DIFFERENTIAL SCANNING CALORIMETRY OF HYDROUS MINERALS UNDER MARS-LIKE CONDITIONS: CALIBRATION STUDIES FOR THE MARS '98 LANDER THERMAL AND EVOLVED GAS ANALYZER (TEGA). D. C. Golden[1], D. W. Ming[2], H. V. Lauer, Jr.[3], R. V. Morris[2], C. Galindo[4] and W. V. Boynton[5], [1]Dual Inc., Houston, TX 77058, d.c.golden1@jsc.nasa.gov, [2]NASA JSC, Houston, TX 77058, [3]Lockheed Martin, Houston, TX 77058, [4]Hernandez Engineering, Houston, TX 77058, and [5]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721.

Introduction. Volatile-bearing minerals (e.g., phyllosilicates, Fe-oxyhydroxides, sulfates, carbonates) may be important phases at the surface of Mars, based upon past climates that were likely warmer and wetter [1]. The Mars '98 Lander carries an instrument - Thermal and Evolved Gas Analyzer (TEGA) - that will be used to characterize these volatile-bearing phases. The Lander is scheduled to begin its mission on the surface in December, 1999. TEGA is made up of a series of single-shot furnaces, which will heat the collected surface materials under a slow stream of N_2 (0.4 sccm) at near 100 Torr N_2. Differences in power consumption between the sample and reference furnaces will be recorded as a function of the temperature and evolved gases will be analyzed. In preliminary experiments using a laboratory differential scanning calorimeter (DSC), carrier gas flow rate and pressure were found to have effects on the onset temperatures and enthalpy of volatile-bearing minerals [2]. Therefore, it is necessary to determine the changes in onset temperatures and enthalpies at reduced pressures and gas flow rates for a wide range of volatile-bearing minerals that might be expected at the surface of Mars.

We have selected lepidocrocite (γ-FeOOH) as a Mars analog mineral to examine the effects of reduced pressure and gas flow rates. Lepidocrocite is an excellent mineral to test because it has two thermal signatures - an endotherm at about 260°C, due to a volatile dissociation event (γ-FeOOH $\rightarrow$ γ-Fe_2O_3), and a higher temperature (424°C) phase transition (γ-Fe_2O_3 $\rightarrow$ α-Fe_2O_3). The objective of this research was to study the effects of two variables, gas flow rate and pressure, on the DSC signatures for lepidocrocite.

Materials and Methods. A Perkin Elmer DSC-7 apparatus was modified to conduct variable pressure experiments. An electronic mass flow meter and a serial vacuum pump, in conjunction with needle valves for flow control, were employed in the modifications to control the gas flow and pressure within the calorimeter oven chamber [3]. The lepidocrocite (LPS2) is a well-characterized synthetic product [4]. Three flow rates and three pressure levels were tested in a factorial combination to see the effects of the N_2 gas flow rate, pressure, and their interaction. Platinum sample ovens were used to heat samples with a temperature ramp rate of 20°C/min. Flow rates are expressed as standard cubic centimeters per minute (sccm). Additional runs were conducted at several operating conditions so that DSC runs could be stopped and analyzed for mineralogy by x-ray diffraction (XRD) analysis.

Results and Discussion. A typical DSC signature for lepidocrocite under standard DSC operating conditions (near 770 Torr N_2 and 20 sccm) is illustrated in Figure 1. The onset temperatures for the dehydroxylation and phase transition were 259°C and 424°C, respectively. Enthalpies for the dehydroxylation and phase transition were 242.7 and -76.9 J/g. These temperatures and enthalpies compare well with previously reported data for ambient operating conditions [2].

Under more Mars-like operating conditions, gas flow rates and pressures collectively affected the DSC signal for onset temperatures and enthalpies (Table 1). For example, a pressure decrease from near 770 Torr to near 70 Torr at near 4 sccm N_2 flow rates resulted in a decrease in onset temperature for the dehydroxylation endotherm from 268.6°C to 254.9°C. A further decrease in pressure to near 7 Torr at a flow rate of 4 sccm resulted in an even lower onset temperature of 248.3°C. The effect on enthalpy measurements is very evident at reduced pressures for the gas evolving transition. Enthalpies for the dehydroxylation endotherm at near 770 and 70 Torr pressure were 232.5 and 662.2

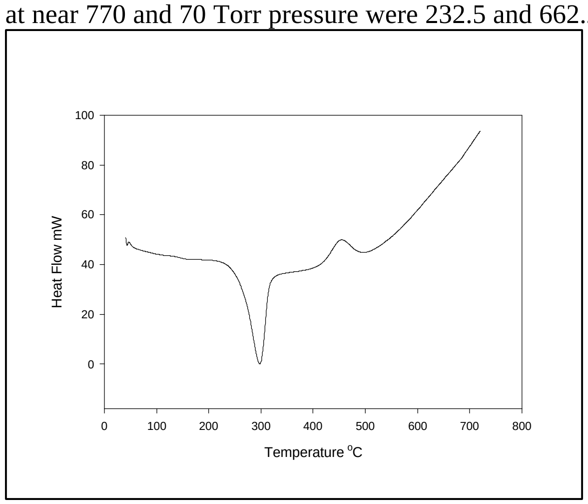

Figure 1. Differential Scanning Calorimetry (DSC) curve at ambient conditions (near 770 Torr and 20 sccm N_2 flow rate) for lepidocrocite (LPS2) showing the onset temperatures for an endoenthalpic peak near 260°C and the exoenthalpic peak near 425°C.

Table 1. Enthalpies and onset temperatures for the thermal analysis of lepidocrocite (LPS2) at varying operating pressures and gas flow rates.

	Sample			*Endotherm		#Exotherm	
Run #	Weight (mg)	Pressure (Torr)	Gas Flow Rate (sccm)	Enthalpy1 (J/g)	Onset1 (^oC)	Enthalpy2 (J/g)	Onset2 (^oC)
L760T20	11.2	771.3	19.75	242.7	259.2	-76.9	424.0
L760T4F	15.3	775.0	3.98	232.5	268.6	-92.8	428.0
L760T1F	11.1	774.0	0.39	233.9	270.4	-116.5	433.8
L760T0F	11.3	773.0	0.07	239.8	270.7	-102.7	430.3
L7020A	10.3	71.0	19.86	379.8	251.2	-105.0	485.6
L70T4FB	13.0	70.0	4.00	662.2	254.9	-112.8	481.0
L70T1FAR1	3.5	73.0	0.98	737.9	254.9	-118.4	480.0
L0720A	13.9	8.0	19.22	408.5	246.5	-119.0	484.7
L0704A	10.3	7.0	4.13	805.4	248.3	-116.1	503.6
L7T1FAR2	4.4	7.0	0.88	1163.9	247.9	-123.0	510.9

* γ-FeOOH → γ-Fe_2O_3; # γ-Fe2O3 → α-Fe_2O_3

J/g, respectively, for ~4 sccm flow rate. A further decease of the pressure to near 7 Torr at 4.1 sccm N_2 resulted in a enthalpy increase to 805.4 J/g. The increase in enthalpy signal at reduced pressures may be due to the adiabaticaly expanding gas cooling the sample holder causing it to require more heat to maintain the temperature. The maghemite to hematite phase transition (exotherm), on the other hand, exhibited an opposite trend to the endotherm. Onset temperatures for phase transition at near 770 and 70 Torr were 428.0°C and 481.0°C, respectively, at a gas flow rate near 4 sccm. The onset temperature increased to 503.6°C at even lower pressures (near 7 Torr) at a gas flow rate of 4 sccm. Enthalpies for the exotherm were somewhat changed by the reduced pressure. For example, the enthalpies at near 770 and 70 Torr were -92.8 and -112.8 J/g, respectively, for gas flow rates near 4 sccm and the enthalpy at near 7 Torr was -116.1 J/g. The reason the onset temperatures increased with decreasing pressure is not known. It is possible that the evolved heat is carried away more efficiently at high pressure than at low pressure (thermal conductivity effect).

Flow rates had a pronounced effect on both onset temperatures and enthalpies. The onset temperatures increased with decreasing gas flow rates for the dehydroxylation endotherm at near ambient pressure conditions (near 770 Torr). Onset temperatures ranged from 259.2°C at a flow rate of near 20 sccm to 270.7°C for a flow rate of 0.07 sccm. Similar effects of the gas flow rate on the onset temperature were noted for reduced pressures. Enthalpies did not change much from reduced flow rates at ambient pressures for the dehydroxylation endotherm; however, apparent enthalpies increased significantly with decreasing flow rates at reduced pressure. Enthalpies also tended to slightly increase with decreasing flow rates for the exotherm phase transition.

In the future these runs will be repeated, bracketing the 0.4 sccm flow rate (operating flow rate for TEGA) in the three pressure ranges, and replicated sufficiently to improve the statistical validity of these measurements, especially in the light of the high variability expected for DSC thermal measurements [5]. The observed changes in the data, for example, the lowering of the onset temperature with decreasing pressure, has been reported in the literature [6]. Normally, a small sample size and large surface area, slow heating rate, block sample holder, and a gas with high thermal conductivity (k) leads to higher resolution of thermal peaks. On the other hand, large sample size and small surface area, fast heating rate, isolated container, and low pressure (low k), leads to higher sensitivity [7]. In our experiments we have attempted to maintain most of these parameters constant, but the sample variation will be something which has to be dealt with in the actual Mars '98 Lander TEGA. Our data suggests that TEGA will work as intended under the instrumental operating conditions on Mars. Reduced pressure and gas flow rates will enhance enthalpy signals and should increase the sensitivity of the instrument. Additionally, the data obtained by simulated runs with modified laboratory DSCs will be useful in interpreting actual data from the Lander. We are currently developing a low-pressure DSC database of Martian analog minerals, "soils", and rocks in support of the Mars '98 Lander mission.

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