DIFFERENTIAL SCANNING CALORIMETRY AND EVOLVED GAS ANALYSIS AT MARS AMBIENT CONDITIONS USING THE THERMAL EVOLVED GAS ANALYSER (TEGA). D. S. Musselwhite[1], W. V. Boynton[1], D. W. Ming[2], G. Quadlander[1], K. E.Kerry[1], R. C. Bode[1], S. H. Bailey[1], M. G. Ward[1], A. V. Pathare[3], R. D. Lorenz[1], D. A. Kring[1], H.V. Lauer[2], Jr. and R. V. Morris[2]. Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721 (donm@lpl.arizona.edu), NASA Johnson Space Center, Mail Code SN2, Houston, Texas 77058, [3]Dept. of Earth and Space Science, University of California, Los Angeles, California 90024

Introduction: Differential Scanning Calorimetry (DSC) combined with evolved gas analysis (EGA) is a well developed technique for the analysis of a wide variety of sample types with broad application in material and soil sciences [1]. However, the use of the technique for samples under conditions of pressure and temperature as found on other planets is one of current development and cutting edge research [2,3]. The Thermal Evolved Gas Analyzer (TEGA), which was designed, built and tested at the University of Arizona's Lunar and Planetary Lab (LPL), utilizes DSC/EGA [4]. TEGA, which was sent to Mars on the ill-fated Mars Polar Lander, was to be the first application of DSC/EGA on the surface of Mars as well as the first direct measurement of the volatile-bearing mineralogy in martian soil.

Experiments: We are conducting DSC/EGA experiments at Mars ambient temperature and pressure using the TEGA engineering qualification model (TEGA-EQM). The TEGA-EQM is a high fidelity simulator of the TEGA flight model (TEGA-FM) that was sent to Mars. The TEGA-EQM is being tested in an environmental chamber capable of reproducing Mars ambient conditions of temperature and pressure. The TEGA-EQM has overall the same design of ovens, manifold plumbing, and EGA (TEGA utilizes a tunable diode laser (TDL) for EGA) and reproduces the gas flow and gas flow geometry of the TEGA-FM. The experiments conducted at LPL are complimentary to experiments done at NASA's JSC and ARC. The tests run at LPL better reproduce the total operating conditions of the TEGA on Mars. The experiments conducted at JSC and Ames utilize conventional lab-bench DSC (but adjusted for lower temperature and pressure operating conditions) and, therefore, they can turn around many more experimental runs than the TEGA-EQM at LPL.

A series of geologic samples have been run in the TEGA-EQM. The analysed materials run include: calcite, lepidocrocite, pyrolusite, hydromagnesite, and free water ice. In addition, Mars soil analogues have been run as unknowns. These illustrate both our ability to accurately determine the mineralogy of martian soil with the TEGA and some of the differences between DSC/EGA run under normal laboratory conditions and those run under Mars ambient conditions. To identify a sample run in TEGA (on Mars or as an unknown on the TEGA-EQM) the following approach is taken: 1) identify onset and peak temperatures in DSC and EGA; 2) assign preliminary composition and mineralogy; 3) run candidate mixtures in Perkin-Elmer DSC at JSC; and 4) run best guess sample in the TEGA-EQM (repeat steps 2, 3 and 4 as necessary).

Discussion: Figure 1 shows the DSC and TDL trace for a representative Mars analogue unknown which was provided to the TEGA Team by R. V. Morris. The Team knew nothing about the chemistry or mineralogy of the unknown sample during the procedure described above. The sample was run with a flow rate of 0.4 sccm yielding an oven pressure of 100 mbar N_2 (unlike a standard DSC, the flow rate and oven pressure are coupled in the TEGA). The sample was heated at 20 °C/min. Two major H_2O releases and two decarbonation events are clearly evident in the TDL data (Fig. 1). The best guess sample composition was formulated by comparing the data for the unknown sample to the large library of low pressure DSC/EGA traces produced at JSC[3]. The data for the best guess sample (Fig. 2), which was run with the same gas flow and temperature ramp rates as the unknown, match the volatile release events for the unknown sample rather well. The mineral composition for the unknown and best guess samples are listed in Table 1. The main difference between the unknown and best guess sample composition is that the best guess sample contains palagonite, which is not present in the unknown sample. The volatile-bearing phases of the unknown were revealed at the end of the 1st best guess run so no iterations of steps 2, 3 and 4 described above were performed. The palagonite was included in the best guess in order to account for the low temperature shoulder (<100°C) in the water release data of the unknown sample. It did not, in fact, reproduce the water-release shoulder well in the TEGA-EQM run and would have been eliminated in the second iterative step.

TABLE 1

Unknown #2[a]		Best Guess	
12.08%	Fe-carbonate	7.62%	siderite[b]
44.07%	Calcite	38.07%	$CaCO_3$ (reagent)[c]
12.51%	1:1 clay (kaolinite)	6.09%	kaolinite (poorly crystalline)[d]
29.06%	goethite (poorly crystaline)	27.91%	goethite (synthetic)[e]
2.27%	quartz	20.30%	palagonite[f]

sample designation, source

a British Chemical Standard, Lincolnshire iron ore BCS No. 301/1 mineral percentages calculated from chemical data
b Wards Scientific
c Fischer Scientific
d Georgia (Clay Minerals Society Reference Clay Kga-2)
e [5]
f Ken Hoblin similar type [6]

Temperatures of features in the TDL data for the unknown and the best guess are shown in Table 2 along with assigned causes of the features. Also listed are onset and peak temperatures from 1 atm DSC/EGA studies. Comparison of the onset temperatures of the

outgassing events in the unknown and best guess samples with literature values for samples run at standard pressure illustrates the effect of the lower pressure. The onset temperature for the dehydration of goethite occurs 10 to 20°C lower for the 100 mbar runs compared with 1atm runs and the dehydration of kaolinite occurs 40°C lower. Temperature of onset for the siderite decarbonation occurs 20 to 50°C lower for the 100 mbar runs compared with 1 atm runs and calcite decarbonation occurs 110 to 235 °C lower.

TABLE 2

event	T (°C) unknown	T (°C) best guess	assigned cause	T (°C) 1 atm data [7]
Onset of 1st H2O peak	200	211	goethite dehydration	220 - 400
1st H2O peak	354	331		
Onset of 2nd H_2O peak	468	469	kaolinite dehydration	510
2nd H_2O peak	527	569		600
Onset of 1st CO_2 peak	451	480	siderite decarbonation	500
1st CO_2 peak	572	587		585
Onset of 2nd CO_2 peak	685	705	calcite decarbonation	830 - 920
2nd CO_2 peak	863	889		830 - 940

Comparing the TDL data between Figures 1 and 2 we see interesting similarities and differences in detail. The relative peak heights of the 1st water release between the two samples is *exactly* what it should be given the (slight) differences in the percentage of goethite between the unknown and best guess samples. Also, the relative peak heights of the 1st and 2nd water releases for the unknown are very close to the relative proportion of water contained in the goethite and kaolinite in the unknown; however, the relative peak heights of the 2nd water release between the unknown and the best guess samples are out of proportion with respect to to their relative kaolinite contents; i.e.,. the second water release in the best guess sample is 2.5 times larger than it "should" be given the proportion of kaolinite relative to goethite in the sample. Thus, an additional high-temperature release of water has occurred in the best guess sample compared with the unknown sample. This is probably due to a difference in composition and or structure of the kaolinite in the best guess sample compared with that of the 1:1 phyllosilicate in the unknown sample. The presence of palagonite in the best guess sample may also have had an effect. The relative heights of the CO_2 release peaks both within and between the samples is fully consistent with the amount of the two carbonate types in each sample.

The enthalpy of decarbonation of the calcite can be seen in the DSC traces for the unknown and best guess samples (Figs. 1 and 2) starting just above 700°C. This corresponds with the CO_2 release seen in the TDL data.

This test of the TEGA-EQM illustrates the outstanding capabilities that a TEGA-like instrument will have on a Mars surface mission (such as the Mars Polar Lander) for detecting and identifying volatile-bearing phases.

References: [1]Hoehne et al.(1996) *Differential Scanning Calorimetry*, Springer, Berlin. [2] Golden et al. (1999) *LPSC XXX*. [3] Lauer et al. (2000) *LPSC XXXI* [4] Boynton et al. (2000) *JGR* (submitted) [5] Morris, R.V. etal, (1985) *JGR*, **90**: 3126-3144. [6] Morris etal. (2000) *JGR* (in press) [7] Blazek (1973) *Thermal Analysis* Van Nostrand Reinhold, London.