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**APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO
VOLCANIC GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN
EMISSIONS, AND VOLCANOLOGICAL STUDIES OF GAS-PHASE
TRANSPORT**

By

Robert Bruce Symonds

A DISSERTATION

Submitted in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

(Geology)

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ABSTRACT

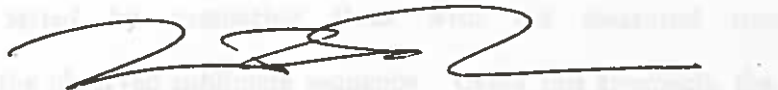
APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO VOLCANIC
GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN EMISSIONS, AND

This dissertation, "Applications of Multicomponent Chemical Equilibria to Volcanic Gases at Augustine Volcano, Volcanic Halogen Emissions, and Volcanological Studies of Gas-phase Transport", is hereby approved in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in the field of Geology.

DEPARTMENT Geological Engineering, Geology, and Geophysics



Thesis Advisor



Head of Department

Date 1 NOV 1990

ABSTRACT**APPLICATIONS OF MULTICOMPONENT CHEMICAL EQUILIBRIA TO VOLCANIC GASES AT AUGUSTINE VOLCANO, VOLCANIC HALOGEN EMISSIONS, AND VOLCANOLOGICAL STUDIES OF GAS-PHASE TRANSPORT**

Dynamic chemical processes in multicomponent volcanic-gas systems were studied using a thermodynamic modeling approach by changing the bulk composition, temperature, or pressure in small increments. To constrain the calculations, a thermochemical data base of >1000 species of gases, solids, and liquids in a 42 element system was compiled. This data base interfaces with computer programs (modified from Reed, 1982) that calculate multicomponent homogeneous and heterogeneous chemical equilibrium in gas-solid-liquid systems.

Applications of the modeling to the 9/81 Mount St. Helens volcanic gases are shown. Constraining the model with samples of gases, sublimates, and magmas from the volcano, the model computes: (1) the amounts of trace elements degassed from magma, and (2) the solids that fractionate from the gas upon cooling. Then the model's predictions were tested by comparing them with the measured trace-element concentrations and the observed sublimate sequence. Using this approach, the following conclusions are reached: (1) most trace elements are volatilized from dacite magma as simple chlorides (e.g., CuCl, AgCl, CsCl) or other types of gas species (e.g., H₂MoO₄, AuS, Fe(OH)₂, Hg, H₂Se); (2) some elements (e.g., Al, Si) exist as rock particles-not gases-in the gas stream; (3) near-surface cooling of the gases triggers sublimation of oxides (e.g., magnetite), sulfides (e.g., molybdenite), halides (e.g., halite), tungstates (e.g., ferberite), and native elements (e.g., gold); (4) equilibrium cooling of the gases to 100°C causes most trace elements, except for Hg, Sb, and Se, to fractionate from the gas by sublimation.

The thermochemical modeling approach was also used to study volcanic halogen emissions. This work shows that HCl and HF are the overwhelmingly dominant species of Cl and F in volcanic gases. It also shows that large explosive volcanic eruptions may inject significant amounts of HCl and HF into the stratosphere and that passively degassing volcanoes are a major source of tropospheric HF.

Finally, the thermochemical models were used to understand the origin and speciation of trace elements in high-temperature, HCl-rich gases collected from Augustine volcano after the spring-1986 eruptions. The study shows that the HCl-rich Augustine gases are very favorable for volatilizing metal chlorides (e.g., FeCl_2 , NaCl, KCl, MnCl_2 , CuCl) from magma.

Acknowledgements

The seed for this project was planted eight years ago when I was employed by Tom Casadevall to help study the SO₂ emissions from Mount St. Helens. Fifteen months of work on an active volcano changed the direction of my life. Thanks Tom for introducing me to a great field of research.

Bill Rose and Mark Reed were exceptionally helpful and inspirational throughout my graduate career. Thanks to the two of you for the many hours of help and encouragement you have provided. Most of all, thanks for being good and caring friends.

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Thermochemical Data and Applications to Studies of High-Temperature Volcanic

Cases with Examples from Mount St. Helens

ABSTRACT

A thermochemical data base, GASTHERM, has been compiled to interface with an Algebraic Programs (Data and Systems, 1981) that handles multicomponent chemical equilibria in gas-solid-liquid systems. GASTHERM provides coefficients for the calculation of the equilibrium constant, K , from 25°-1200°C for various species reactions that are defined by a choice of thermodynamic components. GASTHERM includes 1000 species of gases, solids, and liquids in the 42 element system.

Chapter 1

Detailed chemical equilibria in 2-3 component systems will be provided with our program and data base by using the following:

**Calculation of Multicomponent Chemical Equilibria in Gas-Solid-Liquid Systems:
Thermochemical Data and Applications to Studies of High-temperature Volcanic
Gases with Examples from Mount St. Helens.**

Dynamic chemical equilibria in 2-3 component systems will be provided with our program and data base by using the following:

1. A choice of thermodynamic components for each element.

2. A choice of chemical formulas for each species.

3. A choice of the standard state for each species.

4. A choice of the temperature range for the calculation.

5. A choice of the pressure range for the calculation.

6. A choice of the initial composition for the calculation.

7. A choice of the output format for the calculation.

8. A choice of the output file name for the calculation.

9. A choice of the output file extension for the calculation.

10. A choice of the output file directory for the calculation.