calculation of the temperature range of deposition of various condensed phases may also be compared with that observed in silica-glass sublimation tubes. This comparison permits some evaluation of the validity and application of such equilibrium calculations to the understanding of the volatile phase transport and element speciation in volcanic gas systems.

Two approaches were taken which considered both closed and open systems. For the closed-system calculations, the gas was numerically cooled in 25 °C steps and the element composition was the same in each incremental temperature interval, this approach being similar to those of Symonds et al. (1992) and Getahun et al. (1996). In the open-system calculations, the mass of each element transferred to the condensed phases was removed after each incremental temperature step upon cooling from 1000 to 300 °C.

Input to the computation is the composition of gas sample K95/2 (Tables 1 and 2). All calculations consider heterogeneous systems (i.e., the presence of solids, liquids and a gaseous phase) in which the thermodynamic system is limited to twelve ele-

ments. A consequence of the approaches outlined above is that the gas is calculated to cool along an internal gas buffer defined by the $\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{S} + \frac{3}{2}\text{O}_2$ equilibrium. The calculations commenced with a starting f_{O_2} slightly below the nickel-nickel oxide buffer at 1000 °C as constrained by the restored composition of sample K95/2 (see below). Such a cooling behavior will only partly reflect reality because many of the gas-phase reactions are quenched at 350 to 400°C due to slower reaction kinetics (Giggenbach, 1987). In addition, the cooling behavior of a naturally flowing gas would be expected to be dependent on the flow rate (Saito et al., 1989) and to have an oxygen fugacity intermediate between that of the internal gas buffer and the corresponding rock buffer.

It has to be kept in mind that the calculations presented here focus on the simulation of an artificial situation, that is, the cooling of a high-temperature gas in the sublimation tube. Naturally, the cooling and ascending gases undergo processes much more complex than modeled here. Ascending, cooling magmatic gases may mix with fluids derived from the hydrothermal system of the volcano and will therefore change their major elemental composition upon cooling (see Taran et al., 1995; Giggenbach, 1987; Wahrenberger et al., 2001). In the case of Kudriavy, it can be shown that such processes are also affecting the halogenide composition and elemental ratios at temperatures as high as 700 °C. As chloride is one of the most important ligands involved in trace-element transport in the gas phase, changes in its concentration will severely influence the characteristics of the trace-element transport.

5. GAS CHEMISTRY AND INPUT COMPOSITION

Gases collected in 1995 are similar in composition to those of the 1990-1992 period (see Table 1 and Taran et al., 1995), although H₂O is somewhat elevated in the 1995 discharges (94.2 – 98.9 vol% in 1995 versus 92.1 – 98.5 vol%) giving rise to the higher H₂O / CO₂ ratio of 79 at largely stable CO₂ / S_t ratios of around 1 for gases in the temperature range of 680 – 920 °C. The gases also contain small amounts of ammonia, even at temperatures as high as 920 °C, indicating the admixture of a hydrothermal component to all of the gases measured. This interpretation is consistent with the equilibration of the NH₃/N₂ system within the hydrothermal envelope at conditions governed by the coexistence of a vapor with a brine and buffered by the host-rock (represented by a FeO/FeO_{1.5} buffer; Giggenbach, 1987). It is possible that the measured carbon monoxide con-

Table 1: Composition of gases from Kudriavy volcano, Inurup, as sampled between 8/27 and 9/1/1995. All values in $\mu\text{mol/mol}$. Ar and O_2 are below 1 and 2 $\mu\text{mol/mol}$ respectively.

sample No.	t [°C]	H_2O	CO_2	S_t	HCl	HF	NH_3	He	H_2	N_2	CH_4	CO
K95-2	920	942930.141	16765.084	20309.402	1712.085	744.678	2.929	228.22	5677.386	11077.226	b.d.	561.851
K95-3	710	970898.867	10114.12	12865.856	1756.147	592.847	1.605	1.082	3245.972	506.883	b.d.	15.769
K95-4	680	978110.905	10315.327	6463.196	1364.894	538.76	1.963	1.758	2545.095	640.814	b.d.	15.735
K95-5	619.5	974243.571	10645.083	11721.122	467.925	356.893	1.404	1.483	2006.238	541.773	b.d.	12.989
K95-6	470	984030.032	8297.256	3877.897	3113.444	239.345	0.702	0.182	269.822	169.429	b.d.	1.087
K95-7	190	989821.357	5659.778	3965.457	308.955	16.524	0.54	0.048	21.344	201.185	3.576	b.d.
K95-8	160	986575.935	8998.649	3996.99	206.785	12.439	0.704	0.052	20.248	183.843	3.43	b.d.
K95-9	300	987205.185	6237.959	3935.118	2193.711	43.276	1.292	0.119	199.58	182.83	0.299	0.17
K95-10	620	970152.088	14566.745	10402.265	538.143	443.03	0.912	1.533	3233.463	646.013	b.d.	13.781

Table 2: Composition of condensates from Kudriavyy volcano, Iturup, as sampled between 8/27 and 9/1/1995. b.d. = below detection limit. Elements measured but below detection limit (<0.5-1 ppb) in all condensates are: Li, Be, Sc, Co, Ge, Y, Nb, Pd, Ag, La-Lu, Ta, Re, Os, Ir, Pt, Au, Th, U. All values in ppb with the background/blank values subtracted. Rh and Hg were not measured.

t_{gas} [°C]	920	710	680	470	300	160
sample	K95/2	K95/3	K95/4	K95/6	K95/9	K95/8
	[ng g ⁻¹]					
B	1.05E+04	2.01E+04	1.77E+04	1.19E+04	8.73E+03	1.61E+04
Na	1.32E+04	1.08E+03	3.03E+03	n.a.	n.a.	n.a.
Mg	1.19E+03	4.13E+02	3.34E+02	n.a.	4.04E+02	9.12E+01
Al	8.97E+02	1.04E+03	6.65E+02	6.61E+02	8.41E+03	1.78E+02
Si	3.08E+03	4.66E+03	3.80E+03	4.71E+03	4.70E+02	b.d.
K	1.32E+04	n.a.	n.a.	n.a.	n.a.	n.a.
Ca	1.13E+03	n.a.	1.66E+03	n.a.	n.a.	b.d.
Ti	3.45E+02	1.23E+02	b.d.	1.15E+02	2.19E+04	b.d.
V	1.40E+01	4.18E+00	3.69E+00	3.28E+00	1.99E+01	b.d.
Cr	1.82E+02	2.39E+02	1.03E+02	1.27E+02	1.42E+02	2.83E+01
Mn	3.50E+01	7.31E+00	4.60E+00	1.95E+00	2.68E+04	3.47E+00
Fe	4.78E+03	6.01E+02	3.65E+01	b.d.	1.77E+03	3.18E+02
Ni	1.07E+02	8.44E+01	4.19E+02	4.55E+01	4.78E+01	7.35E+01
Cu	5.44E+01	3.33E+01	2.05E+01	1.16E+01	3.11E+01	3.40E+01
Zn	1.28E+03	6.40E+02	5.01E+02	1.15E+02	1.26E+02	3.33E+02
Ga	2.81E+01	1.88E+01	9.46E+00	5.56E+00	4.79E+00	b.d.
As	1.86E+03	2.55E+03	2.40E+03	2.32E+03	1.68E+02	2.64E+02
Se	b.d.	b.d.	7.00E+02	b.d.	b.d.	3.38E+01
Br	6.85E+03	1.04E+04	4.54E+03	4.82E+03	2.92E+03	5.78E+02
Rb	6.21E+01	5.33E+01	2.30E+01	2.66E+00	1.52E+00	b.d.
Sr	b.d.	b.d.	b.d.	4.63E+00	5.07E+01	b.d.
Zr	4.33E+01	2.71E+01	1.59E+01	1.03E+01	2.71E+00	b.d.
Mo	2.04E+02	1.27E+02	1.07E+01	3.04E+00	5.61E-01	1.13E+00
Cd	5.54E+01	b.d.	3.95E+01	1.20E+00	b.d.	b.d.
In	4.37E+01	3.89E+01	4.69E+01	1.08E+01	b.d.	b.d.
Sn	2.87E+02	1.97E+02	4.20E+02	7.53E+01	3.26E+01	9.97E+00
Sb	1.45E+01	2.21E+01	4.06E+01	b.d.	2.58E+00	2.58E+00
Te	2.77E+04	1.96E+01	1.60E+01	2.23E+01	4.94E+00	1.04E+00
I	2.00E+03	3.07E+03	1.72E+03	1.63E+03	1.89E+03	4.69E+02
Cs	9.36E+00	1.39E+01	4.14E+01	2.74E+00	b.d.	b.d.
Ba	8.50E+02	8.92E+02	4.14E+02	1.84E+02	8.09E+01	3.29E+01
W	1.82E+01	1.21E+01	9.80E+00	1.25E+01	6.69E+00	1.10E+01
Tl	7.72E+01	5.46E+01	3.74E+01	2.73E+01	1.43E+01	b.d.
Pb	7.91E+02	6.68E+02	4.70E+02	5.61E+02	1.09E+02	1.38E+01
Bi	6.45E+01	7.29E+01	3.18E+01	6.72E+01	3.38E+00	2.69E+00

tent is underestimated due to slow reaction with NaOH (to form formate) in the sampling bottles during storage as noted previously by Giggenbach and Matsuo (1991).

The data presented in this study (Table 2) indicate that the majority of trace elements are somewhat less concentrated than measured by Taran et al. (1995) in the 1990-1992 period. Of interest is the much higher Br content of the gases measured in this study (approx. 6.85 ppm as compared to 0.75 ppm at 920 – 940°C as reported by Taran et al., 1995). Further significant differences are the lower Si, Al and Zr contents obtained

in the 1995 samples. Elements such as Bi, As, B, Tl, Pb, Sn, Mo, Cd and W are highly enriched in comparison to the average wall rock as reported by Avdeiko et al. (1992) (i.e., weight-based, Mg-normalized enrichment factors are $EF_1 > 3$). Of low ($EF_1 < 3$) or negative EF_1 are: Fe, Ti, V, Mn, Si and Al.

To obtain an appropriate input composition for computational modeling, gas sample K95/2 was restored to its last equilibrium composition following the methods outlined by Symonds et al. (1994). The restoration procedure is based on independent f_{O_2} measurements obtained by solid-state electrode

where f_{O_2} was found to vary with temperature according to $\log f_{O_2} = -32.64 + 0.0174 T[K]$ (Rosen et al., 1993). To restore sample K95/2, the conversion of 6 mmol H_2O to H_2 and of 0.25 mmol CO to CO_2 was necessary to match all "correspondence temperatures" (CT's) within ± 10 °C (see Gerlach and Casadevall, 1986). The last equilibrium temperature is calculated to 984 °C at a $\log f_{O_2} = -10.989$. The presence of N_2 , NH_3 and small amounts of Ar (i.e. $< 2 \mu\text{mol}^{-1}$) in the gas was neglected. As discussed by Taran et al. (1995), Kudriavy exhalations as well as many other volcanic gases do contain "excess" nitrogen. The resulting input composition was obtained by combining the restored gas and condensate analyses of sample K95/2 and this is presented in Table 3.

6. RESULTS AND DISCUSSION

6.1. Silica-Tube Sublimate Mineralogy

Data on the composition of the sublimate phases and their elemental distribution in the silica tube as a function of temperature are given in Figure 2. A number of important rock-forming silicate minerals were found to have sublimed in the higher-temperature regime (i.e., aegerine, $NaFeSi_2O_6$, ferrosilite/enstatite, $(Fe,Mg)SiO_3$; magnetite, Fe_3O_4 and SiO_2 ; no feldspars were detected). Chloride and sulfide phases were the dominant phases deposited over a wide temperature range. The chloride sublimate phase, $(Na,K)Cl$ contained traces of F, Br and I. Rhenium was detected as a trace element in FeS_2 and in solid solution with MoS_2 but was not detected as a discrete rhenium compound as noted in the natural fumarole sublimate deposits. The rhenium concentration in the condensate collected from the same fumarole into which the sublimation tube had been inserted was below detection limit. A number of phases whose exact stoichiometry could not be determined were also observed. Native iron was detected in a sylvite (KCl) matrix between 770 and 874 °C. Other native elements have been reported in sublimation tube experiments at Kudriavy.

6.2. Natural Fumarole Sublimates

The sublimates which have deposited naturally around various fumaroles at Kudriavy (Table 4) are also distinctly zoned with respect to temperature and distance from the discharging vent. The silicate phases were deposited at the highest temperatures, the oxides and sulfides at lower temperatures and the halides and sulfates at intermediate temperatures. The zonation reflects the changing volatility of trace elements in response to changes in gas

chemistry, temperature and air admixture. The extent and significance of the air admixture is as yet unknown.

A number of mineral groupings were recognized in the Kudriavy fumarole sublimates and are as follows:

Pb-Bi sulfides: Cannizzarite ($Pb_4Bi_6S_{13}$), and cosalite ($Pb_2Bi_2S_5$), as well as several other phases with varying (Pb + Bi) / S ratios were identified. These Pb-Bi sulfides concentrate In, Sn, and Zn

Table 3: Composition of sample K95/2 as an input to thermodynamic modeling. All data in mol%. Main composition restored according to Symonds et al. (1994). Below detection limits (< 0.5 -1 ppb) are: Li, Be, Sc, Ge, Y, Nb, Pd, Ag, lanthanides (Ce-Lu), Hf, Ta, Re, Os, Ir, Pt and Au.

T_{eq} [°C]	984		
$\log f_{O_2}$ [bar]	-10.9889		
H_2O	94.792		
H_2	1.165		
CO_2	1.720		
CO	0.033		
CH_4	0.815E-11		
SO_2	1.834		
H_2S	0.192		
S_2	0.012		
COS	0.237E-03		
HCl	0.173		
HF	0.075		
HBr	0.154E-03		
B	1.72E-03	As	4.39E-05
Na	1.01E-03	Rb	1.29E-06
Mg	8.70E-05	Zr	8.40E-07
Al	5.89E-05	Mo	3.76E-06
Si	1.94E-04	Cd	8.73E-07
K	5.98E-04	In	6.75E-07
Ca	5.00E-05	Sn	4.29E-06
Ti	1.28E-05	Sb	2.12E-07
V	3.96E-07	Te	3.84E-04
Cr	6.20E-06	I	2.79E-05
Mn	1.12E-06	Cs	1.25E-07
Fe	1.52E-04	Ba	1.10E-05
Co	4.30E-08	La	7.15E-09
Ni	3.22E-06	W	1.75E-07
Cu	1.52E-06	Tl	6.69E-07
Zn	3.46E-05	Pb	6.76E-06
Ga	7.13E-07	Bi	5.46E-07

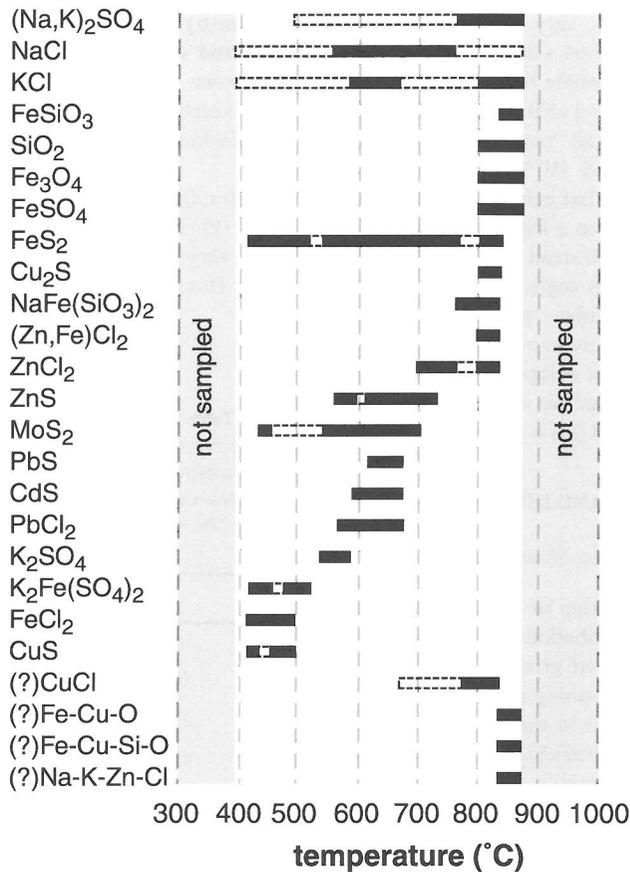


Figure 2: Phases identified in the sublimation tube by semi-quantitative SEM-EDAX spectra. Filled boxes indicate more than five positively identified spectra per 5-cm tube sector and dashed boxes between three and five phases. Question marks designate phases of uncertain stoichiometry. See text for further discussion.

in significant amounts (1 – 10 wt%) and minor Fe and Cu (≈ 1 wt%). In some cases, this incorporation leads to phases with chemistries not attributable to known mineral phases. For example, the In content of Pb-Bi sulfides reaches 13 wt%.

Cd-Zn sulfides: Both end members (i.e., greenockite and wurtzite) were identified. However, solid solutions of intermediate chemistry are more prevalent. Minor amounts up to 1 wt% of Fe, Cu and In apparently substitute for Cd and Zn.

Mo minerals: The Mo-containing minerals detected were powellite at higher temperatures with molybdenite at intermediate temperatures and ilsemannite ($\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$), forming at the lowest temperatures; tugarinovite (MoO_2) and molybdate (MoO_3) were also present as reported previously by Bykova et al. (1995); a rhenium

sulfide mineral also occurs at temperatures below 650 °C (see also Korzhinsky et al., 1994) and apparently, a solid solution occurs between ReS_n and MoS_2 where n varies widely with an average value of ~ 1.5 to 2.0.

Silicates: Mg- and Ca-dominated silicates of the olivine, garnet and (clin-)pyroxene group minerals were detected in the highest temperature zones (i.e., > 750 °C) of the Kudriavyy fumarolic field.

Chlorides: Na, Ca and K chlorides have also been identified; a complete solid solution series, $(\text{Na,K})\text{Cl}$ has been detected.

These sublimate minerals can be assigned to different temperature assemblages, such as olivine-pyroxenes-magnetite-hematite; powellite-anhydrite-molybdenite ReS_n -garnet (andradite); greenockite-wurtzite-cos-

alite-cannizzarite and halite-sylvite-hematite. Data on mineral phases presented here confirm and supplement the database already published by Bykova et al. (1995) and Korzhinsky et al. (1996).

6.3. Closed-System Cooling

Closed-system calculations were used to provide insight into the dominant transporting species and investigate the possible coexistence of solid and liquid (i.e., condensed phases). Specifically, the saturation of the gas (with respect to condensed compounds) at near magmatic temperature has to be discussed in the light of possible contamination of the condensate by wall-rock particles. A comparison of predicted solid/liquid phases with the observed sublimate mineralogy provides some test of the validity of the numerical simulation. In total, 27 trace elements were considered in the closed-system equilibrium calculations. All condensed (solid/liquid) species calculated to be stable between 300 and 1000 °C are given in Figure 5 and are discussed in detail below. In the case of gaseous species, representative results for a number of elements are given in Figures 3 and 4.

The results of the closed-system equilibrium calculations can be summarized as follows. Systematic trends in the affinity of trace elements to certain ligands in the gas phase are evident. There is a change from fluoride-dominated, major volatile species to chloride/bromide and in extreme cases iodide complexes with increasing atomic number within the same group, as would be expected. For example, B is mainly volatile as $B(OH)_3(g)$, Al as $AlOF_2(g)$ and $NaAlF_4(g)$, Ga as $GaCl(g)$ and $GaCl_3(g)$ and Tl as $TlCl(g)$. At higher temperatures, sulfur (as sulfide) becomes more important as a ligand with first-row transition elements, while O, OH and F decrease in importance relative to chloride as the major transporting ligand, reflecting the well known Irving-Williams stability order. The same order was reported for Mt. St. Helens gas chemistry (Symonds and Reed, 1993). In addition, bromide and iodide complexes become more important in comparison to chloride species with decreasing temperature. The calculations also show that complexes with simple carbonyl and halocarbon ligands are also stable although they are present at low concentrations; for example, at 1000 °C and 1 bar, $\log f = -28.8$ for $Ni(CO)_4$, $\log f = -34.8$ for $SiH_3(CCl_3)(g)$ and $\log f = -29.3$ for $SiH_3(CF_3)(g)$.

Therefore, the nature of trace-element transport in Kudriavy gases is calculated to be very similar to those of Mt. St. Helens and Merapi (Symonds and Reed, 1993; Symonds et al., 1987). Some differences to St. Augustine (Symonds et al., 1992) are observed

by comparing the temperature range between 860 and 1000 °C. For example, $Fe(OH)_2(g)$ and $Ni(OH)_2(g)$ are important species in Kudriavy and Mt. St. Helens gases but at Mt. St. Augustine, $FeCl_2(g)$ and $NiCl_2(g)$ dominate by three orders of magnitude over the respective hydroxide species. $PbCl_2(g)$ as well as $PbCl_4(g)$ dominate strongly over $PbS(g)$ at Augustine which is the opposite to Kudriavy. $MoOCl_2(g)$ is the most abundant gaseous Mo-containing species at Augustine below 940 °C, whereas at Kudriavy, this is only true below 375 °C. These differences possibly arise from the higher chloride concentrations (up to 6 vol%) at St. Augustine in comparison to Kudriavy (0.3 vol%, see Table 1). We note also the similar stabilities of volatile species in Kudriavy gases calculated by Churakov et al. (2000) with our calculations with minor discrepancies (e.g., copper) arising from differences in the thermodynamic data bases employed.

Forty three condensed phases are calculated to be in equilibrium with Kudriavy gases at various temperatures between 300 to 1000 °C, some of which match the natural sublimation assemblage or the sublimation tube observations as given in Figure 5. However, a number of significant discrepancies between calculated assemblages and those occurring naturally were observed. Iron is calculated to occur only in magnetite and pyrite but occurs both in natural sublimates and in the sublimation tubes, predominantly in silicates and oxide compounds such as olivine ($(Mg,Fe)SiO_4$), augitic-pyroxene ($(Ca,Na)(Mg,Fe,Al)Si_2O_6$), andradite ($Ca_3Fe_2Si_3O_{12}$), hematite (Fe_2O_3), magnetite (Fe_3O_4). Pyrite (FeS_2) and rozenite ($FeSO_4 \cdot 4H_2O$) are found in the natural sublimates. However, they are of limited importance in comparison to the other phases. The thermochemical database comprises data for the pure end members only. In the closed-system calculations, lead is predicted to remain in the gas phase at all temperatures considered. In contrast, lead is found in phases such as cannizzarite ($Pb_4Bi_6S_{13}$), cosalite ($Pb_2Bi_2S_5$) and other Pb-Bi sulfides both in nature and in the sublimation tube. Qualitatively, the actual sublimate phases are correctly predicted by the equilibrium thermodynamic calculations. However, the latter fail to predict the specific paragenesis (e.g., the natural coexistence of powellite and molybdenite with garnet (andradite), as well as the correct temperature ranges of deposition in the sublimation tube (e.g., the deposition of alkali sulfates above 750 °C; the stability range of chalcocite or the dominance of NaCl above 600 °C).

Symonds and Reed (1993) observed the same problem with lead volatility in the case of gases from Mt. St. Helens and invoked inaccuracies in the thermochemical data for the gaseous species to account for such discrepancies. In the case of cannizzarite and

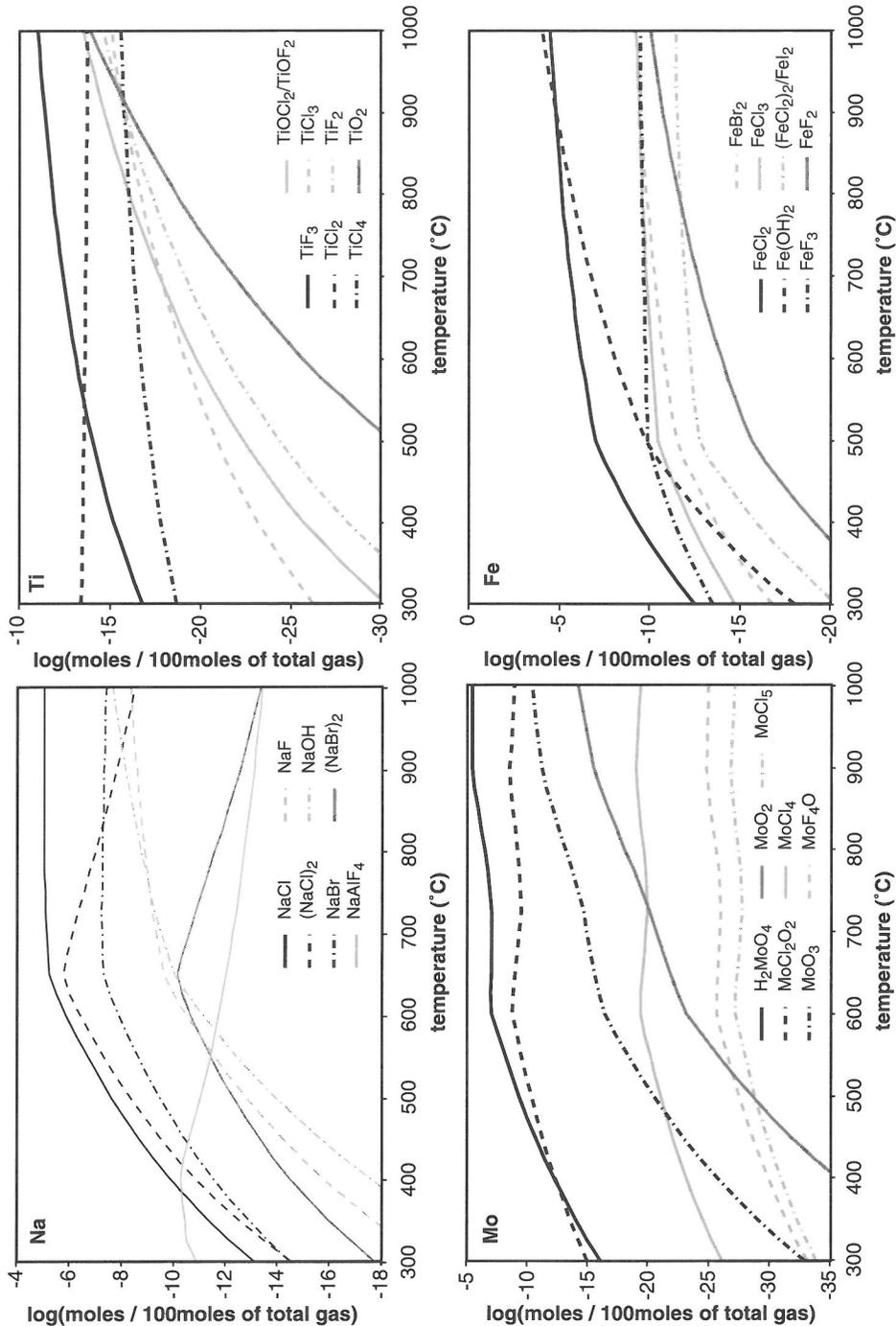


Figure 3: Distribution of (a) sodium (Na, Group IA), (b) titanium (Ti, group IVA), (c) molybdenum (Mo, group VIA) and (d) iron (Fe, group VIIIA) amongst its gaseous species at closed-system equilibrium cooling conditions for the systems: X-Na-Al-Si, X-Ti, X-Ca-Mo-Si and X-Fe-Mg-Si. For solids stable in equilibrium with the gas phase see Fig. 5. Not shown are species which are calculated to be stable but at concentrations below 10^{-25} mol/mol at all temperatures considered, i.e., $(\text{TiCl}_3)_2(\text{g})$, $\text{TiI}_4(\text{g})$, $\text{Ti}(\text{g})$, $\text{TiI}(\text{g})$, $\text{TiBr}(\text{g})$, $\text{TiI}_3(\text{g})$, $\text{TiCl}(\text{g})$, $\text{TiI}_2(\text{g})$, $\text{TiBr}_2(\text{g})$, and $\text{TiS}(\text{g})$; $\text{MoI}_3(\text{g})$, $\text{Mo}(\text{g})$, $\text{MoF}(\text{g})$, $\text{MoBr}(\text{g})$, $\text{MoI}(\text{g})$, $\text{MoO}(\text{g})$, $\text{MoF}_2(\text{g})$, $\text{MoBr}_2(\text{g})$, $\text{MoF}_4(\text{g})$, and $\text{MoBr}_3(\text{g})$; $(\text{FeI}_2)(\text{g})$.

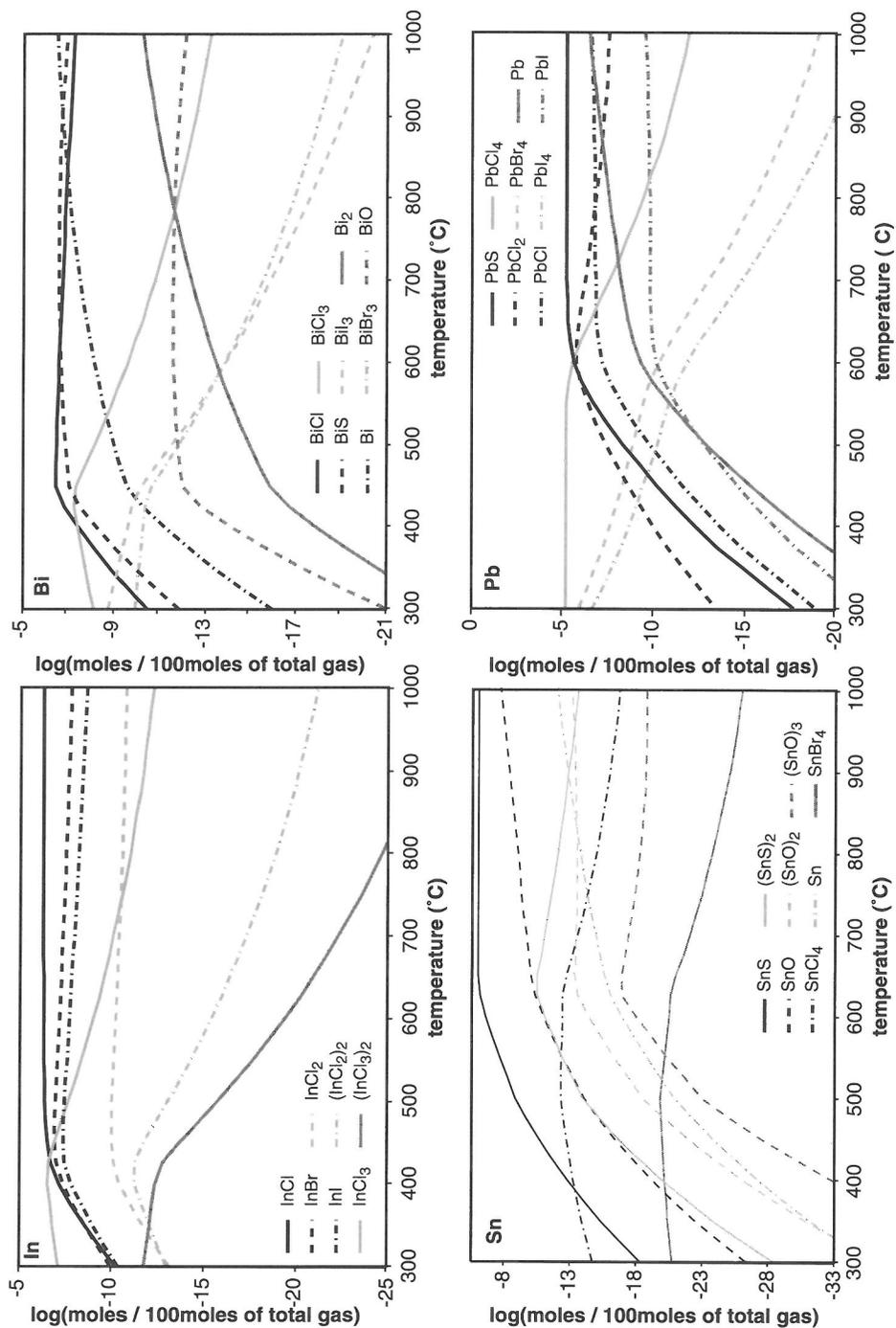


Figure 4: Distribution of (a) indium (In, group IIIB), (b) bismuth (Bi, group VB), (c) tin (Sn, group IVA) and (d) lead (Pb, group IVB) amongst its gaseous species at closed-system equilibrium cooling conditions (for stable solids see Fig. 5). For the systems X-In, X-Bi, X-Sn and X-Pb-Si, all stable gaseous species considered in the calculations are shown.

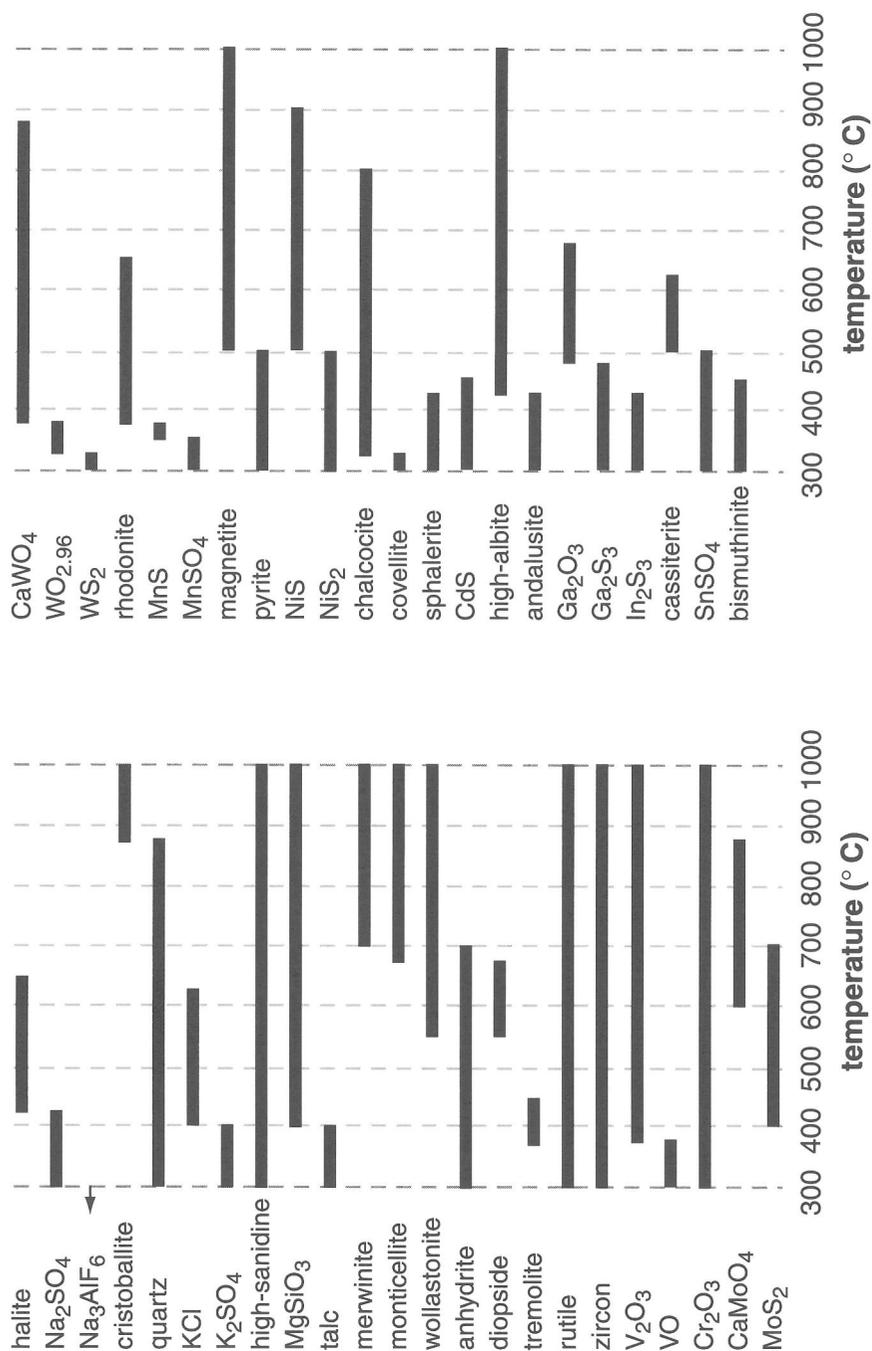


Figure 5: Condensed phases calculated to be stable within the temperature range and the elemental systems considered in the text. The condensed phases of calcium molybdate and tungstate ($\text{CaMoO}_{4(c)}$ / $\text{CaWO}_{4(c)}$) as well as magnetite ($\text{Fe}_3\text{O}_{4(c)}$) are calculated to be stable on the basis of an extrapolated C_p° function. See text for further discussion.

cosalite, adequate thermodynamic data do not exist and their sublimation could not be considered in the calculations. Alternatively, one could assume that the content of Pb in the condensate was underestimated. Korzhinsky et al. (1996) have shown that siderophile elements are precipitated in the sulfur-containing particles forming in the condensate during sampling and that current analytical techniques do not fully account for the multiphase composition of the condensate. Consequently, the concentrations of elements such as Ag and Pb might be underestimated by an order of magnitude. In the case of sample K95/2, this explanation seems to be insufficient. $\text{PbS}_{(c)}$ is only predicted to be stable under the assumption of an underestimation of Pb by at least two orders of magnitude. The failure of the model to predict Fe-pyroxene partly arises because solid solutions are not considered in the calculations. Pure ferrosilite is stable only at pressures above 10 kbars (at 600 °C; Lindsley, 1980). Consequently, the assemblage fayalite + quartz would be expected as a result of these calculations. One of the most important results of the closed-system calculations is the saturation of the gas with respect to major rock-forming minerals at 1000 °C. These phases are: enstatite (MgSiO_3), rutile (TiO_2), zircon (ZrSiO_4), V_2O_3 , Cr_2O_3 , magnetite (Fe_3O_4), high-albite ($\text{NaAlSi}_3\text{O}_8$), monticellite (CaMgSiO_4), wollastonite (CaSiO_3) and merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$).

No thermochemical data are available for silicates of V, Ti and Cr. These elements are thought to be distributed amongst Fe-Ti oxides and pyroxenitic phases. Similar results have been obtained for St. Augustine, Merapi and Mt. St. Helens gases (Symonds and Reed, 1983; Symonds et al., 1992, 1987). However, it should be noted for example, that at Izalco volcano (Costa Rica), a variety of different vanadium oxides have been observed as sublimation products (e.g., Stoiber and Rose, 1974). Theoretically, several interpretations could account for the calculated supersaturation of the gas phase with respect to rock-forming minerals such as the presence of the phases cited above as aerosols in the gas stream, non-equilibrium behavior (i.e., supersaturation of the gas because of kinetic effects), abrasion, entrainment and dissolution of wall-rock particles in the condensates and incorrect or missing thermochemical data on gaseous and condensed species.

In the case of gases from St. Augustine, Symonds et al. (1992) favored wall-rock contamination as the most plausible explanation for the calculated supersaturation. The basis for this conclusion is the low and similar enrichment factors for wall-rock elements and the absence of silicate phases in the sublimation tubes. However, in the case of Kudriavy, olivine, pyroxenes, iron oxides and SiO_2 are found as natural fu-

marole sublimates as well as in the sublimation tube. A much stronger argument in favor of wall-rock contamination rather than the use of unreliable and frequently misleading enrichment factors is the fact that the gas is calculated to be saturated with respect to silicate minerals (i.e., SiO_2 , Al_2SiO_5) at temperatures above 1300 °C, surpassing a reasonable temperature of the host melt. Therefore, the measured elements are thought to be derived to some extent from wall-rock contamination. It is difficult to judge the extent of this contamination. Symonds et al. (1992) have considered this problem by computationally reacting wall-rock with the measured gas at fixed temperature and pressure.

Generally, the assumption of closed-system cooling seems to oversimplify various aspects of the highly dynamic systems investigated. The observation that solids form not only in the cooler peripheral parts of the vents where processes of air admixture occur (e.g., Getahun et al., 1996) but also on the actual vent walls in contact with the moving gas stream, indicates that the system is open with respect to the retrieval of certain trace elements.

6.4. Open-System Cooling

Twenty elements were considered in open-system calculations of which twelve can be directly compared to the elemental distribution data from the silica tube. The results are presented in Figures 6 to 8 and are also directly compared to sublimation tube mineralogy as outlined above and presented in Figure 2. As the results cannot be compared on a quantitative basis, the amount of each phase has been normalized to its maximum abundance. Note that each condensed phase is considered and scaled separately and therefore, additional features of the results such as the calculated dominance of $\text{NaCl}_{(c)}$ over $\text{Na}_2\text{SO}_{4(c)}$ are not represented in the graphs. In the discussion below, the elemental systems (where $\text{X}=\text{C-S-O-H-S-Cl-Br-F-I}$) used for the calculation are discussed separately. The systems X-Na-Al-Si; X-K-Al-Si(Na); X-Ca-Al-Si(Na) and X-Ca-Mg-Fe-Si (Figures 6a-c) are summarized as follows:

feldspars: anorthite, high-sanidine and high-albite are calculated to be stable in very narrow temperature intervals of 1000 – 960 °C and 1000 – 840 °C; all feldspar condensed phases decrease in abundance by at least seven orders of magnitude in the first 20 °C cooling step.

orthosilicates: $\text{CaSiO}_{3(c)}$ (wollastonite), $\text{MgSiO}_{3(c)}$ (enstatite), $\text{Ca}_3\text{MgSi}_2\text{O}_{8(c)}$ (merwinite) are all only stable at 1000 °C; $\text{CaMgSiO}_{4(c)}$ (monticellite) is stable above 800 °C and $\text{Mg}_2\text{SiO}_{4(c)}$ is

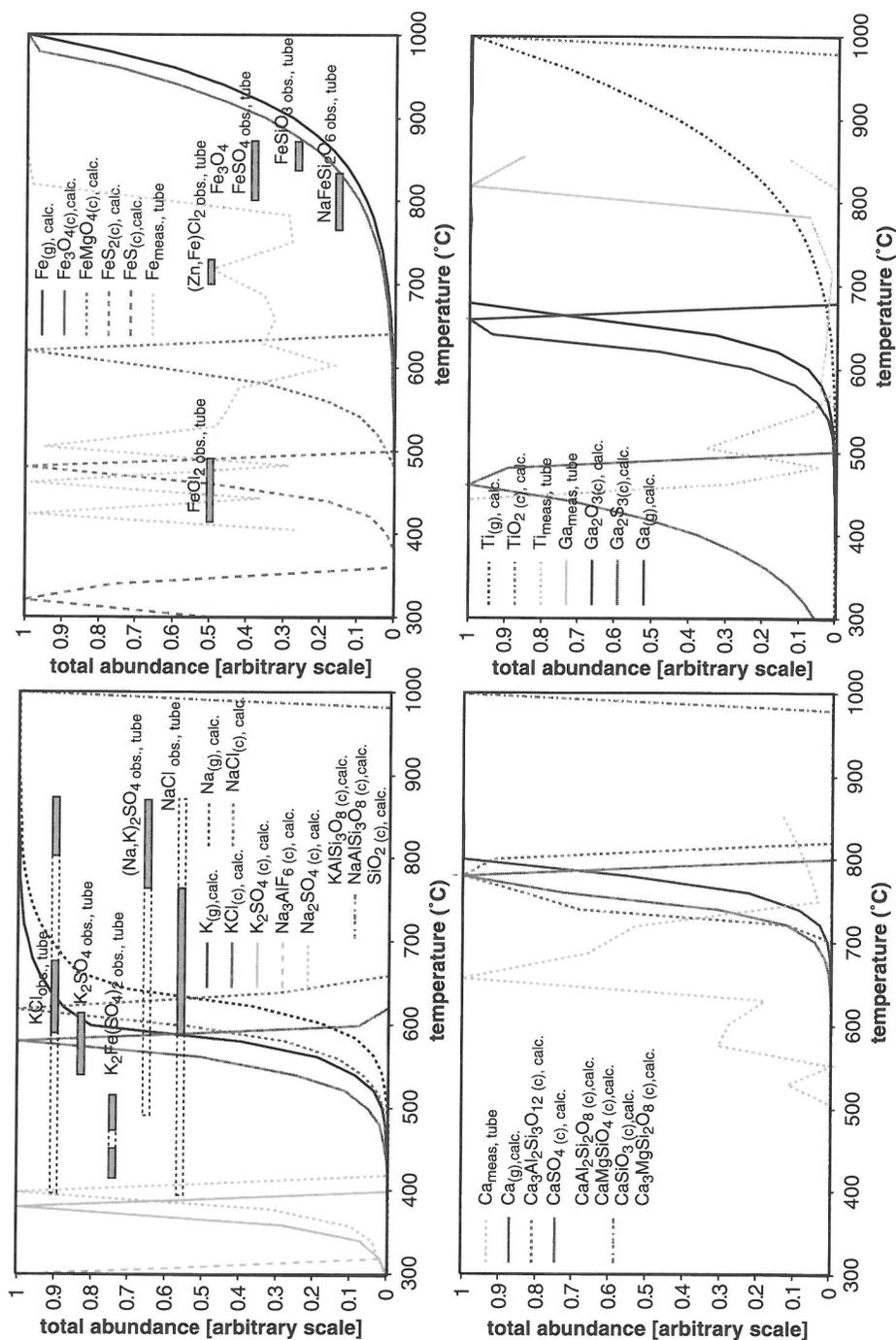


Figure 6: (a) Na/K, (b) Fe, (c) Ca and (d) Ti/Ga phase behavior in open-system calculations as compared to sublimation tube mineralogy. The boxes indicate the presence of solid phases positively identified in the sublimation tubes. Note that $Fe_3O_{4(c)}$ is calculated to predominate over $FeS_{2(c)}$ by two orders of magnitude whereas the sublimation tube chemistry indicates similar strong deposition of iron between 400 and 500 °C as is detected at 800 °C. Titanium is found as a minor constituent in salts of the sublimation tube. See text for further discussion.

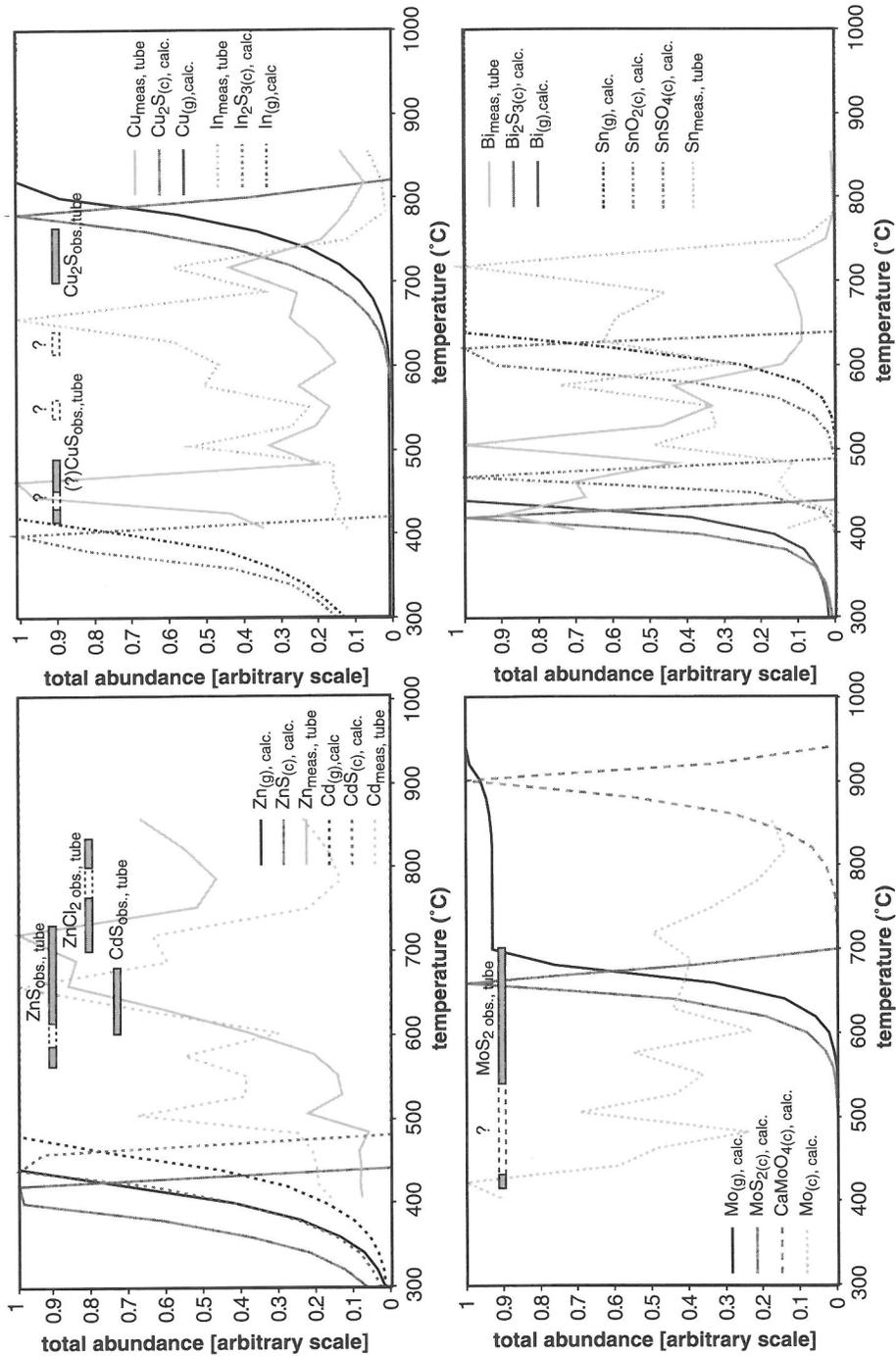


Figure 7: (a) Zn/Cd, (b) Cu/In, (c) Mo and (d) Bi/Sn phase behavior in open-system calculation as compared to sublimation tube chemistry and mineralogy. Indium is found as a constituent of Zn-Cd phases. Tin is found as a constituent of Zn-Cd and Pb-Bi phases in the sublimation tube. Bismuth is found as a constituent in Pb-phases in the sublimation tube.

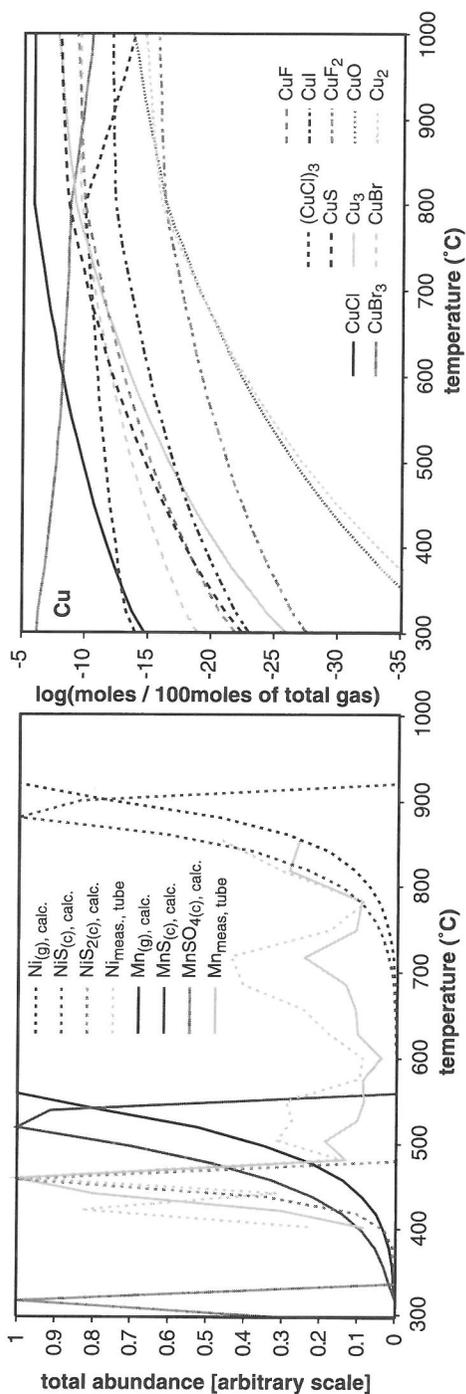


Figure 8: (a) Mn/Ni phase behavior in open-system calculations as compared to sublimation tube chemistry. Again, as discussed in the case of iron (Fig. 6) NiS_(c) is calculated to predominate over NiS_{2(c)} which is deposited at lower temperatures whereas the sublimation tube chemistry indicates the maximum deposition at 400 to 500 °C. (b) Distribution of copper (Cu, group IB) amongst its gaseous species at closed-system equilibrium cooling conditions (for stable solids see Fig. 5) in the system X-Cu. All stable gaseous species considered are shown. Note that Cu is predicted to be transported as the CuBr_{3(g)} species below 600 °C. See text and Fig. 7 for further discussion.

calculated to be stable between 980 and 800 °C; grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12(c)}$), becomes stable upon cooling to 820 – 700 °C; $\text{Al}_2\text{SiO}_5(c)$ (andalusite) is stable between 960 and 920 °C.

chlorides and sulfates: $\text{NaCl}(c)$ (halite) and $\text{KCl}(c)$ (sylvite) are stable between 640 – 460 °C and 600 – 460 °C respectively, $\text{Na}_2\text{SO}_4(c)$ (thenardite) and $\text{K}_2\text{SO}_4(c)$ (arcanite) between 420 – 300 °C and 380 – 300 °C respectively; $\text{Na}_3\text{AlF}_6(c)$ (cryolite) occurs only at 300 °C. $\text{CaSO}_4(c)$ (anhydrite) has a wide stability ranging from 780 to 300 °C. However, this phase decreases in abundance by four orders of magnitude above 600 °C.

sulfides: Pyrite ($\text{FeS}_{2(c)}$) and troilite ($\text{FeS}(c)$) are stable from 560 – 400 °C and from 340 to 300 °C, respectively.

oxides: Magnetite ($\text{Fe}_3\text{O}_4(c)$) decreases from its maximum abundance at 1000 °C and is stable within a 500 °C interval (i.e., 1000 – 500 °C) with the amount being deposited decreasing by two orders of magnitude in the first 200 °C; $\text{MgFe}_2\text{O}_4(c)$ (magnesioferrite) is stable between 620 and 480 °C and predominates over $\text{MgO}(c)$; it is the only phase that is stable over two temperature intervals, one from 840 to 640 °C and a second one from 440 to 300 °C (having an abundance of four orders of magnitude lower than the first one); cristobalite, $\text{SiO}_2(c)$, shows the same features as the orthosilicates: it is only stable at 1000 °C; corundum, $\text{Al}_2\text{O}_3(c)$, is stable over a wide temperature interval ranging from 940 to 300 °C while only decreasing in abundance by three orders of magnitude.

Other systems

X-Ti (Figure 6d): $\text{TiO}_2(c)$ (rutile) is theoretically stable from 1000 to 440 °C; its abundance changes by seven orders of magnitude in the first 20 °C.

X-Zr-Si, -Cr and -V (not shown): The trends are similar to those for Ti, in contrast to Cr and Zr where only one stable phase exists at 1000 °C (i.e., $\text{Cr}_2\text{O}_3(c)$ and $\text{ZrSiO}_4(c)$ (zircon)), V has two stable phases: $\text{V}_2\text{O}_3(c)$ at 1000 °C and $\text{VO}_2(c)$ at temperatures below 340 °C.

X-Zn, -Cd and -In (Figures 7a,b): $\text{ZnS}(c)$ (sphalerite), $\text{CdS}(c)$ and $\text{In}_2\text{S}_3(c)$ are deposited over similar temperature intervals (440 – 300 °C, 480 – 300 °C and 420 – 300 °C) and are calculated to be the only stable condensed phase for each element.

X-Cu and -Mn-Si (Figures 7b, 8a): $\text{Cu}_2\text{S}(c)$ has a stability interval of 800 to 580 °C; the phase covellite, calculated to be stable in the closed system (see above), is not predicted to be stable; $\text{MnSiO}_3(c)$ (rhodonite) is not calculated to be

stable in the open system; the reason for this is the high-temperature deposition of Si as cristobalite; $\text{MnS}(c)$ is stable from 540 – 340 °C and $\text{MnSO}_4(c)$ between 320 – 300 °C.

X-Bi, -Sn and -Mo-Ca-Si (Figures 7c,d): $\text{SnSO}_4(c)$ is deposited between 480 and 300 °C; cassiterite ($\text{SnO}_2(c)$) deposits from 600 to 500 °C. $\text{Bi}_2\text{S}_3(c)$ (bismuthinite), the only stable Bi-containing phase, is calculated to be stable between 400 and 300 °C; therefore, both minerals coexist theoretically within an interval of 60 °C.

X-Ga and -Ni-Si (Figures 6d, 8a): Each of these elements forms two stable phases. $\text{Ga}_2\text{O}_3(c)$ and $\text{Ga}_2\text{S}_3(c)$ are deposited in the intervals from 920 – 620 °C and 480 – 300 °C respectively; $\text{NiS}_2(c)$ and $\text{NiS}(c)$ are stable between 900 and 480 °C.

6.5. Discussion

The features of the open-system calculations can be summarized as follows:

- The results reflect the observed deposition of minerals over restricted temperature intervals in sublimation tubes
- The separation of mineral phases occurs with respect to temperature, such as for example,

$$T\left(\frac{\text{max. subl.}}{\text{NaCl}}\right) = 620^\circ\text{C}, \quad T\left(\frac{\text{max. subl.}}{\text{Na}_2\text{SO}_4}\right) = 400^\circ\text{C}$$

$$T\left(\frac{\text{max. subl.}}{\text{KCl}}\right) = 580^\circ\text{C}, \quad T\left(\frac{\text{max. subl.}}{\text{K}_2\text{SO}_4}\right) = 380^\circ\text{C}$$

However, the corresponding spatial separation in the tube will be a function of the temperature gradient and hence depend directly on the flow rate.

- In some cases, open-system calculations reproduce distinct mineral assemblages found in sublimation tubes and in the natural environment, e.g., garnet-molybdenite-anhydrite or Bi-sulfide (represented by bismuthinite, ($\text{Bi}_2\text{S}_3(c)$) in the calculations) – ZnS-CdS.
- Open-system calculations indicate the deposition of silicate minerals whereas they were calculated to be supersaturated in the closed system, over small temperature intervals of only 20 °C; an exception is TiO_2 .
- The results of the calculations differ for open and closed systems with respect to the condensed phases found to be stable; in most cases, the open-system calculations fail to reproduce the correct temperature range of maximum deposition found in the sublimation tubes.

Nevertheless, the open-system calculations are to some extent able to reproduce the processes of subli-

Table 4: Sublimate minerals collected at Kudriav in 1995.

Temperatures indicate the approximate temperature range of the gas in which the sample was collected. Note that flow conditions will vary across the surface of a rock specimen as will the temperature. Additional information for phase identification beside SEM-EDAX spectra is indicated. n.d. = not detected.

mineral	theoretical formula	additional information	observed temperature [°C]
olivine	(Mg,Fe)SiO ₄	single X-tal X-ray	>750
enstatite	Mg ₂ Si ₂ O ₆	single X-tal X-ray	>750
augitic pyroxene	(Ca,Na)(Mg,Fe,Al)Si ₂ O ₆	shape	650 – 750
wollastonite	Ca ₂ Si ₃ O ₆	shape	650 – 750
andradite	Ca ₃ Fe ₂ Si ₃ O ₁₂	single X-tal X-ray	650 – 750
powellite	CaMoO ₄	single X-tal X-ray	650 – 750
anhydrite	CaSO ₄	single X-tal X-ray	550 – 650
haematite	Fe ₂ O ₃	single X-tal X-ray	550 – 650
magnetite	Fe ₃ O ₄	single X-tal X-ray	550 – 650
unnamed	ReS _n n ≈ 1-4 (?)	shape, reflectivity	550 - 650
molybdenite	MoS ₂	single X-tal X-ray, reflectivity	550 – 650
greenockite	CdS	single X-tal X-ray, powder X-ray	450 – 550
wurtzite	ZnS (Zn/Cd) _m ≈ .4-.8 and ((Zn+Cd)/S) _m ≈ 1.0-.75	shape	450 – 550
cannizzarite	Pb ₄ Bi ₅ S ₁₁	single X-tal X-ray	450 – 550
cosalite	Pb ₂ Bi ₂ S ₅	shape	450 – 550
pyrite	FeS ₂	shape	450 – 550
crystoballite	SiO ₂	powder X-ray	450 – 550
halite	NaCl	shape, single X-tal X-ray	450 – 550
rozenite	FeSO ₄ · 4H ₂ O	single X-tal X-ray	350 – 450
ilsemannite	Mo ₃ O ₈	colour, shape	350 – 450
sinjarite	CaCl ₂ · 2H ₂ O	powder X-ray	n.d.
sylvite	KCl	shape	n.d.

mation occurring in a moving gas stream. The differences in the calculated sublimation assemblages as compared to the results of the closed-system approach presented above are partly a consequence of the retrieval of the major elements, Si and Al, in the first 20 °C step of calculation. However, the failure of the model to reproduce the actual observed tempera-

ture range of sublimate deposition deserves a more detailed discussion. Two cases may be distinguished:

- (i) elements where the calculated volatility is underestimated, i.e.,

$$T\left(\frac{\text{max. subl.}}{\text{calc.}}\right) > T\left(\frac{\text{max. subl.}}{\text{obs.}}\right),$$

(e.g., Ni, Mo, Mn, Cu and Fe).

- (ii) elements where the calculated volatility is overestimated, i.e.,

$$T\left(\frac{\text{max. subl.}}{\text{calc.}}\right) < T\left(\frac{\text{max. subl.}}{\text{obs.}}\right),$$

(e.g., Ga, Sn, Bi, In, Cd and Zn).

The temperature differences between calculated and observed maximum sublimation discussed are >100 °C (with the exception of Mn where the difference is around 75 °C). While it is correct that the temperature measured along the tube's axis is a maximum estimate of the actual sublimation temperature, the difference in the temperature between the inner tube wall and that along the tube's axis is less than ± 50 °C as determined by direct measurements during the experiment. Therefore, the temperature differences discussed here are significant.

In the case of underestimation of the volatility of trace elements, incorrect or missing thermochemical data as well as dynamic or kinetic effects will be important. Indeed, it would be expected that actual sublimation processes taking place in the tube are intermediate between a closed and an open system. Sublimates forming in the gas stream initially as aerosols might be retained and only deposited at lower temperatures. The behavior of molybdenum may be such an example. In the case of copper, such an argument may be premature. As exemplified in the closed-system approach discussed above and shown in Figure 8b, Cu is predicted to be dominantly volatile as the $\text{CuBr}_{3(g)}$ complex below 600 °C. The change in the oxidation state of copper at this temperature is a consequence of the internal gas buffer dominating the redox environment. However, there are no thermochemical data for the hypothetical $\text{CuCl}_{3(g)}$ complex. Hence, the volatility of copper is underestimated at temperatures below 600 °C due to a lack of data for a dominant gaseous complex of copper.

It should also be mentioned that other, potentially important volatile species have not been considered in the calculations because thermodynamic data pertaining to their stability are currently unavailable. For example, many volatile species forming in a volcanic gas will be hydrated complexes such as $\text{AgCl}(\text{H}_2\text{O})_{3(g)}$, $\text{CuCl}(\text{H}_2\text{O})_{n(g)}$, $\text{AgCl}(\text{H}_2\text{O})_{n(g)}$, $\text{AuCl}(\text{H}_2\text{O})_{n(g)}$, and $\text{SnCl}_2(\text{H}_2\text{O})_{n(g)}$ (Migdisov et al., 1999; Archibald et al., 2000; Williams-Jones et al., this volume) but the stability of these in high-temperature Kudriavy gases has not been considered. In addition, the formation and high-temperature stability of sulfur-containing species such as polysulphanes (Migdisov et al., 1998) and molecular complexes such as $\text{Sb}_2\text{S}_3(\text{H}_2\text{S})_{(g)}$ (Zakaznova-Iakovleva et al., 2001) may be important in volcanic gas systems but

have not been considered in our calculations. We have also not considered ionic clustering reactions within the vapor phase (Likholyot, 2000) although these are probably unimportant in volcanic gas systems.

Similarly, erroneous thermochemical data might explain the overestimation of the volatility of certain trace elements. It should also be noted, that most elements do not sublime as pure substances. As demonstrated in Figure 7, elemental distribution of Cd, Zn and In on the one hand, and Pb and Bi on the other, correlate strongly. Therefore, it may be possible to stabilize certain elements in solid solutions at temperatures higher than would be expected for the respective pure substances.

7. CONCLUSIONS AND COMMENTS

The comparison of open-system equilibrium calculations with the results from a silica-tube experiment allows some assessment of the validity of current thermochemical equilibrium modeling as applied to trace-element transport in volcanic gases. At this stage, it has to be concluded that equilibrium models only qualitatively reproduce the sublimation tube chemistry and hence trace-element volatility in the Kudriavy gas. It was shown above that this may be partly explained by unavailable or incorrect thermochemical data as well as the lack of consideration of solid solutions. The latter are believed to stabilize certain sublimates to temperatures higher than predicted by the models, thus causing an overestimation of the volatility of specific elements by the calculation. The models used here are themselves expected to only approximate the real processes in the sublimation tubes which are considered to behave in an intermediate way between a closed and open system, depending on the flow rate.

It was already pointed out above that many of the gaseous equilibria are quenched below 350 – 400 °C. The occurrence of diffusion processes (see also Korzhinsky et al., 1996) and the dependence of gaseous equilibria on the flow rate of a fumarole (Saito et al., 1989) indicate that disequilibrium processes must also occur at much higher temperatures. Therefore, the use of thermochemical equilibrium computations to model heterogeneous equilibria in dynamic volcanic gas systems such as Kudriavy must be treated with caution and regarded as a crude approximation of reality.

Finally, the data reported in this work further emphasize the importance of volcanic gases in transporting heavy-metals and other compounds to the earth's surface and atmosphere. The importance of magma degassing in supplying a metal flux to ore depositing hydrothermal convectional cells is further noted.

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