Geochemistry of Surface-Atmosphere Interactions on Venus Paul Withers 13 April 1999 Physical Geochemistry

- Planets and their Atmospheres -Lewis, Prinn; 1984
- Venus Hunten, Colin, Donahue, Moroz (Eds); 1983
- Venus II Bougher, Hunten, Phillips (Eds); 1997
- Fegley, Klingelhofer, Lodders, Widemann, 591-636 in Venus II

Why should we care about this?

- Atmosphere is chemically reactive, optically thick, with T~ 740K, p ~ 100bars
- Little mechanical weathering
- Evolution of surface mineralogy controlled by thermochemically driven atmosphere-surface reactions
- Little direct surface information

Venus - pre 1960 view

- Similar mass, radius as Earth
- Closer to Sun
- Covered by thick clouds
- CO₂ detected in atmosphere
- Very small upper limits on H₂O,
 O₂ in atmosphere
- Earth's twin?



Atmosphere of Venus

- 740K, 100 bars at surface
- 97% CO₂, 3% N₂, 0.1% trace
- H₂O, CO, HCl, HF, SO₂, H₂S, COS, O₂, Noble gases
- Greenhouse effect from CO₂ causes high T
- H₂SO₄ clouds block light
- Near-surface composition of atmosphere not measured
- Inferred surface $f_{O2} = 10^{-21}$ bars



Surface of Venus

- Metre-scale light, flat, sharpedged slabs and darker soil
- Soil is ash or weathered rock
- Similar in appearance to ocean floor or arid regions on Earth
- Mostly lava floods and shield volcanoes basaltic
- Less than 500 Myr old

Geological processes on Venus

- Volcanism
- Tectonism
- No freeze-thaw, no sedimentation, no water erosion, no sand-blasting
- Thermochemical weathering
- Small amount of physical weathering to soils?
- Presence of atmosphere limits temperature fluctuations and impact processes

Thermochemical Weathering

- Lava + weathering = surface
- Equilibrium processes...?
- ...Regional variations in supply rates of gas and rock, p, T, and atmospheric composition
- ...Kinetics
- What are the major minerals?
- What is the oxidation state of the surface?

Carbonates on Venus

- $CaCO_3 + SiO_2 = CaSiO_3 + CO_2(g)$
- Psurface = Pbuffer @ Tsurface
- Other carbonates also stable
- Interpretation of X-ray fluorescence data suggests ~ 5% by mass of carbonates
- Likely source alkaline igneous rocks

Hydrogen Halides on Venus

- More HCl, HF than on Earth
- Constant abundances suggests buffering by alkali silicates and water
- Corrosive acids likely to be reacting with surface
- Likely source volcanic activity
- CO₂, HF, HCl buffers consistent with mineralogy of terrestrial alkaline igneous rocks

Oxidation State of the Surface

- $2\text{CO} + \text{O}_2 = 2\text{CO}_2 \text{ controls O}_2$
- Lack of data near surface
- $f_{O2} \sim 10^{-21}$ bars, CO = 10 ppm
- $\operatorname{CO}_2 + 2\operatorname{Fe}_3\operatorname{O}_4 = \operatorname{CO} + 3\operatorname{Fe}_2\operatorname{O}_3$
- CO/CO₂ also controlled by redox reactions with Fe silicates
- CO/CO_2 and hence f_{O2} independent of total pressure
- Calculate stable Fe minerals given p, T and CO/CO₂

Magnetite or Haematite?

- One, other, or both stable
- Images suggest presence of haematite
- Attempts to use CO/CO₂ limits rely on equilibrium models...
- ...But lab experiments suggest CO/CO₂ mixture more oxidising than equilibrium models

Sulphur on Venus

- Important due to clouds and greenhouse effect
- Complicated due to SO, SO₂, SO₃, H₂S, OCS, H₂SO₄, etc.
- S in lower atmosphere is kinetically controlled
- $CaCO_3 + SO_2 = CaSO_4 + CO$ removes SO_2 , deposits $CaSO_4$
- FeS₂ decomposes to Fe₇S₈
- Likely source volcanic activity
- Require recent volcanism ~ 1 km³ yr⁻¹ to keep H₂SO₄ clouds

Conclusions

- We lack direct information on the surface mineralogy and oxidation state of Venus
- Useful constraints can be found from models assuming thermodynamic equilibrium between the surface and the atmosphere
- Better results are obtained if lab experiments are used to constrain reaction rates
- Need more data, new spacecraft instruments

Handy Minerals

- SiO₂ Quartz
- CaCO₃ Calcite
- Fe_3O_4
- Fe_2O_3

- FeS₂

• CaSiO₃ Wollastonite Magnetite (reduced) Haematite (oxidised) • $CaSO_4$ Anhydrite • Fe₇S₈ Pyrrhotite Pyrite