CHEMIN-V: A DEFINITIVE MINERALOGY INSTRUMENT FOR THE VENERA-D MISSION. D.F. Blake¹, P. Sarrazin², T. S. Bristow¹, R. Walroth¹, R. Downs³, M. Gailhanou⁴, A. Yen⁵ and K. Zacny⁶, ¹Exobiology Branch, MS 239-4, NASA Ames Research Center, Moffett Field, CA 94035 (david.blake@nasa.gov), ²SETI Institute, Mountain View, CA, ³Univ. of Arizona, Tucson, AZ, ⁴IM2NP-Aix Marseille Universite²-CNRS, ⁵Jet Propulsion Laboratory, Pasadena, CA, ⁵Honeybee Robotics, Pasadena, CA.

The Case for Scientific Exploration of the Venus Surface: Venus and Earth were presumably formed from the same protoplanetary material, at a similar radial distance from the center of the solar nebula and it is likely that both had similar early histories. Venus should be Earth's twin, but current conditions on the surface of Venus and in its atmosphere are radically divergent from those of Earth. What events transpired to yield present-day Venus: Surface temperatures of 470°C, a 90 bar CO₂ atmosphere and the absence of a magnetic field? Did conditions ever exist on Venus that could have fostered the origin of life? How and why did the evolutionary paths of Venus and Earth diverge? These are questions posed by the Report of the Venera-D Joint Science Definition team [1].

Science Objectives of the Venera-D Lander: Science objectives of the Venera-D Lander include [1]: <u>L6</u>. Surface elemental composition ("Determine the elemental composition of surface rocks with emphasis on trace elements including the radioactive isotopes of K, U and Th)," and <u>L7</u>. Mineral phases ("Identification of mineral phases, containing Fe (Fe²⁺, Fe³⁺, Fe⁶⁺) to address atmosphere and surface evolution along with surface minerals (search for any possible bound water e.g., phyllosilicates?))." As a result of the limited lifetime of the lander on the surface of Venus, these objectives must be met within 1 hour.

The Importance of Mineralogy to Planetary Exploration: Minerals are thermodynamic phases that have a unique structure and a limited range of composition. Minerals are stable under known and specific ranges of pressure, temperature and element activity. An assemblage of minerals can be used to characterize the conditions under which it was formed and any post-depositional changes that modified its chemistry or resulted in secondary mineralization.

Mineralogical Analysis using X-ray Diffraction and X-ray Fluorescence (XRD/XRF): XRD is the only *in-situ* technique able to definitively identify, quantify and determine the elemental composition of minerals present in planetary regolith. XRD can also determine the quantity of X-ray amorphous material present in a regolith sample, and when combined with XRF, the elemental composition of the amorphous component(s). Taken together, these techniques pro-

vide a comprehensive analysis of regolith mineralogy that can only be improved upon by sample return.

The CheMin instrument on Mars Science Laboratory. X-ray diffraction was deployed in robotic planetary exploration for the first time on the Mars Science Laboratory Curiosity rover. During its 6-year employment on Mars, CheMin established the quantitative mineralogy of the Mars soil [2], characterized the first habitable environment on another planet [3], and provided the first in-situ evidence of Martian silicic volcanism [4]. CheMin is now employed in characterizing the depositional and diagenetic environments of basaltic lacustrine mudstones that comprise the lower strata of Mt. Sharp in Gale Crater - elucidating for the first time, the early aqueous and oxidative history of Mars. Descriptions of all of the samples analyzed by CheMin as well as raw XRD patterns, the CheMin team's preferred analytical result and all publications related to the analyses can be viewed and downloaded from the CheMin website: https://odr.io/Chemin.

The Terra Instrument – A CheMin Spinoff. During its refinement prior to flight, a prototype portable CheMin instrument called "Terra" was developed. Terra shares its diffraction geometry with CheMin, but in many ways exceeds CheMin's performance. Terra delivers more X-ray flux to the sample, yielding much improved diffraction intensity as well as slightly improved 2θ resolution. Terra became a commercial product in 2009 and currently more than 600 instruments are in daily use in the oil & gas, minerals and pharmaceutical industries.

The Terra XRD/XRF Instrument, a Prototype for CheMin-V: A basalt cobble from Hawai'i was analyzed in a Terra instrument for 15 minutes, then reanalyzed for 8 hours in a Rigaku laboratory X-ray Diffractometer. The XRD pattern from the 15 minute integration (100 frames collected for 10 seconds each) is shown in Fig. 1. Table 1 shows the resulting Rietveld refinement and quantitative analysis from Terra, compared to that of the Rigaku instrument. Compositions (formulae) for minerals having variable chemistry are derived from the refined lattice parameters for andesine, augite, pigeonite and forsterite from the Terra instrument.

With the exception of andesine, results are within error of each other. The benefit of increased integration time is an improved detection and measurement of minor and trace phases; however all major phases are identified, quantified, and their major element chemistry determined.

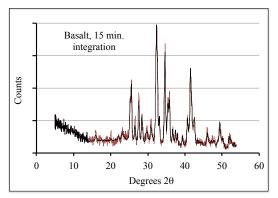


Fig. 1: 15 minute analysis of basalt from Hawai'i with the Terra XRD/XRF instrument. Brown = raw pattern, black = fitted model pattern from Rietveld refinement.

Table 1: Rietveld refinement of basalt cobble, 15 minute analysis vs. Rigaku laboratory XRD. Sparingly crystalline minerals such as palagonite/allophane and nontronite were identified and quantified using full pattern fitting and laboratory standards.

		Terra 15 minutes	Rigaku 8 hours
Phase	Formula	(Wt %)	(Wt %)
Andesine	Ca _{0.24} Na _{0.26} (Al _{0.735} Si _{3.265})O ₈	34.9	27.9
Augite	Mg _{0.82} Fe _{0.52} Ca _{0.66} Si ₂ O ₆	15.4	19.9
Pigeonite	(Mg _{0.54} Fe _{0.46}) SiO ₃	10.8	13.3
Forsterite	(Mg _{0.69} Fe _{0.31}) SiO ₄	7.3	7.5
Ilmenite	FeTiO ₃	0.8	1.5
Hematite	Fe_2O_3	0.3	0.4
Magnetite	Fe ₃ O ₄	ND	1.1
Cristobalite	SiO ₂	5.1	2.6
Palag./Allophane		20.3	20.9
Nontronite 10.0		4.4	4.0
Total		99.2	99.1

The CheMin-V instrument for the Venera-D lander. Fig. 2 shows a 3D model of the CheMin-V XRD/XRF geometry. A single X-ray source emits a cone of $CoK\alpha$ radiation intercepted by two pinhole collimators. The two collimators produce $\sim 70~\mu m$ diameter parallel beams of X-rays directed at the centers of two sample cells. The direct beams from the source/collimators strike opposite ends of a 256X1024 pixel CCD, and the diffracted beams from each sample are detected by the CCD along its long dimension. The CCD is split into two halves, yielding two separate 128X1024 pixel detectors, each recording an XRD pattern. Silicon Drift Diode detectors (SDD) are

placed on the X-ray entrance side of each sample cell, recording an XRF spectrum of each sample.

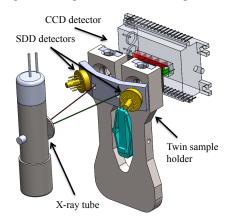


Fig. 2: Geometry of the CheMin-V diffraction experiment. Two samples are analyzed at the same time on a single CCD detector. SDD detectors record the XRF spectrum from each sample.

Powdered samples delivered to the sample cells are vibrated, producing a random motion of the grains in the X-ray beam (as in the CheMin and Terra instruments). CheMin-V can return quantitative mineralogical results from two different samples in 15 minutes, leaving margin for sample delivery and data transmission. If desired, two additional samples can be analyzed with a second sample cell pair, rotated into position by a single actuator (not shown). Estimated dimensions of the instrument are 27X18X15 cm with a mass of 5 kg (Fig. 3).

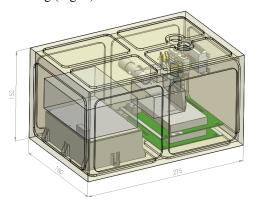


Fig. 3: Notional model of the flight instrument.

References: [1] Venera-D JSDT, (2017), https://www.lpi.usra.edu/vexag/reports/Venera-D-STDT013117.pdf [2] Blake, D.F., et al., (2013), *Science*, 341, 1239505; doi: 10.1126/science.1239505. [3] Vaniman et al., (2013), *Science*, 10.1126/science.1243480. Grotzinger et al., (2013), *Science*, 10.1126/science.1242777. [4] Morris, R.V., (2016), PNAS: doi: 10.1073/pnas.1607098113.