

THERMAL AND EVOLVED GAS ANALYSES AT REDUCED PRESSURES: A MINERAL DATABASE FOR THE THERMAL EVOLVED GAS ANALYZER (TEGA). H. V. Lauer Jr.¹, D. W. Ming², D. C. Golden³, I-C. Lin⁴, R. V. Morris², and W. V. Boynton⁵, ¹Lockheed-Martin SMS&S, 2400 NASA Rd1, Houston, TX 77058 (howard.v.lauer1@jsc.nasa.gov); ²SN2 NASA/JSC, Houston, TX 77058 (douglas.w.ming1@jsc.nasa.gov; richard.v.morris1@jsc.nasa.gov); ³Hernandez Engineering Inc., Houston, TX 77058 (d.c.golden1@jsc.nasa.gov); ⁴SN2 NASA/JSC; Houston; TX 77058(i-ching.lin1@jsc.nasa.gov); ⁵University of Arizona, Tucson, AZ 85721 (wboynton@lpi.Arizona.edu).

Introduction: Volatile-bearing minerals (e.g., Fe-oxyhydroxides, phyllosilicates, carbonates, and sulfates) may be important phases on the surface of Mars. The Thermal Evolved Gas Analyzer (TEGA), which was part of the Mars Polar Lander payload, was to detect and identify volatile-bearing phases in the Martian regolith. The TEGA instrument is composed of a differential scanning calorimetry (DSC) interfaced with an evolved gas analyzer (EGA) [1]. The EGA consists of a Herriott cell of a tunable-diode laser (TDL) spectrometer that determines CO₂ and H₂O abundances. The sample chamber in TEGA operates at about 100 mbar (~76 torr) with a N₂ carrier gas flow of 0.4 sccm.

Essentially no information exists on the effects of reduced pressure on the thermal properties of volatile-bearing minerals. Here we present a database for the thermal behavior of volatile-bearing phases under reduced pressure conditions.

Experimental Setup: We have developed a testbed that simulates the operating conditions of TEGA. Our testbed consists of a commercial DSC, quadrupole mass spectrometer (QMS), vacuum pump, digital pressure gauge, electronic mass flow meter, gas bottles and dryers, and high and low pressure regulators connected together using a collection of shut off and needle regulating valves. The setup has been designed to enable us to vary and control the pressure and carrier gas flow rate inside the calorimeter oven chamber.

We have selected a suite of well-characterized natural and synthetic minerals and phases to analyze in our TEGA testbed (Table 1). The sample suite includes phyllosilicates, carbonates, sulfates, Fe-oxyhydroxides, and amorphous phases. We have attempted to include all of the potential volatile-bearing phases that might be encountered on the surface of Mars. Representative samples were accurately weighed into an alumina crucible and then placed in the DSC sample chamber. The system was then closed off and pumped down to its ultimate limit using the main system vacuum pump. The system was then back-filled with an ultra pure N₂ carrier gas. The system was evacuated again and back filled with N₂ several more times to ensure that all atmospheric contamination was removed from the system. The main vacuum system was then shut off and all of carrier gas was sent to the QMS. DSC runs were conducted at a

temperature ramp rate of 20°C/min under an atmosphere near 100 Torr N₂ carrier gas flowing at 8 sccm (note: The 8 sccm flow rate was analogous to the 0.4 sccm flow rate used in the TEGA Engineering Qualification Model (EQM)). Evolved gases (H₂O, CO₂, O₂ and SO₂) were quantified in the QMS, which was previously calibrated by a suite of well-characterized geological samples.

Results: The thermal and evolved gas behaviors of the volatile-bearing minerals and phases under reduced pressure are summarized in Table 1. We have presented the peak temperatures for endothermic and exothermic events. In nearly all cases, both DSC and EGA detected thermal response events. However, in some cases, DSC events were not evident during a gas release (e.g., water evolving from 2-L ferrihydrite).

We cannot address the effects of reduced pressure for each phase presented here; however, in general, gas release events occurred at lower temperatures under reduced pressure conditions compared to ambient pressures (i.e., 760 Torr N₂). For example, the peak temperature for the dehydroxylation of lepidocrocite occurs at around 265°C under reduced pressure conditions and around 300°C at ambient pressure [2,3]. In another example, the peak temperature of the decarbonation of hydromagnesite under reduced pressure is 450°C compared to 550°C at ambient pressure [4]. The DSC heat flow curves were also very different under the two pressures [4].

The database developed here was used to identify a geologic unknown sample in the TEGA-EQM located at the University of Arizona. We were able to correctly identify the unknown sample [5]. The database presented here will be instrumental in identifying and detecting volatile-bearing phases on Mars when TEGA-like instruments are included as part of the lander payload.

References: [1] Boynton et. al, *JGR*, in press. [2] Golden D. C. et. al. (1999) *LPSC XXX, CD-ROM*. [3] Lin et. al. (2000) *LPSC XXXI, CD-ROM*. [4] Lauer Jr. H. V. et. al. (2000) *LPSC XXXI, CD-ROM*. [5] Musselwhite et. al. (2000) *LPSC XXXI, CD-ROM*.

Table 1. Thermal and evolved gas analyses (peak temperatures) of Mars analog materials under reduced pressure conditions (100 Torr N₂). Temperatures in parathensis were only detected by evolved gas analysis in the quadrupole mass spectrometer. All other reported temperatures were detected by both DSC heat flow and evolved gas analysis. Note the upper temperature of our TEGA testbed was 730 °C.

	Endotherm 1	Endotherm 2	Endotherm 3	Endotherm 4	Exotherm
	Temp/evolved gas	Temp/evolved gas	Temp/evolved gas	Temp/evolved gas	Temperature
	{°C}	{°C}	{°C}	{°C}	{°C}
Iron Oxides/Oxyhydroxides/sulfides					
Goethite synthetic (GTS5)	300 H ₂ O				
Goethite nat. (Biwabek Mn)	330 H ₂ O				
2-L Ferrihydrite	(150) H ₂ O				419
6-L Ferrihydrite	235 H ₂ O				
Akaganeite	210 H ₂ O				559
Schwertmannite	180 H ₂ O	590 SO ₂			490
Hematite					
Nanophase Hematite	(180) H ₂ O				318
Lepidocrocite	265 H ₂ O				528
Phyllosilicates					
Na-Montmorillonite (SWy-1)	(150) H ₂ O	697 H ₂ O			
Ca-Montmorillonite (STx-1)	120 H ₂ O	680 H ₂ O			
Nontronite (API-33)	150 H ₂ O	290 H ₂ O	460 H ₂ O		
Nontronite (NG-1)	400 H ₂ O				
Nontronite (SWA)	(150) H ₂ O	(275) H ₂ O	460 H ₂ O		
Kaolinite (KGa-1)	540 H ₂ O	630 H ₂ O			
Kaolinite (KGa-2)	512 H ₂ O				
Sepiolite (SepNev-1)	112 H ₂ O	260 H ₂ O	500 H ₂ O		
Vermiculite (VTx-1)	593 H ₂ O				
Sulfates					
Gypsum	119 H ₂ O				350
Kieserite	165 H ₂ O	390 H ₂ O	702 SO ₂		
Jarosite (GCJAR1)	434 H ₂ O				503, 630
H ₂ O-K Jarosite	(150) H ₂ O	(300) H ₂ O	439 H ₂ O	650 SO ₂	503, 588
Carbonates					
Calcite	>730 CO ₂				
Dolomite	>730 H ₂ O				
Magnesite	615 CO ₂				
Siderite (SIDDM)	533 CO ₂	600 CO ₂			
Siderite (SIDCS)	500 CO ₂				
Rhodocrocite (C3ML)	524 CO ₂	545 CO ₂			
Rhodocrocite (C29ML)	560 CO ₂	610 CO ₂			
Mg-Fe carbonate (solid sol'n)	613 CO ₂				
Smithsonite	495 CO ₂	>730 CO ₂			
Nesquehonite	170 H ₂ O	455 CO ₂	537 CO ₂		
Hydromagnesite	240 H ₂ O	450 CO ₂			
(NH ₄) ₂ CO ₃	95 H ₂ O, CO ₂				
Palagonites					
HWMK515	(150) H ₂ O	425 H ₂ O	600-650 SO ₂		-550
HWMK964A (Alunite+palag.)	436 H ₂ O	532 H ₂ O	>730 SO ₂		
PH13	(150) H ₂ O	>730 H ₂ O			
HWMK602	(150) H ₂ O				
Oxides/Peroxides					
Pyrolusite	600 O ₂				
BaO ₂	580 O ₂				
KO ₂	155 H ₂ O, O ₂	390 O ₂			
Sedimentary Zeolites					
Clinoptilolite	125 H ₂ O				
Chabazite	128 H ₂ O				