[Geophysical Research Letters]

Supporting Information for

[The methane diurnal variation and micro-seepage flux at Gale crater, Mars as constrained by the ExoMars Trace Gas Orbiter and Curiosity observations]

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Introduction

This SI section provides information on the Adsorptive-Diffusive Model along with the new function produced for this paper (S1).

Text S1.

Adsorptive-Diffusive Model Modifications

The adsorptive-diffusive model employed in this paper is a modified version of the model described in detail within *Moores et al.* (2019). As described in the main text, the major changes undertaken to adapt the model to the scenario described in this letter were (1) to set the background level of methane to zero outside of the thin PBL overnight and (2) to increase the resolution of the model during the overnight period. Each of these modifications will be discussed in turn. Outside of these modifications, it was seen that good matches could not be achieved if the enthalpy of adsorption of methane was set to 31.5 kJ mol^{-1}, however, a relatively wide range of lower values served provided improved fits and as such we selected the value derived in the laboratory by *Gough et al* (2010) for Mars-analogue materials of 18 kJ mol^{-1}.

(1) Setting the background level of methane to zero outside of the overnight period was achieved by forcing the atmospheric content of the atmosphere in contact with the regolith stack to zero at the end of each timestep.
(2) Increasing the resolution of the model overnight was achieved by creating a separate function with a resolution of 10 seconds, as compared to the main model which steps forward in time by 0.01 sols. Implementing this function also allowed us to sequester all additional components of the model, including the direct modeling of the expanding diffusion front and thereby the thickness of the overnight PBL. This function is provided below as implemented in Matlab and may be employed by adding a call to the function within the code available as part of *Moores et al.* (2019). Because of the smaller timestep, additional effort was expended to ensure that the temperature of the near subsurface was accurate, spinning up the temperature model over one sol previous to the start of the overnight period using REMS data appropriate to the specific observation sol (*Martinez et al., 2017*) – this was found to have relatively little impact on the result.

The new function is provided below. The main code can be found in Moores et al. (2019) and all components of the code may be downloaded from www.yorku.ca/jmoores/GRLmethane2019.zip

```
function [OvernighConc,HRtime,SAMconc] =
DiffSorpSeepOvernightHR(deltaH,setFLUX,tau,hPBL,T,intp,intf,theta,m,pCO2in,myThetaH2Oin,p
ATMin,mATMin,TMAXsurfin,IngestTime,TaATingest,atmoD)

dt = 10;         % Timesetep in seconds

setFLUX = setFLUX*dt;  % adjust flux at the bottom of the stack for the new timestep

Tg_REMS_Highest_Confidence_Means_Std_PY_Ls_Warm_1_2167
Ta_REMS_Means_Std_1_Ls_1_2167
```

```
for i = 1:length(TgIN(:,1))
    TgIN(i,1) = TgIN(i,1)+TgIN(i,2)./24;   %convert to fractional sol
end

for i = 1:length(TaIN(:,1))
    TaIN(i,1) = TaIN(i,1)+TaIN(i,2)./24;   %convert to fractional sol
end

LeadCoeff = 6.073e-6;                        %% Leading Coefficient in keq equation
lifetime = 88775*668;            %% lifetime of methane in the martian atmosphere (1
Martian year = 1.881 Earth Years)
DesCoeff = 1;
SSA = 0.3e5;                            %% Specific Surface Area 1.06e5 typical, 0.3e5
based on Meslin 2013

% Temperature Model of the Subsurface
k = 0.5;         %Heat Conductivity of the surface
rhoCp = 3.2e5;   %Consistent with TI = 400 (mks)
T0 = 233;        %Average yearly temperature at Gale

% Temporal and Spatial Meshes
N = 15;                                 %% Number of points in spatial grid
rN = N;                                 %% Number of spatial points
z = linspace(0,30,N);
rSorption = max(z);                     %% thickness of the regolith stack
r = linspace(-1.*rSorption,0,rN);       %% The radii of the points (Spatial Mesh)
dr = rSorption/(rN-1);                  %% Radiusstep
nsteps = tau/dt;                        %% Number of time steps required
time = linspace(dt,tau,nsteps);         %% Temporal mesh

% Derived/Invariant Constants between runs
R = 8.314;                              %% Universal gas constant
RstarCH4 = 8314/16;                     %% Specific Gas Constant, methane
RstarCO2 = 8314/44;                     %% Specific Gas Constant, CO2
MLmass = 1300*SSA*(1.3847e-07);         %% mass of a monolayer of methane

%Initialization of temporal and spatial meshes
deltaHsurf = deltaH;                    %% adsorptive enthalpy change at surface

OvernighConc = pATMin; %initial value of the atmospheric methane pressure
mATM = 0;
pATM = 0;

%equilibrate the temperature diurnal cycle over the previous day
TequilibTime = HRtime-88770/88775;
for n = 1:8877
    T(1) = T0;
    for j = 2:rN-1
        T(j) = T(j)+(k./rhoCp)*dt/(dr^2)*(T(j+1)-2*T(j)+T(j-1));   %% solve diffusion
equation
    end
    T(rN) = interp1(TgIN(:,1),TgIN(:,3),TequilibTime);
    TequilibTime = TequilibTime+10/88775;
end

%% TIME STEPPING
for n = 1:nsteps

    %Solve temperature diffusion
    T(1) = T0;
    for j = 2:rN-1
        T(j) = T(j)+(k./rhoCp)*dt/(dr^2)*(T(j+1)-2*T(j)+T(j-1));   %% solve diffusion
equation
    end
    T(rN) = interp1(TgIN(:,1),TgIN(:,3),HRtime(n));
    pCO2(n) = pCO2in;

    myThetaH2O(n) = myThetaH2Oin;    %Surface coverage of water, assumed constant

    keq = LeadCoeff.*exp(deltaH./(R.*T(1)))./(T(1)).^1.5;
    psi = RstarCH4*T(1)*MLmass; %Chevrier Constant
    D0 = (1e-5/3)*sqrt(8*R*T(1)/(pi*0.016));
    ch4des = DesCoeff.*exp(-45.41)*1.38e-23*T(1)/6.626e-34;
```

```
    alpha  = keq;
    dthetadp = alpha/(1+alpha*intp(1))^2*(1+(alpha*intp(1)*ch4des*dt*(1+alpha*intp(1))-
1)*exp(-1*ch4des*(1+alpha*intp(1))*dt));
    D(1) = D0/(1+psi*dthetadp);

    intf(1) = intf(2) - (setFLUX*( z(2)-z(1) )./(dt*D(1))) * ( RstarCO2*T(1)./pCO2(n) );
%% Enforce RHS Bound Cond (seep Flux = const)
    intp(1) = intf(1)*pCO2(n)*(RstarCH4/RstarCO2);

    theta(1) = keq*intp(1)/(1+keq*intp(1));            % fractional surface coverage
    m(1) = intf(1)*(pCO2(n)/(RstarCO2*T(1)))*( z(2)-z(1) ) + theta(1)*MLmass*( z(2)-z(1)
);   % total mass of methane in layer

    for j = 2:rN-1
        keq = LeadCoeff.*exp(deltaH./(R.*T(j)))./(T(j)).^1.5;

        psi = RstarCH4*T(j)*MLmass; %Chevrier Constant
        D0 = (1e-5/3)*sqrt(8*R*T(j)/(pi*0.016));
        ch4des = DesCoeff.*exp(-45.41)*1.38e-23*T(j)/6.626e-34;
        alpha = keq;

        dthetadp =
alpha/(1+alpha*intp(j))^2*(1+(alpha*intp(j)*ch4des*dt*(1+alpha*intp(j))-1)*exp(-
1*ch4des*(1+alpha*intp(j))*dt));
        D(j) = D0/(1+psi*dthetadp);

        intp(j) = intp(j)+D(j)*dt/(dr^2)*(intp(j+1)-2*intp(j)+intp(j-1));   %% solve
diffusion equation

        if(intp(j) < 0)
            intp(j) = 0;
        end

        intf(j) = (intp(j)/pCO2(n))*RstarCO2/RstarCH4;    % mass fraction of methane in
vapor
        theta(j) = keq*intp(j)/(1+keq*intp(j));            % fractional surface coverage
        m(j) = intf(j)*(pCO2(n)/(RstarCO2*T(j)))*( z(2)-z(1) ) + theta(j)*MLmass*( z(2)-
z(1) );     %% total mass of methane in layer

    end

    TMAXsurf(n) = interp1(TgIN(:,1),TgIN(:,3),HRtime(n));

    keq = LeadCoeff.*exp(deltaH./(R.*TMAXsurf(n)))./(TMAXsurf(n)).^1.5;
    psi = RstarCH4*TMAXsurf(n)*MLmass; %Chevrier Constant
    D0 = (1e-5/3)*sqrt(8*R*TMAXsurf(n)/(pi*0.016));
    ch4des = DesCoeff.*exp(-45.41)*1.38e-23*TMAXsurf(n)/6.626e-34;
    alphaTOP(n) = keq;

    dthetadpTOP(n) =
alphaTOP(n)/(1+alphaTOP(n)*intp(rN))^2*(1+(alphaTOP(n)*intp(rN)*ch4des*dt*(1+alphaTOP(n)*
intp(rN))-1)*exp(-1*ch4des*(1+alphaTOP(n)*intp(rN))*dt));

    D(rN) = D0/(1+psi*dthetadpTOP(n));

    intf(rN) = (intp(rN)/pCO2(n))*RstarCO2/RstarCH4;    % mass fraction of methane in
vapor
    fluxIN(n) = dt*D(rN-1)*(pCO2(n)/(RstarCO2*T(rN-1)))*(intf(rN-2)-intf(rN-1))./( z(2)-
z(1) );    % flux from below

    hPBL = sqrt(6*atmoD*n*dt);  % new PBL height
    airTemp = interp1(TaIN(:,1),TaIN(:,3),HRtime(n));
    pATM(n) = mATM(n)*RstarCH4*airTemp/hPBL;

    ch4ads = keq*ch4des;

    chi = keq*RstarCH4*TMAXsurf(n)*MLmass*(z(2)-z(1))/hPBL; %constant for calculating
deltheta
    mTotal = theta(rN)*MLmass*(z(2)-z(1))+mATM(n);  %total mass in surface-atmosphere
interacting
    m(rN) = mTotal*chi/(1+chi); % solve for ideal mass in adsorbed layer
    newTheta  = m(rN)/(MLmass*(z(2)-z(1))); %convert that mass to fractional adsorption
    deltheta(n) = newTheta - theta(rN);
```

```
    %check desorption kinetics
    if(deltheta(n) < 0 )
        if( deltheta(n) < -1*ch4des*theta(rN)*dt )
            deltheta(n) = -1*ch4des*theta(rN)*dt;
        end

        %the regolith cannot give up more methane than it has
        if(deltheta(n) < -1*theta(rN) )
            deltheta(n) = -1*theta(rN);
        end
    end

    if(deltheta(n) > 0 )    %if deltheta is < 0  it is giving up mass to the atmosphere,
so we don't consider that case
        if( deltheta(n) > dt*ch4ads*pATM(n)*(1-theta(rN)) )
            deltheta(n) = dt*ch4ads*pATM(n)*(1-theta(rN));
        end
        if( deltheta(n)*MLmass*( z(2)-z(1) ) > mATM(n) )
            deltheta(n) = mATM(n)/( MLmass*( z(2)-z(1) ) ); % the top layer of regolith
cannot gain more mass than the atmosphere has available
        end
    end

    theta(rN) = theta(rN)+deltheta(n);

    delH2Otheta = 0;

    if(theta(rN) < 0)
        theta(rN) = 0;
    end

    delATMO(n) = -1*deltheta(n)*MLmass*(1-myThetaH2O(n)) + fluxIN(n);

    mATM(n+1) = mATM(n)+delATMO(n) ;  % add the mass that moves to the atmosphere,
adjusted for water vapor
    if(mATM(n+1) < 0 )
        mATM(n+1) = 0;
    end

    pATM(n+1) = mATM(n+1)*RstarCH4*TMAXsurf(n)/hPBL;

    intp(rN) = theta(rN)/keq;
    intf(rN) = (intp(rN)/pCO2(n))*RstarCO2/RstarCH4;    % mass fraction of methane in
vapor

    OvernighConc(n+1) = pATM(n+1)./pCO2(n);
    HRtime(n+1) = HRtime(n) + dt./88775;
end

SAMconc = OvernighConc(length(OvernighConc));
```

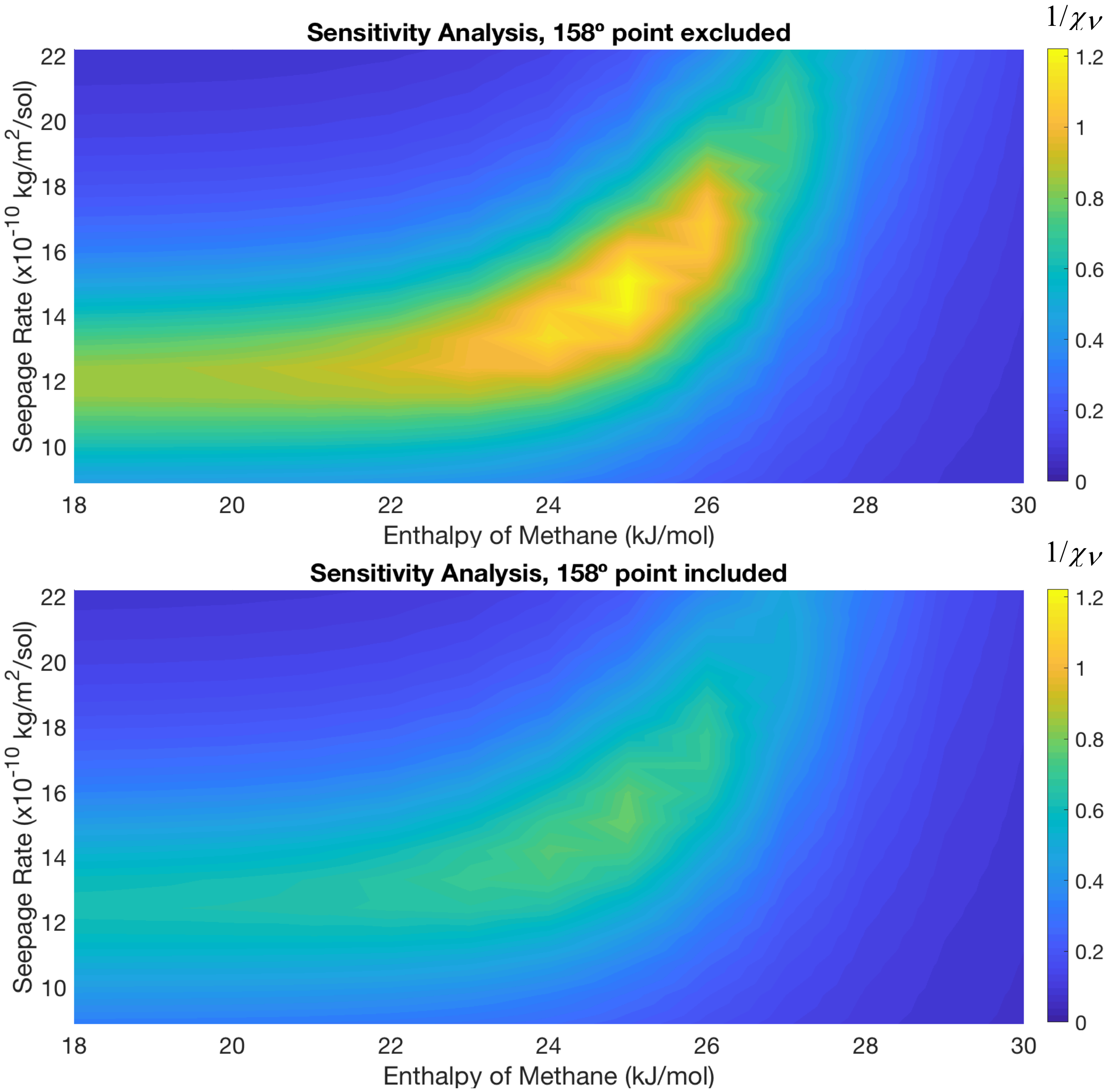

Figure S1.

Solution Sensitivity Results

Caption: To find the best combination of adsorption enthalpy and seepage rate, the code described in section 3.2 and text S1 was run at a variety of different values of both variables. Peaks in the value of the reduced chi-squared statistic were seen both in cases where the L_S = 158º point was either excluded as an outlier (top panel) or included as a part of the set (bottom panel). The value for L_S = 331º was excluded in both cases, as described in the main text. In both cases, the best fit (greatest value of $1/\chi_\nu$, shown in yellow) was seen at similar values of the adsorption enthalpy and seepage rate: approximately 25 kJ mol^{-1} and 1.5 x 10^{-10} kg m^{-2} sol^{-1}. Where 158º was excluded, the best fit is characterized by χ_ν= 0.820, corresponding to a goodness of fit of 0.547 whereas for the inclusive analysis, χ_ν= 1.28 producing a goodness of fit of 0.165. Both values indicate the results are consistent with a constant source at depth.

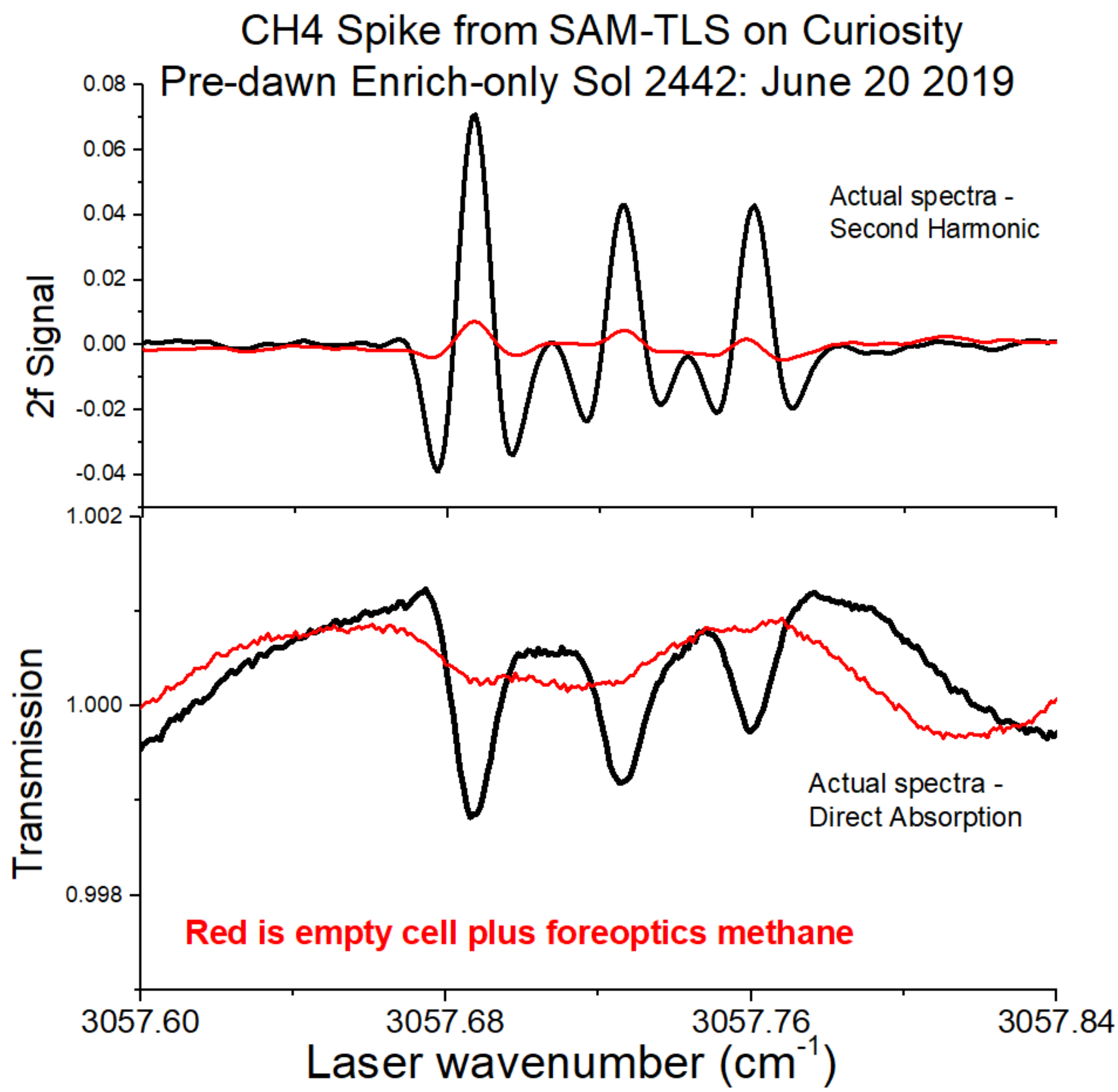

Figure S2.

High Methane Result on Sol 2442

Caption: An enrichment run was completed on Sol 2442 with gas ingest beginning at 03:53 LMST (2442.16) in order to test the theory of this paper that methane concentration should increase overnight towards dawn. The completed run shows exceptionally high methane content, 19.5 ± 0.18 ppbv at the 1 SEM level (at the 95% confidence interval, 2 SEM, the value for the sol 2442 spike is 19 ± 3.0 ppbv). In both panels, the black curve shows the full cell while the red curve shows the empty cell plus the methane present in the fore-optics (for details on the measurement protocol, please consult *Webster et al., 2018*). Note that the absorption is seen clearly in both the direct transmission (bottom) as well as the high signal-to-noise 2nd harmonic (top). The high value of methane observed strongly suggests a plume event was taking place at this time.