### VOLATILES

- A volatile is a chemical species that favors the gaseous state
- An equilibrium exists between gas and liquid
- How do volatiles effect magmas?

### ROLE OF VOLATILES

- Effect viscosity
- Control eruption characteristics
- May modify climate

### VOLCANIC GAS SPECIES

- **H$_2$O**, **CO$_2$**, **SO$_2$**, **H$_2$S**, **SO$_3$**
- **CO**, **COS**, **CH$_4$**, **HCl**, **HF**
- **H$_2$**, **O$_2$**, **S$_2$**, **N$_2$**, **CS$_2$**, **NH$_4$**, **B**, **Br**
- Noble gases, Volatile metals
- Rare earth elements

### Main Gaseous Elements in Volcanoes

- **H**, **C**, **O**, **S**, **Cl**, **F**, **N**

### ATMOSPHERIC COMPOSITION

- N$_2$ ~ 80%
- O$_2$ ~ 20%
- Ar < 1%

### QUANTIFICATION OF VOLATILES

- Measured as partial pressure of a gas
  \[ \sum p_i = P \]
IDEAL GAS LAW

\[ V = \frac{RT}{P} \]

EXAMPLE OF WATER

• The case of liquid-gas equilibrium
  – This system has one component and two phases and thus is univariant
  – For any pressure, liquid and vapor water are at equilibrium at a single temperature, below the critical point

WATER PHASE DIAGRAM

The critical point is where liquid boils without a change in volume

For water: \( T_c = 374 \, ^\circ\text{C}, \, P_c = 221 \, \text{bars} \)

Water Equilibrium

\[ 2H_2 + O_2 = 2H_2O \]

\[ K = ??? \]

WATER CO₂ EQUATION

\[ H_2 + CO_2 = CO + H_2O \]

\[ K = \frac{[P_{CO}][P_{H2O}]}{[P_{H2}][P_{CO2}]} \]

Hydrogen Sulfide

Species \( H_2, S_2, H_2S \)

Equilibrium \( 2H_2 + S_2 = 2H_2S \)
### Sulfur Dioxide

<table>
<thead>
<tr>
<th>Species</th>
<th>$H_2$, $S_2$, $SO_2$, $H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>$4H_2 + 2SO_2 = S_2 + 4H_2O$</td>
</tr>
<tr>
<td>Constant</td>
<td>$K = [S_2][H_2O]^4/[H_2]^4[SO_2]^2$</td>
</tr>
</tbody>
</table>

### Influence of Volatiles

- Evolution of mantle and crust
- Rheological properties of earth materials
- Formation of atmosphere and oceans
- Appearance and evolution of life
- Sedimentary processes
- Geochemical cycles

### Volatile Cycle

- Topology of the cycle (reservoirs and connections)
- Mass of reservoirs
- Volatile concentrations in reservoirs
- Estimate fluxes between reservoirs

### Main Volatile Reservoirs

- Earth interior (mantle and core)
- Earth crust (contained in minerals)
- Atmosphere
- Oceans
- Groundwater

### Source of Volatiles in Magmas

- Juvenile gases (mantle)
- External sources
  - meteoric water
  - subducted hydrated crust

### CARBON DIOXIDE

- Second most abundant magmatic gas
- Controls composition of mafic magnesian sources
- Governs magma vapor pressure at high temperatures
- Propellant for mafic magmas (diatremes)
### Sulfur

- Major component of magmatic gas
- Equilibrium depends on
  - T, P, Fe content
- S exists in multiple oxidation states
- SO$_2$ escapes when magmas rise

### Main Classes of Volatile Tracers for Earth Systems

- Helium
  - Traces exhalation of primordial volatiles from mantle
- Nobel gases (in general)
  - Provide age relations of reservoirs
- Major Volatiles
  - Describe present day cycles

### What is an Isotope?

- Two or more species of a chemical element
- Same atomic number (# of protons) but different atomic mass
- Same position in Periodic Table
- Nearly the same chemical behavior but different physical properties

### Noble Gases

- Helium
- Argon
- Neon
- Xenon

### Helium

- Primary reference reservoir is solar plumes
- Secondary reference reservoir are meteorites
- Nearly no He exists in the atmosphere
  - Short residence time (10$^6$ years), lost immediately
- $^3$He/$^4$He ($R_A$) = 1.4 x 10$^6$

### Sources of Atmospheric He

- MORB degassing
  - Volcanism releasing deep gases
- Continental degassing
  - Radiogenic decay of minerals containing $^{238}$U, $^{235}$U, and $^{232}$Th to yield $^4$He
- Cosmogenic input
### MORB flux of He
- MORB basalts contain $8 R_A$ of He
- Source is primordial He ($>100 R_A$)
- This indicates that the present mantle still contains primordial gases
- He isotopes can trace oceanic circulation

### Arc Volcano Flux of He
- Arc volcanoes contain 8 to 1 $R_A$ He
- Lower ratios are not from radiogenic decay in subducted crust (time too short)
- This indicates that incorporation of radiogenic He from continental crust

### Atmospheric Argon
- Argon Isotopes are $^{36}$Ar, $^{38}$Ar, and $^{40}$Ar
- Only $^{40}$Ar is radiogenic
- Atmospheric $^{40}$Ar/$^{36}$Ar ratios = 300
- MORB samples have $^{40}$Ar/$^{36}$Ar ~20,000
- MORB is purely radiogenic Ar
- Mantle is degassed in primordial Ar

### ROLE OF TEMPERATURE
- Increasing temperature forces water out
- Changes relative abundance of gas species

### ROLE OF PRESSURE
- Decreasing pressure releases water
- Clausius-Clapeyron relation for a gas
  \[ \frac{dT}{dP} = \frac{T \Delta V}{\Delta H} \]

### GAS MEASUREMENT
- Direct collection from fumaroles
- Remote Sensing (COSPEC, etc.)
- Glass and fluid Inclusions in crystals
- Total volatile loss on heating (LOI)
- Experimental studies (also theoretical calculations)
Oxygen Isotopic Characteristics

- Mantle sources
- Standard sea water
- Meteoric water

SOLUBILITY OF GAS IN MAGMA

During the crystallization of anhydrous phases:

\[ X_r (1 - f) = X_i \]

During the crystallization of a hydrous phase:

\[ X_r (1 - f) = X_i - X_{OH} f' \]

Where:
- \( X_r \) is the resulting water concentration in the magma
- \( X_i \) is the initial water concentration in the magma
- \( X_{OH} \) is the concentration of water in the hydrous phase
- \( f \) is the fraction of anhydrous phase that crystallized
- \( f' \) is the fraction of hydrous phase the crystallized

Volatile in Magma Chambers

- Roofward increase in volatiles
  - Lowers the magma liquidus
  - First pumice erupted may contain few crystals
- F & Cl are more soluable than H₂O
- Hydrous silicates (hornblende and biotite) form at roof of magma chamber

Physical Effects Of Water On Magma

- Increases crystallization
- Decreases viscosity
- Increases eruption pressure