In Situ Analysis of Geochemistry and Mineralogy on the Venus Surface

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Possibilities for Venus In-Situ Measurements

**Geochemistry**
- LIBS: Laser-Induced Breakdown Spectroscopy
- APXS: Alpha-Particle X-Ray Spectrometer
- XRF: X-ray Fluorescence
- GRS: Gamma-ray Spectroscopy

**Mineralogy**
- XRD: X-ray Diffraction
- Raman Spectroscopy
- Reflectance/Emission Spectroscopy
Laser-Induced Breakdown Spectroscopy (LIBS)
LIBS Advantages

- Quantify elements from H to Pb
- Plasma is very high T and thus insensitive to 740K
- No sample collection, no interlocks
- Probe multiple locations: 1000’s in a hour
- Rapid analysis: minutes/spot
- Prototype built with PIDDP and internal LANL funding
- Easily coupled with Raman
- Flight heritage from ChemCam + SuperCam
- Concurrent development for deep sea applications

Venus = 92 bars, ocean floor = 1000 bars
LIBS Disadvantages

• Issues needing further study include:
  • Plasma stability (repeatability)
  • Effects of turbulence
  • Lack of large calibration databases
  • Effects of sample porosity
  • More calibration data under Venus pressures needed to support calibration transfer
• Pressure effects need to be studied

Pink font = “we’re working on it”
Manifold Alignment Techniques overcome variations in calibration suites

In LIBS, ionization states of the plasma are a direct function of plasma temperature so emission spectra vary with power density on targets.
Manifold Alignment shows great potential for all types of instrument cross-calibration and merging of datasets acquired under varying conditions.
APXS

- Exposes material to α particles and x-rays emitted by decay of $^{244}$Cm
- Emitted x-rays from rock/soil measured with detectors
- Data take 1-10 hours to acquire and improve with length of acquisition
- Needs to be contact or close to rocks/soil
- Tremendous flight heritage
- Would need a different kind of detector that can detect x-rays at Venus surface conditions or be inside pressure vessel and use sample delivery
X-ray Fluorescence

Advantages
• “gold standard” for bulk chemical analyses of geological samples

Disadvantages
• Would need a different kind of detector that can detect x-rays at Venus surface conditions, or use sample delivery
• Would have to develop a Be window on the pressure/temperature shell, so you could bring the sample up to the window without breaking containment
• Sample handling and preparation important – lots of moving parts
PING: Probing \textit{In situ} with Neutrons and Gamma Rays

PING uses high energy neutrons and gamma rays to penetrate Venus’ surface and measure the bulk elemental composition over a large volume: ~20 cm deep, ~50 cm radius

- PING is located inside the Venus lander pressure vessel
- No moving parts
- No arm for sample manipulation required
- No window required

Slides courtesy of Ann Parsons
How PING Works

- PING’s Pulsed Neutron Generator (PNG) emits isotropic pulses of 14 MeV neutrons.

- These energetic neutrons penetrate the pressure vessel walls, the dense atmosphere and Venus’ surface.

- Nuclear reactions between the 14 MeV neutrons and the Venus subsurface materials produce gamma rays with energies specific to the element and nuclear process involved.

- The resulting gamma rays are energetic enough to pass through the surface materials, atmosphere and pressure vessel to be detected by the LaBr₃ Scintillator Gamma Ray Spectrometer (GRS).

- GRS gamma ray spectra are analyzed to determine the elemental composition via their spectral signature.
PING Pros and Cons

Pros:
- established technique in drill hole chemical analysis
- excellent precision and accuracy
- bulk measurement
- no moving parts
- no window required
- located inside pressure vessel
- Flexibility in placement/orientation within pressure vessel

Cons:
- mixed flight heritage (DAN on Curiosity, GRS from Chang’e)
- TRL 5 due to robust oil field heritage
- current units are proprietary
- requires massive rock blocks for calibration and testing
- as yet no robust calibration model
SUMMARY
Geochemical Measurements on Venus

**LIBS:** Laser-Induced Breakdown Spectroscopy
data processing still in development

**APXS:** Alpha-Particle X-Ray Spectrometer
contact instrument requires moving parts
interior instrument requires breaking interlock

**XRF:** X-ray Fluorescence
no good detector options for external use
requires breaking interlock for interior use

**GRS:** Gamma-ray Spectroscopy
mixed flight heritage; testing, calibration needed
X-Ray Diffraction (XRD)

- Powdered sample exposed to collimated x-ray beam
- Diffracted x-rays are identified by energy, creating a diffraction pattern
- Diagnostic patterns for minerals all well-understood
X-Ray Diffraction Pros and Cons

**Pros:**
- “Gold standard” for terrestrial mineral identification
- Definitive mineral identification

**Cons:**
- Data acquisition takes >10 hours (even on Mars)
- Extensive sample handling needed to drill, sieve, and deliver sample
Raman peaks are diagnostic of mineral species.
Same mineral, different samples

Same exact sample, different spectrometers
Mineral mixing is non-linear
No methodology currently exists for unmixing
Equivalent of “absorption corefficients” does not exist

Calcite + Diamond Mixture

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<th>Mixture</th>
<th>Peak Intensity</th>
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Raman shift (cm⁻¹)
Raman Spectroscopy

Pros:
• Excellent accuracy when identifying single minerals
• Can be stand-off technique requiring no sample contact
• Flight heritage from Mars 2020 and ExoMars

Cons:
• Rocks and soils require methods for unmixing Raman spectra non-existent
• If microscope is used, must bring sample to window or inside to use microscope to ID
• Pure mineral databases exist but are not verified (e.g., RRUFF is only 64.1% XRD’d)
• Need techniques to align data from different instruments
Reflectance/Emission Spectroscopy
VNIR, IR, mid-IR

Emission = 1 - Reflectance

Best range for emissivity measurements on Venus
Emissivity:

Existing spectral databases (e.g., ASU TES Lab Spectral Library) cover 0-100°C.

Higher-T databases needed (Helbert lab).

Pressure effect theoretically small.

Could possibly align existing databases.

Helbert et al. (2013)
What about reflectance?

Wagner and Schade (1996): Thermal emission must be taken into account when considering reflectance at IR to mid-IR wavelengths. "...drastic weakening of features with increasing temperature" because emission mutes reflectance features.
SUMMARY
Mineralogical Measurements on Venus

XRD: X-ray Diffraction
- requires sample handling
- requires yet-to-be-developed detectors

Raman Spectroscopy
- promising for both stand-off and close-up
- needs better databases
- needs development of unmixing algorithms

Reflectance/Emission Spectroscopy
- reflectance spectra have emittance contribution
- all spectra have shifts from temperature
- needs better databases
- pressure effects need study