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1 **Independent confirmation of a methane spike on Mars and a source region east**  
2 **of Gale Crater**

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20 † This paper is dedicated to the memory of our wonderful colleague, Dr. Vittorio Formisano, former  
21 PI for PFS-Mex, who recently passed away.

23 **Reports of methane detection in the Martian atmosphere have been intensely debated. The**  
24 **presence of methane could enhance habitability and may even be a signature of life. However,**  
25 **no detection has been confirmed with independent measurements. Here we report a firm**  
26 **detection of  $15.5 \pm 2.5$  parts per billion by volume of methane in the Martian atmosphere**  
27 **above Gale crater on 16 June 2013, by the Planetary Fourier Spectrometer onboard Mars**  
28 **Express, one day after the in-situ observation of a methane spike by the Curiosity Rover.**  
29 **Methane was not detected in other orbital passages. The detection uses improved**  
30 **observational geometry as well as more sophisticated data treatment and analysis, and**  
31 **constitutes a contemporaneous, independent detection of methane. We perform ensemble**  
32 **simulations of the Martian atmosphere, using stochastic gas release scenarios to identify a**  
33 **potential source region east of Gale crater. Our independent geological analysis also points to**  
34 **a source in this region, where faults of Aeolis Mensae may extend into proposed shallow ice of**  
35 **the Medusae Fossae Formation and episodically release gas trapped below or within the ice.**  
36 **Our identification of a likely release location will provide focus for future investigations into**  
37 **the origin of methane on Mars.**

38

39 Since its discovery in the Martian atmosphere<sup>1-4</sup>, there has been a continuing debate about  
40 the origin of methane (CH<sub>4</sub>), and several generation mechanisms, both abiotic and biotic, have been  
41 proposed<sup>5-17</sup>. Despite various detections reported by separate groups and different experiments, the  
42 methane debate still splits the Mars community. Although plausible mechanisms have been  
43 proposed to explain the observed abundance, variability, and lifetime of methane in the current  
44 Martian atmosphere<sup>18-34</sup>, doubts about its very existence still arise. Previous detections have been  
45 considered tentative<sup>35</sup> due to either the challenge of discriminating telluric and Martian features  
46 when observing from Earth (claims later rebutted<sup>23</sup>) or the limited spectral resolving power and/or  
47 signal-to-noise ratio of space-borne observations<sup>18-20</sup>. In-situ detection of CH<sub>4</sub> at Gale crater<sup>4</sup> by the  
48 Tunable Laser Spectrometer-Sample Analysis at Mars (TLS-SAM) on Curiosity has also been

49 questioned<sup>36</sup> as potentially coming from the rover itself, although that possibility was ruled out by  
50 the Curiosity team<sup>24</sup>. However, while several non-detections have been reported, none of the  
51 positive detections have been confirmed so far with independent measurements.

52

### 53 **Methane detection by the Planetary Fourier Spectrometer (PFS)**

54 The Mars Express (MEx) spacecraft<sup>37</sup> was designed to operate in several science pointing  
55 modes, including nadir pointing and spot pointing. Most PFS<sup>38</sup> observations are acquired in nadir  
56 pointing<sup>2,18,19</sup>. The spot-tracking mode, which points the optical instruments to a surface feature on  
57 Mars and tracks it, was exploited in this study for the first time. These observations are particularly  
58 suitable for methane retrievals because they allow acquisition of several hundred spectra over one  
59 area in a relatively short time (typically a few tens of minutes). The ensemble average of these  
60 measurements enhances the statistical importance of the PFS observations, as detailed in the  
61 Supplementary Information (noted hereafter SI). In Supplementary **Table S1**, we summarize the list  
62 of spot-tracking observations over Gale crater performed by the PFS from December 2012 to July  
63 2014, which roughly corresponds to the first 20-month period of methane measurements at Gale  
64 crater by Curiosity's TLS-SAM<sup>4</sup>.

65 PFS observed elevated levels of methane of  $15.5 \pm 2.5$  ppbv, column-integrated abundance,  
66 in orbit 12025, on June 16, 2013 (**Table 1**). This date just follows Martian solar day (*sol*) 305 after  
67 the landing of the Curiosity rover<sup>24</sup>, when the TLS-SAM also reported a methane spike of  $5.78 \pm$   
68  $2.27$  ppbv. Our results, therefore, provide the first contemporaneous detection of methane in the  
69 Martian atmosphere by *in situ* and remote sensing measurements. In **Fig. 1a**, we show the PFS  
70 average spectrum for orbit 12025 (280 measurements collected in about 45 minutes in spot-tracking  
71 mode) compared to synthetic best-fit spectra. In **Fig. 1b** we subtract the synthetic best-fit spectrum  
72 with no methane to the PFS spectrum. The CH<sub>4</sub> absorption band observed by PFS becomes evident  
73 in the differential spectrum (**Fig. 1b**). The relatively high spectral resolution and the new data

74 handling allow unambiguous identification of the CH<sub>4</sub> Q-branch at 3018 cm<sup>-1</sup> by the PFS near-  
75 infrared spectra. Considering the 1-σ uncertainty, methane abundances ranging from 13 to 18 ppbv  
76 are consistent with the observed intensity of the CH<sub>4</sub> absorption band. A detailed description of the  
77 new PFS data treatment and of the improved characterization of the PFS apodized instrument line  
78 shape is reported in in SI-1. The algorithm adopted for the CH<sub>4</sub> retrievals is described in the  
79 Methods section.

80 In the almost two-year period of spot-tracking observations reported here (22 in total), there  
81 was no other occasion on which PFS made a positive detection of methane over Gale crater (see  
82 **Table S1**). PFS did not perform any spot-tracking observation during the second TLS-SAM high-  
83 methane period (sol 466 to sol 526), but there are 10 spot-tracking observations in the later period  
84 when no methane was detected, with a detection limit of 2-4 ppbv. This is consistent with the low  
85 methane measurements by TLS-SAM in the same period. In addition, no evidence of methane was  
86 found in 3 nadir observations performed a few days apart from sol 306 in the area surrounding Gale  
87 crater (**Table 1 and Fig. S12a**). An example of non-detection is shown in **Fig. S12b** for MEx orbit  
88 12018 (one sol before the TLS-SAM spike detection on sol 305, **Table 1**). An upper-limit of 3 ppbv  
89 of CH<sub>4</sub> is retrieved from the average of 276 PFS measurements collected in this orbit.

90

### 91 **The search for CH<sub>4</sub> source regions**

92 The contemporaneous detection of methane provides unique information to use in search for  
93 its source locations. The available data in a 14-sol time window (Sols 304 – 318; **Table 1**) provide  
94 evidence that the sol 305-306 observations by the PFS and the TLS-SAM sampled the same  
95 methane release event, and that this event is limited in time. Although several production  
96 mechanisms and sources of methane have been discussed in the literature<sup>6-17</sup>, terrestrial analogues  
97 argue that subsurface accumulations are the most likely sources (see SI-2). Subsurface methane  
98 could have been produced by either abiotic or biotic processes and stored in clathrates, zeolites, or

99 reservoir rocks (any permeable or fractured rock) sealed by permafrost or other impermeable rocks  
100 before being outgassed through fractures and faults<sup>16</sup>. Accordingly, in this paper, we focus on the  
101 hypothesis of surface release. Exogenous processes that may add methane to the Martian  
102 atmosphere<sup>17</sup> are not considered in this work.

103         It was argued that a gas emission possibly explaining the detection by TLS-SAM on sol 305  
104 was most likely weak and local (possibly inside the crater) and took place to the north of Curiosity  
105 because the prevailing daytime near-surface winds are southwards<sup>4</sup>. However, the vertically-  
106 integrated methane abundance measured by PFS one sol later changes our understanding of the  
107 release event. The amount of methane measured by PFS corresponds to ~39-54 tonnes that were  
108 present in the area of ~49,000 km<sup>2</sup> observed from orbit (**Fig. 2**). The combination of PFS and TLS  
109 observations strongly suggest that the emission took place outside the crater (see SI-3), making a  
110 general circulation model (GCM) an appropriate choice for a first interpretation of these  
111 observations. To simulate methane transport, we applied the three-dimensional GEM-Mars  
112 model<sup>28,40,41</sup> (see Methods). Wind fields simulated in the GCM show a variability with local time  
113 and with height (see **Fig. S17**), increasing the complexity of methane transport compared to  
114 previous assumptions<sup>4</sup>.

115         The search for the source of methane based on a few observations is an under-constrained  
116 problem. The constraints provided by the available observations (**Table 1**) suggest that the release  
117 event was relatively short and occurred not very far from the crater. Methane released from a  
118 localized source would rapidly disperse<sup>28</sup> whereas a distant source would require very large  
119 amounts of methane to be emitted, which is inconsistent with the observations. Preliminary model  
120 tests led to the following assumptions that restrict the problem: (i) the source is unlikely to be more  
121 distant than ~800 km from the crater, and (ii) the emission did not start prior to sol 302. We  
122 considered 30 model grid cells within a 24°×20° area centered at Gale as potential emission sites  
123 (**Fig. 2**). The problem remains weakly constrained as no direct information is available on the

124 source's location, and the initial time, duration, temporal variations and strengths of gas fluxes  
125 characterizing the release pattern. For this reason, we developed an *ensemble approach* considering  
126 a very large sample of possible emission scenarios in order to identify the most likely sources *in*  
127 *terms of probability*.

128 We considered methane emission patterns (release intensity, duration, temporal variation)  
129 that are based on gas seepage theory and consistent with methane seepage phenomena observed on  
130 Earth<sup>42</sup> (see SI-2 for details). We assumed an “episodic” seepage scenario for the methane release  
131 (**Fig. S7**), which is most consistent with previous detections<sup>1-4</sup>. An episodic emission may be  
132 characterized by one single major pulse or a series of short-term seepage oscillations (SI-2). From  
133 each of the 30 possible emission sites considered in the model, a series of 30-minute-long methane  
134 pulses was applied for a total duration of 5 sols (from sol 302 to 307). Exploiting the linear  
135 additivity of the methane tracers (as the methane is chemically inert on the considered timescale,  
136 and the feedback of methane on the atmospheric dynamics is negligible), the tracers were linearly  
137 combined by random numbers to produce release scenarios composed of stochastic fluxes. A total  
138 of  $10^6$  different combinations was generated for each of the 30 considered release sites. For these  
139 patterns, the initial times and durations of emission were also generated randomly. As a result, the  
140 constructed episodic emission scenarios last from 30 minutes to 5 sols. The large number ( $10^6$ ) of  
141 emission scenarios considered in each of the model grid cells forms a statistically representative  
142 sample of all possible release scenarios from a specific site (**Fig. S16**).

143 The simulated scenarios were then compared with the observational constraints in **Table 1**.  
144 The number of scenarios consistent with the observations divided by the sample size then gives the  
145 probability that a methane release from a given emission site fits the observations (see Methods).  
146 The result is shown in a *probability map* (**Fig. 3**). Sites to the north, west and south-west of Gale  
147 have no significant probability for being source locations. The sites to the east and south-east of  
148 Gale crater yield the highest probabilities as source locations, especially Blocks E8 and ESE with

149 probabilities of 42.4% and 54.0%, respectively, meaning that about half of all the generated  
150 emission patterns released from these sites can reproduce the entire set of observations in **Table 1**.  
151 The total mass of methane released from E8 (ESE) in 95% of scenarios fitting the observations is  
152 1,170 – 2,740 tonnes (1,590 – 4,050 tonnes), which corresponds to an enhancement of ~0.1 – 0.3  
153 ppbv (0.2 – 0.4 ppbv) to the global mean mixing ratio, after the gas is well-mixed around the planet.  
154 These abundances can be considered as upper limits for the mass released, given the coarse  
155 resolution of the GCM.

156

### 157 **Geological context**

158 We investigated the Martian geological context in search of structures that might be  
159 associated with methane release (e.g., faults, hydrothermal-volcanic vents, springs, and mud  
160 volcanoes<sup>16</sup>), applying knowledge of relationships between gas seepage and tectonic/morphological  
161 structures, as observed on Earth<sup>42</sup>. Gas seepage occurs along faults, of any type, regardless the  
162 tectonic conditions. Details of terrestrial gas seepage and geological assessment of the Martian area  
163 of interest determined from atmospheric modelling (**Fig. 2**) are provided in SI-2. Conclusions about  
164 relative merits of different grid blocks were reached independently from the GCM analysis, by a  
165 separate team.

166 Potential methane release structures were identified along the eastern side of the grid, in  
167 Block E8 and subordinately in Blocks ENE, E12, ESE, and ESEE (**Fig. 4**). Block E8 includes the  
168 Noachian-Hesperian fretted terrain of Aeolis Mensae<sup>43</sup> in contact with the younger, Hesperian-  
169 Amazonian, Medusae Fossae Formation (MFF) and in close proximity to locations where the MFF  
170 has been proposed to contain shallow bulk ice (from water-equivalent-hydrogen > ~26%<sup>44</sup>). Since  
171 permafrost is one of the best seals for methane<sup>16</sup>, it is possible that bulk ice in the MFF may trap  
172 and seal subsurface methane. That methane could be released episodically along faults that break  
173 through the permafrost due to partial melting of ice, gas pressure build-up induced by gas



174 accumulation during migration, or stresses due to planetary adjustments or local meteorite impact<sup>16</sup>  
175 (see also SI-2). The distribution of geological outcrops suggests that Aeolis Mensae deposits  
176 underlie the area of bulk ice (**Fig. 4**). Faults of Aeolis Mensae, being associated with the Martian  
177 dichotomy, may be deeply rooted<sup>16</sup> (SI-2) and may have provided long-lived conduits for migrating  
178 methane and liquid water, the latter perhaps contributing to accumulation of shallow ice in the  
179 MFF. In addition, the many fault intersections of Aeolis Mensae may enhance permeability and thus  
180 degassing, as on Earth<sup>42</sup>. Several lineations appear to offset dunes and yardangs in the MFF of  
181 Block E8 (**Fig. S8**) and may be relatively recent. These lineations have orientations similar to faults  
182 of Aeolis Mensae and may be surface expressions of reactivated Aeolis Mensae/dichotomy faults at  
183 depth, providing pathways for gas seepage through an otherwise sealing permafrost.

184         Blocks ESE and ESEE contain extensions of Aeolis-Mensae dichotomy faults in their north-  
185 eastern and northern portions, respectively. Block ESE is farther from the bulk ice (**Fig. 4**) than  
186 Block E8, and Block ESEE is still farther. Block ESE however contains unusual flow-like  
187 structures (**Fig. S8**), and work is continuing to assess whether these might be methane-release  
188 structures. Other blocks are of lesser merit (see SI-2).

189         Thus, the eastern sector of the grid contains features that could trap subsurface methane and  
190 account for its present-day, episodic release. Of these, Block E8 is the highest ranked, as it has  
191 potentially recent faults closest to the proposed ice. Because the area affected by faults and ice is  
192 large ( $10^2$ - $10^4$  km<sup>2</sup>; **Fig. 4**), methane flux from either diffuse microseepage or seeps along faults in  
193 the ice could account for the methane detected by the PFS (see SI-2 and **Fig. S10**).

194

## 195 **A first step to understanding the origin of methane on Mars**

196         This work presents the first independent confirmation of methane detection on Mars and the  
197 first synergistic approach to the search for potential sites of methane release, integrating orbital and  
198 ground-based detections with Martian geology and atmospheric simulations (using gas emission

199 scenarios based on terrestrial seepage data). This approach provides a template for future efforts  
200 aimed at locating sites on Mars of methane release from the subsurface. While this work relies on  
201 the hypothesis of a surface release, other explanations remain possible, but given a surface release,  
202 our work provides the first constraints for source locations.

203         The results of the GCM and geological analyses are remarkable, as each line of investigation  
204 independently pointed to the same area east/southeast of Gale as the most likely source location for  
205 the methane (**Figs. 3-4**). Block E8 is singled out, as it contains multiple faults and fault intersections  
206 of Aeolis Mensae along with possible extensions of those faults into proposed shallow ice in the  
207 overlying MFF. Such ice could have sealed subsurface methane and recent reactivation of Aeolis  
208 Mensae/dichotomy faults could have penetrated the ice, episodically opening enhanced release  
209 pathways.

210         The results presented in this work not only corroborate previous detections by Curiosity but,  
211 in a broader perspective, might change our view of methane occurrence on Mars. Rather than by  
212 large emissions and a global presence, our data suggest that the presence of methane on Mars might  
213 be characterized by small, short emissions and transient events. This possibility has been raised  
214 before<sup>35,42</sup>, but further investigations are required to understand processes of rapid methane loss and  
215 reconcile these new PFS findings with the anticipated TGO results<sup>47</sup>.

216         We do not address the ultimate origin of the detected Martian methane. Many abiotic and  
217 biotic processes can generate methane on Mars<sup>6-17</sup>. However, the first step to understanding the  
218 origin of any Martian methane is to determine its release location. From there, detailed follow-up  
219 should eventually reveal the mode of generation and significance of detected methane<sup>48</sup>. The PFS  
220 instrument will continue its monitoring of the Martian atmosphere. The new approach, described  
221 here, to PFS data selection, processing and retrieval will also be applied to the entire PFS dataset for  
222 a complete re-analysis. In addition, spot-tracking observations will be performed over geologically-  
223 determined potential source regions of methane, including the region identified in this work,

224 providing a test of the model of subsurface release. The ExoMars Trace Gas Orbiter payload<sup>49,50</sup>  
225 will also continue its search for methane from Mars orbit, and coordinated observations with PFS  
226 are being planned.

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362

363 **Author Contributions**

364 M.G. and S.A. developed the new approach to PFS data selection and treatment. M.G. performed  
365 the CH<sub>4</sub> retrieval. A.A., P.W. and S.A. supervised the PFS science operations, planning,  
366 commanding, and data archiving. A.C.-M. provided ancillary data and other geometrically relevant  
367 models for PFS and MEx through the SPICE software suite. A.C.-M., J.M.-Y.P. and D.M.  
368 contributed to the planning of PFS observations and to the successful implementation and execution  
369 of PFS spot-tracking observations. V.F. developed the concept and was the former PI for PFS-MEx.  
370 S.V., F.D. and L.N. developed and performed the GCM simulations and analysis. G.E. and D.O.  
371 performed the geological analysis and the evaluation of terrestrial seepage patterns. M.A. were  
372 responsible for the PFS-MEx project from the Italian Space Agency side. All authors contributed to  
373 interpretation of the results and the preparation of the manuscript.

374

375 **Competing interests**

376 The authors declare no competing interests.

377

378 **Figure captions**

379

380 **Fig. 1 | PFS retrieval of CH<sub>4</sub> abundance from orbit 12025.** **a**, Synthetic best-fit spectra (black  
381 curves) are compared to the PFS average spectrum (red). H<sub>2</sub>O abundance is 350 ppm in all spectra.  
382 Water vapor and solar lines are also indicated. **b**, The best-fit synthetic spectrum with 0 ppbv of  
383 methane shown in **a** is subtracted from the PFS average spectrum (black) and from the synthetic  
384 spectra with 13 and 18 ppbv of methane (red and blue curve, respectively). The orange line marks  
385 the zero level. 1- $\sigma$  error-bars are shown in (a) and (b) (see SI-1 for details).

386

387 **Fig. 2 | Location map and regional setting.** Basemap, MOLA elevation on MOLA Hillshade.  
388 White grid is area of interest from atmospheric modelling. Red lines, extensional faults; blue lines,  
389 compressional faults<sup>39</sup>. Black outline around Gale crater is the envelope of PFS footprints for orbit  
390 12025. Yellow triangle, location of the Curiosity rover.

391

392 **Fig. 3 | Probabilities estimated for the 30 emission sites.** The probability is defined as the number  
393 of release scenarios consistent with the observations divided by the sample size. Basemap as in **Fig.**  
394 **2.**

395

396 **Fig. 4 | Geological context of grid blocks.** MFF, Medusae Fossae Formation. Black dots, sites with  
397 Water-Equivalent-Hydrogen > 26 %<sup>44</sup>. Dark red line, outline of lower member of MFF. Green line,  
398 aligned knobs<sup>45,46</sup>. Black arrows, Aeolis Mensae outcrops within the MFF. Yellow triangle,  
399 Curiosity rover location. Basemap, stretched MOLA elevation over MOLA Hillshade.

400

401 **Methods**

402

403 *Computation of synthetic spectra and CH<sub>4</sub> retrieval algorithm.*

404 We developed an algorithm to retrieve methane abundance (volume mixing ratio, vmr) on Mars  
405 from the PFS SWC spectra. The algorithm includes a radiative transfer (RT) code developed for the  
406 analysis of PFS SWC spectra with a full treatment of the multiple scattering (MS) problem. The  
407 retrieval algorithm relies on the Levenberg-Marquardt approach<sup>51,52</sup>.

408 The computation of synthetic spectra relies on the DISORT (Discrete Ordinates Radiative  
409 Transfer Program for a Multi-Layered Plane-Parallel Medium) solver implemented in the ARS  
410 code<sup>53</sup> and specifically developed for the analysis of PFS spectra. DISORT is a general and versatile  
411 plane-parallel radiative transfer program applicable to problems from the ultraviolet to the radar  
412 regions of the electromagnetic spectrum<sup>54</sup>, which includes a full treatment of atmospheric multiple  
413 scattering by suspended particles. The synthetic spectra are obtained performing the line-by-line  
414 computation and then filtering the result with the newly retrieved PFS apodized instrumental line  
415 shape (ILS) described above. We use HITRAN 2012<sup>55</sup> as spectroscopic database. The absorption  
416 coefficients  $k(\nu, p, T)$  at the  $i$ -th atmospheric layer [ $\text{cm}^{-1}$ ] are defined as:

417 
$$k_i(\nu, p, T) = \text{ACS}_i(\nu, p_i, T_i) \cdot n_i$$

418 where  $\nu$  is the wavenumber [ $\text{cm}^{-1}$ ],  $p_i$  and  $T_i$  are the pressure [mbar] and the temperature [K] at the  $i$ -  
419 th layer, respectively.  $\text{ACS}_i$  is the absorption cross section calculated from HITRAN 2012 using a  
420 Voigt profile [ $\text{cm}^{-1}/(\text{molecule} \times \text{cm}^{-2})/\text{cm}^{-1}$ ] and  $n_i$  is the number density [ $\text{cm}^{-3}$ ] calculated from the  
421 pressure and temperature using the perfect gas law. The absorption coefficients are calculated using  
422 a line-by-line approach<sup>54</sup>.

423 The use of an appropriate solar spectrum is also important for analysis of infrared spectra, in  
424 particular with relatively high spectral resolution, because Fraunhofer lines mix up with H<sub>2</sub>O  
425 absorption features in the considered spectral range. The PFS team has made a significant effort to

426 construct a high-resolution Solar spectrum<sup>56</sup> used in this analysis. The commonly used spectrum<sup>57</sup>  
427 has disadvantages, being either purely theoretical within the H<sub>2</sub>O bands, and undersampled for our  
428 purpose (1-cm<sup>-1</sup> bins).

429 In order to calculate the synthetic spectra, a series of parameters that describe the atmospheric  
430 layers at the time of the observations must be specified as input parameters to the RT code. The  
431 initial guess for the H<sub>2</sub>O abundance (vertical profile) and the surface pressure are the only  
432 parameters extracted from the General Circulation Model (EMCD v5.2<sup>58,59</sup>), at the time (Solar  
433 Longitude L<sub>s</sub>, and Local Time LT) and location (latitude and longitude) of the PFS measurements.  
434 For the surface pressure we make use of pres0, a routine to estimate surface pressure with high  
435 accuracy, using high resolution (32pix/deg.) MOLA topography, provided with EMCD 5.2. The  
436 initial abundance of methane is set to 0 ppbv. All the other relevant atmospheric, namely the  
437 atmospheric temperature profile as a function of pressure and altitude, the surface temperature, and  
438 the integrated dust and water ice opacity, are retrieved<sup>60,61</sup> from the PFS LWC measurements  
439 acquired simultaneously to those of the SWC used for the CH<sub>4</sub> retrievals.

440 In order to retrieve methane abundance, the synthetic spectra calculated as described above, are  
441 best-fitted to the PFS average spectra. The retrieval algorithm relies on the minimization of the sum  
442 of the squares of the differences between the measured radiances and a parameterized function  
443 (least squares problem). To solve the nonlinear least squares problem, we adopted the Levenberg-  
444 Marquardt approach<sup>51,52</sup>.

445 To retrieve methane mixing ratio we use PFS SWC average spectra in the reduced spectral  
446 range 3001 – 3031 cm<sup>-1</sup>, which includes several absorption bands of water vapor, a Solar band, and  
447 the CH<sub>4</sub> Q-branch at 3018 cm<sup>-1</sup> (e.g., **Figs. S2, S5 and S6**). Three parameters are considered in the  
448 iterative retrieval: the surface albedo, the water abundance, and the methane mixing ratio. The  
449 goodness of fit between radiance measurements and synthetic spectra is checked at each iteration by

450 using chi-squared error criterion  $\chi^2(a)$ . The improvements  $\Delta a$  of a retrieved parameter  $a$  are  
451 performed by using the non-dimensional scalar factor  $\lambda$  presented in the formula:

452

$$453 \quad [J^T W J + \lambda \cdot \text{diag}(J^T W J)] \cdot \Delta a = J^T W (y - y') \quad (\text{Eq. 1})$$

454

455 where:

456  $J$  – Jacobian matrix, derivative of fitted function with respect to each parameter;

457  $W$  – inverse of the measurement error covariance matrix;

458  $y$  – measured spectrum;

459  $y'$  – synthetic spectrum.

460

461 The steps required and implemented in our algorithm for the Levenberg-Marquardt approach<sup>62</sup> can  
462 be summarized as follows:

463 1) Calculate the  $\chi^2(a)$  using a first-guess of the parameters  $a$  to be retrieved;

464 2)  $\Delta a$  is calculated by **Eq. 1** assuming an initial modest value for  $\lambda$  in the first iteration:  $\lambda = \lambda_0$ ;

465 3) calculate the synthetic spectrum with updated parameters  $a + \Delta a$ ;

466 4) evaluation of  $\chi^2(a + \Delta a)$ ;

467 5) update value of  $\lambda$ :

468 a. if  $\chi^2(a + \Delta a) \geq \chi^2(a)$ , increase  $\lambda$  by a “substantial” factor  $f_+$ :  $\lambda_{i+1} = \lambda_i \cdot f_+$ , ( $i$  is the  
469 iteration number);

470 b. if  $\chi^2(a + \Delta a) < \chi^2(a)$ , decrease  $\lambda$  by a “substantial” factor  $f_-$ :  $\lambda_{i+1} = \lambda_i / f_-$ ;

471 6) repeat steps 3) to 5) until final solution is approached;

472 7) the algorithm is stopped when the convergence criterion is reached.

473

474 The Levenberg-Marquardt parameters  $\lambda_0$ ,  $f_+$ , and  $f_-$  have been estimated from preliminary tests  
475 on the retrieval algorithm by assuming a wide range of possible values and by the comparison of  
476  $\chi^2(a)$  and  $\chi^2(a + \Delta a)$  in the various iterations. A good compromise between accuracy of retrieval  
477 (minimization of  $\chi^2(a)$ ), number of iteration required to reach the convergence criterion, and the  
478 required computational time is found for the following values of the above parameters, which have  
479 been adopted in the final implementation of the algorithm:  $\lambda_0=10^{-2}$ ;  $f_+=10^5$  and  $f_- = 10$ .

480 Also necessary is a condition for stopping. Iterating to convergence (to machine accuracy or to  
481 the round-off limit) is generally wasteful and unnecessary since the minimum is at best only a  
482 statistical estimate of the parameters ( $a$ ). A change in the parameters that changes  $\chi^2$  by an amount  
483  $\ll 1$  is never statistically meaningful<sup>61</sup>. In practice, it is recommended to stop iterating on the first  
484 or second occasion that decreases by a negligible amount, being either less than 0.01 absolutely or,  
485 in case round-off prevents that being reached, some fractional amount like  $10^{-3}$  <sup>(62)</sup>. It is also  
486 recommended to avoid a stop after a step where  $\chi^2$  increases: that only shows that it has not yet  
487 adjusted itself optimally<sup>61</sup>. In our case, as a convergence criterion we stop iterating when the  
488 following conditions are satisfied:  $\chi^2(a + \Delta a) - \chi^2(a) < 0$  and  $|\chi^2(a + \Delta a) - \chi^2(a)| < \chi^2(a + \Delta a) \cdot 10^{-3}$ .

489 We applied the retrieval algorithm described above to the PFS spot-tracking observations over  
490 Gale crater listed in **Table S1** as well as to the standard nadir observations listed in **Table 1**. Only  
491 dayside observations with  $> 200$  measurements were considered. Methane is only detected in orbit  
492 12025, where PFS collected 280 measurements in about 45 minutes in spot-tracking mode. The  
493 results are shown in **Fig. 1**. The actual footprints of PFS observations and the retrieved atmospheric  
494 temperature profiles used as input for the computation of synthetic spectra are shown in **Fig. S9a,b**.

495

496

497



498 *GCM simulations.*

499 The GEM-Mars three-dimensional general circulation model (GCM) for the atmosphere of  
500 Mars<sup>40</sup> applied in this work was operated at a 4°×4° horizontal resolution and with 103 vertical  
501 levels extending from the surface to  $\sim 7 \times 10^{-6}$  Pa ( $\sim 140$  km). The vertical resolution in the lowermost  
502 atmosphere is fine: the spacing between levels is  $\sim 15$  m near the surface and  $\sim 1$  km at 10 km in  
503 height. The model time step is 1/48 of a sol ( $\sim 30$  minutes). The model was extensively validated  
504 against multiple datasets<sup>40</sup>, and was previously applied for the study of fine dust layers observed by  
505 the Phoenix Mars mission<sup>41</sup>, for the simulation of the annual cycles of water vapour and carbon  
506 monoxide on Mars<sup>63</sup>, for the simulation of the Mars dust cycle<sup>64</sup>, and for the transport of methane  
507 upon surface release<sup>28</sup>. GEM-Mars forms an integral part in the analysis and interpretation of data  
508 from the NOMAD spectrometer on the ESA-Roskosmos ExoMars Trace Gas Orbiter<sup>47,65,66,67</sup>.

509 The accuracy of the simulated wind fields can be optimized by constraining the dynamical  
510 model fields by available observations. To do this, the atmospheric dust content in the GCM was  
511 imposed to be in accordance with the dust observations by the PFS obtained during MEx orbits  
512 12018 (nadir) and 12025 (spot-tracking) (**Table 1** and **Fig. S9c**). GEM-Mars has an active dust  
513 lifting scheme but the simulated dust optical depth (OD) was scaled at all times to the  
514 climatological values for Martian year 31<sup>68</sup>, binned over 10° L<sub>s</sub>. In the region of Gale crater, the  
515 climatological value for L<sub>s</sub>=330°–340° (OD=0.62) was considerably larger than that measured by  
516 PFS (average OD  $\sim 0.30$ ). The model dust OD was scaled globally in this time window by the ratio  
517 0.30/0.62 to ensure that the dust OD in the Gale crater area matches the PFS value at the time of the  
518 observations (**Fig. S9c**). It was verified that the simulated temperature profile at the time of the PFS  
519 observation matched with the PFS retrieved temperature profile during orbit 12025 (**Fig. S9b**). The  
520 model temperature profile shown in **Fig. S9b** is an average of 70 profiles that are randomly  
521 distributed within the PFS orbit 12025 footprint (**Fig. S9a**) at 9:40 LTST on sol 306. These model  
522 profiles were interpolated from the model grid and corrected for pressure taking into account the

523 height difference between the coarse-grained model grid and the high-resolution MOLA  
524 topography.

525 For each of the 30 grid cells considered as emission sites, a simulation was performed  
526 involving the release of 120 tracers (see below). The simulations were fully parallelized on 24  
527 nodes of BIRA-IASB's High-Performance cluster.

528

529

530 *Statistical approach.*

531 The statistical approach adopted here, belonging to the Monte-Carlo-type approaches, is based  
532 on the assumption that the inert tracers (such as methane, on the considered timescales) simulated in  
533 a GCM are linearly additive. This was explicitly verified by test simulations (relative error of  
534  $\sim 0.05\%$ ). As a corollary, they can also be scaled by any factor. In addition, while the model time  
535 step is  $\sim 30$  minutes, the average of two tracers released at an interval of one hour describes fairly  
536 well the evolution of the tracer released in between (relative error of  $\sim 3\%$ ). In practice, in this  
537 model study, 120 tracers were released successively every hour from any model grid cell.  
538 Exploiting the last assumption, the tracers released at the 119 model time steps in between can be  
539 reasonably considered as the average of tracers on both sides, so raising to 239 the total number of  
540 available tracers.

541 Let  $N = 239$  and  $M_r = 10^5$  kg be respectively the number of tracers and the initial mass of  
542 each tracer  $T_i$  released at time  $t_i$ . If the mass of tracer  $T_i$  is scaled by a factor  $\varphi_i(t_i)$  arbitrarily  
543 chosen, the mass  $M_{0i}$  of  $T_i$  released into the atmosphere becomes:  $M_{0i} = \varphi_i(t_i)M_r$ .

544 In order to match the first and last observational constraints (**Table 1**), it was verified from test  
545 simulations that the event started at the earliest at midnight on sol 302, and lasted no longer than  
546 until the end of sol 306. On the other hand, the event started necessarily prior to sol 305 at 13h, i.e.  
547 at the time of the methane detection by Curiosity. Finally, the minimum emission duration is 30

548 Mars minutes (i.e. one model time step). Thus, being  $t_0$  the initial time and  $\tau$  the duration of the  
 549 event, we have

550

$$0 \text{ h} \leq t_0 \leq 85 \text{ h (i. e. between sol 302 at 0 h and sol 305 at 13 h)}$$

$$\tau_{\min} \leq \tau \leq \tau_{\max} \quad \text{where} \quad \begin{cases} \tau_{\min} = 30 \text{ minutes} \\ \tau_{\max} = 5 \text{ sols} \end{cases}$$

551

552 where  $\tau_{\min}$  and  $\tau_{\max}$  are the minimum and maximum durations, respectively. As a result,  
 553 depending on  $t_0$  and  $\tau$ ,  $T_i(t_i)$  is zeroed if its emission time  $t_i$  is outside the time period of the event.

554 These conditions can be rewritten in terms of Heaviside step functions as

555

$$\theta_1(t_i - t_0) = \begin{cases} 1, & t_i \geq t_0 \\ 0, & t_i < t_0 \end{cases}$$

$$\theta_2(t_0 + \tau - t_i) = \begin{cases} 1, & t_i \leq t_0 + \tau \\ 0, & t_i > t_0 + \tau \end{cases}$$

556

557 and the effective mass  $M_{0i}$  of  $T_i$  released at time  $t_i$  takes the form

558

$$M_{0i} = \varphi_i(t_i, t_0, \tau) M_r = \varphi_i(t_i) \theta_1(t_i - t_0) \theta_2(t_0 + \tau - t_i) M_r = \begin{cases} \varphi_i(t_i) M_r, & t_0 \leq t_i \leq t_0 + \tau \\ 0, & t_i < t_0 \text{ or } t_i > t_0 + \tau \end{cases}$$

559

560 The total mass  $M_0$  of tracers released during the event occurring between  $t_0$  and  $t_0 + \tau$  is thus given

561 by

$$M_0 = \sum_{i=1}^N \varphi_i(t_i, t_0, \tau) M_r$$

562

563 For the sake of conciseness, Greek and Latin letters will indicate the measurements (retrieved  
 564 abundance of methane) and the corresponding model variables (mean abundance for the same area

565 and temporal interval of the observations), respectively. Let  $\{\alpha, \beta, \gamma, \delta, \varepsilon, \zeta\}$  be the set of  
 566 observational constraints reported in **Table 1**:

567

$$\begin{aligned}
 \text{MSL (sol 305): } & \alpha \pm \Delta\alpha = 5.78 \pm 2.27 \text{ ppbv} \\
 \text{PFS (sol 306): } & \beta \pm \Delta\beta = 15.5 \pm 2.5 \text{ ppbv} \\
 \text{MSL (sol 313): } & \gamma \pm \Delta\gamma = 2.13 \pm 2.02 \text{ ppbv} \\
 \text{PFS (sol 304): } & \delta = 3 \text{ ppbv} \\
 \text{PFS (sol 316): } & \varepsilon = 5 \text{ ppbv} \\
 \text{PFS (sol 318): } & \zeta = 5 \text{ ppbv}
 \end{aligned}$$

568

569 Let  $\{A, B, C, D, E, F\}$  be the set of model variables that must fit the observational dataset  
 570  $\{\alpha, \beta, \gamma, \delta, \varepsilon, \zeta\}$ . A release scenario is said consistent with the observations if and only if the  
 571 following relations are satisfied:

$$\left\{ \begin{array}{l}
 \alpha - \Delta\alpha \leq A \leq \alpha + \Delta\alpha \\
 \beta - \Delta\beta \leq B \leq \beta + \Delta\beta \\
 \gamma - \Delta\gamma \leq C \leq \gamma + \Delta\gamma \\
 0 \leq D \leq \delta \\
 0 \leq E \leq \varepsilon \\
 0 \leq F \leq \zeta
 \end{array} \right.$$

572

573 Let  $\{A_{0i}, B_{0i}, C_{0i}, D_{0i}, E_{0i}, F_{0i}\}$  be the set of model variables that result from the emission of the  
 574 initial mass  $M_r$  of the single tracer  $T_i$ . Those variables are obtained by linear interpolation at the  
 575 time and location of the corresponding observations. As they depend linearly on  $M_{0i}$ , they are  
 576 scaled by the same factor  $\varphi_i(t_i, t_0, \tau)$ . Consequently, the model variables  $\{A_0, B_0, C_0, D_0, E_0, F_0\}$   
 577 can be written as

578

$$\begin{cases} A_0 = \sum_{i=1}^N \varphi_i(t_i, t_0, \tau) A_{0i} \\ B_0 = \sum_{i=1}^N \varphi_i(t_i, t_0, \tau) B_{0i} \\ \vdots \\ F_0 = \sum_{i=1}^N \varphi_i(t_i, t_0, \tau) F_{0i} \end{cases}$$

579

580 We generate  $10^6$  potential release events for each of the 30 emission sites considered by generating

581 the same amount of random combinations of the parameters  $\varphi_i, t_0, \tau$ . Then, for each single event,

582 the model variables can be scaled by a factor  $f$  in order to match the observations, when possible.

583 This factor must satisfy six constraining relations in terms of the six observations:

584

$$\begin{cases} \frac{\alpha - \Delta\alpha}{A_0} \leq f_A \leq \frac{\alpha + \Delta\alpha}{A_0} \\ \frac{\beta - \Delta\beta}{B_0} \leq f_B \leq \frac{\beta + \Delta\beta}{B_0} \\ \frac{\gamma - \Delta\gamma}{C_0} \leq f_C \leq \frac{\gamma + \Delta\gamma}{C_0} \\ 0 \leq f_D \leq \frac{\delta}{D} \\ 0 \leq f_E \leq \frac{\varepsilon}{E} \\ 0 \leq f_F \leq \frac{\zeta}{F} \end{cases}$$

585 or, more simply:

$$\mathbf{f}_{\min} \leq \mathbf{f} \leq \mathbf{f}_{\max}$$

586

587 where  $\mathbf{f} = \{f_A, f_B, f_C, f_D, f_E, f_F\}$ .

588

589 A scenario is said to be consistent with the observations if it exists  $f$  such that:

590

$$\max(\mathbf{f}_{\min}) \leq f \leq \min(\mathbf{f}_{\max})$$

591

592 If so,  $f$  is arbitrarily chosen as the mean value between  $\max(\mathbf{f}_{\min})$  and  $\min(\mathbf{f}_{\max})$ :

593

$$f = \frac{\max(\mathbf{f}_{\min}) + \min(\mathbf{f}_{\max})}{2}$$

594

595 As described above, a sequence of stochastic fluxes is generated to produce a release pattern that  
596 mimics an episodic seepage event. In practice, this procedure consists in generating *randomly*  
597 factors  $\{\varphi_i(t_i)\}$  given by a probability distribution function.  $\varphi_i(t_i)$  was defined as the factor scaling  
598 the initial mass  $M_r$  of tracer  $T_i$ , so that

599

$$\varphi_i(t_i) = \frac{M_{0i}}{M_r}$$

600

601 If a mass  $M_{0i}$  is released from a surface area  $S$  during one model time step  $\Delta t$ , the resulting release  
602 rate  $\chi_{0i}(t_i)$  of  $T_i$  is given by:

$$\chi_{0i}(t_i) = \frac{M_{0i}}{S\Delta t}$$

603

604 Therefore,  $\varphi_i(t_i)$  takes the form

605

$$\varphi_i(t_i) = \frac{S\Delta t}{M_r} \chi_{0i}(t_i)$$

606

607 Let  $P(\chi)$  be a probability distribution function of the release rate  $\chi$  used to generate randomly a  
608 release pattern. Given that the time evolution of gas fluxes is not known even on Earth, we chose  
609 the simplest function, i.e. the uniform distribution function:

610

$$P_u(\chi) = \frac{1}{X_0}; \quad 0 \leq \chi \leq X_0$$

611

612 where  $X_0$  was fixed to  $150 \text{ mg m}^{-2} \text{ day}^{-1}$ . This value is arbitrary but does not affect the final results  
613 because the tracers are all scaled by a factor  $f$  afterwards. Any other distribution function could be  
614 used. In our study, in order to test the sensitivity of the analysis to the variability of gas fluxes and  
615 to estimate the robustness of the statistical results, we also considered a Gaussian distribution  
616 function:

617

$$P_G(\chi) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(\chi - \mu)^2}{2\sigma^2}\right); \quad 0 \leq \chi \leq \infty$$

618

619 where  $\mu = 75 \text{ mg m}^{-2} \text{ day}^{-1}$  and  $\sigma = 20 \text{ mg m}^{-2} \text{ day}^{-1}$ . The good agreement between the so-obtained  
620 probability map (not shown) and that displayed in **Fig. 3** indicates that the probabilities of fitting the  
621 observations do not depend dramatically on the gas flux variability, which emphasizes the robustness of  
622 our results.

623 Finally, the initial time  $t_0$  and duration  $\tau$  of the release event are generated randomly using a  
624 uniform distribution function.

625 An example scenario is presented in **Figs. S13-S15**. **Fig. S13** illustrates the procedure followed to  
626 produce one release pattern. **Fig. S14** shows the time evolution of the simulated methane abundance  
627 at Gale crater and the procedure to scale the tracers in order to match the observations. **Fig. S15**  
628 finally shows maps of the simulated methane abundance for the times of the available observations.

629

630

631

632

633 ***Geological analysis.***

634 For the GCM simulations, we considered terrestrially realistic methane emission patterns (i.e.,  
635 release intensity, duration, variation and area), based on gas seepage theory and experimental data  
636 acquired on Earth (e.g., ref. <sup>42</sup> and references therein). For definition and description of the various  
637 “seepage” terms used here, the reader may refer to refs <sup>42, 69-76</sup>. Details are provided in SI-2.

638 For Martian geological context, we analysed image data from the Mars Orbiter Laser Altimeter  
639 (MOLA) on Mars Global Surveyor as well as the Context camera (CTX) and High Resolution  
640 Imaging Science Experiment (HiRISE) on Mars Reconnaissance Orbiter, incorporating information  
641 from published geological maps and reports. We initially evaluated a wide area, ~1000-km-radius,  
642 surrounding Gale crater. However, GCM simulations indicated that features more than ~800 km  
643 from Gale would be unlikely to account for the Gale detections. Emphasis was then placed on the  
644 grid areas used in the GCM simulations. All data were mapped using Esri’s ArcGIS software and  
645 the U.S. Geological Survey Mars Global GIS v2.1 (outline of the Medusae Fossae Formation from  
646 geological global map I-1802ABC). Details are provided in SI-2.

647

648 **Data availability**

649 The PFS data used in this study are publicly available via the ESA Planetary Science Archive.  
650 References of terrestrial gas seepage data are reported in the SI. Data used to map water-equivalent-  
651 hydrogen are available from Jack T. Wilson (Durham University, UK). All other geological data of  
652 Mars used in this study are in the public domain and include published papers, data provided in the  
653 U.S. Geological Survey MarsGlobal GIS v2.1 (which can be accessed on their Mars GIS FTP site -  
654 file name: MarsGIS\_Equi0\_v21.zip [note: v21 used in the file name for v2.1]), and CTX and  
655 Visible data image mosaics provided by Google Earth (Mars).

656

657



658 **Code availability**

659 The core GEM model used for this work is publicly available through  
660 <http://collaboration.cmc.ec.gc.ca/science/rpn.comm/>. The routines that were modified for the  
661 application to Mars were explained in *ref.*<sup>40</sup> and are available upon request from authors L.N., F. D.  
662 and S. V. The model output used in this paper is available by request from authors S.V., F.D. and  
663 L.N. The equations for the statistical analysis are included in Methods. The computer code to  
664 reproduce them is available from author S.V.

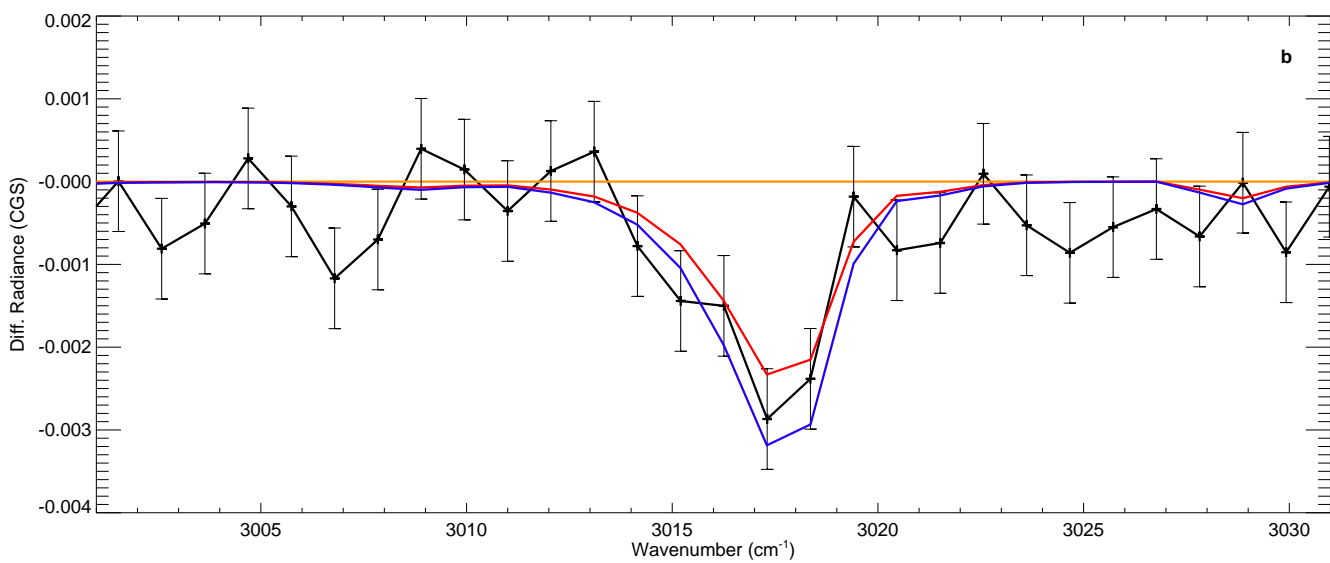
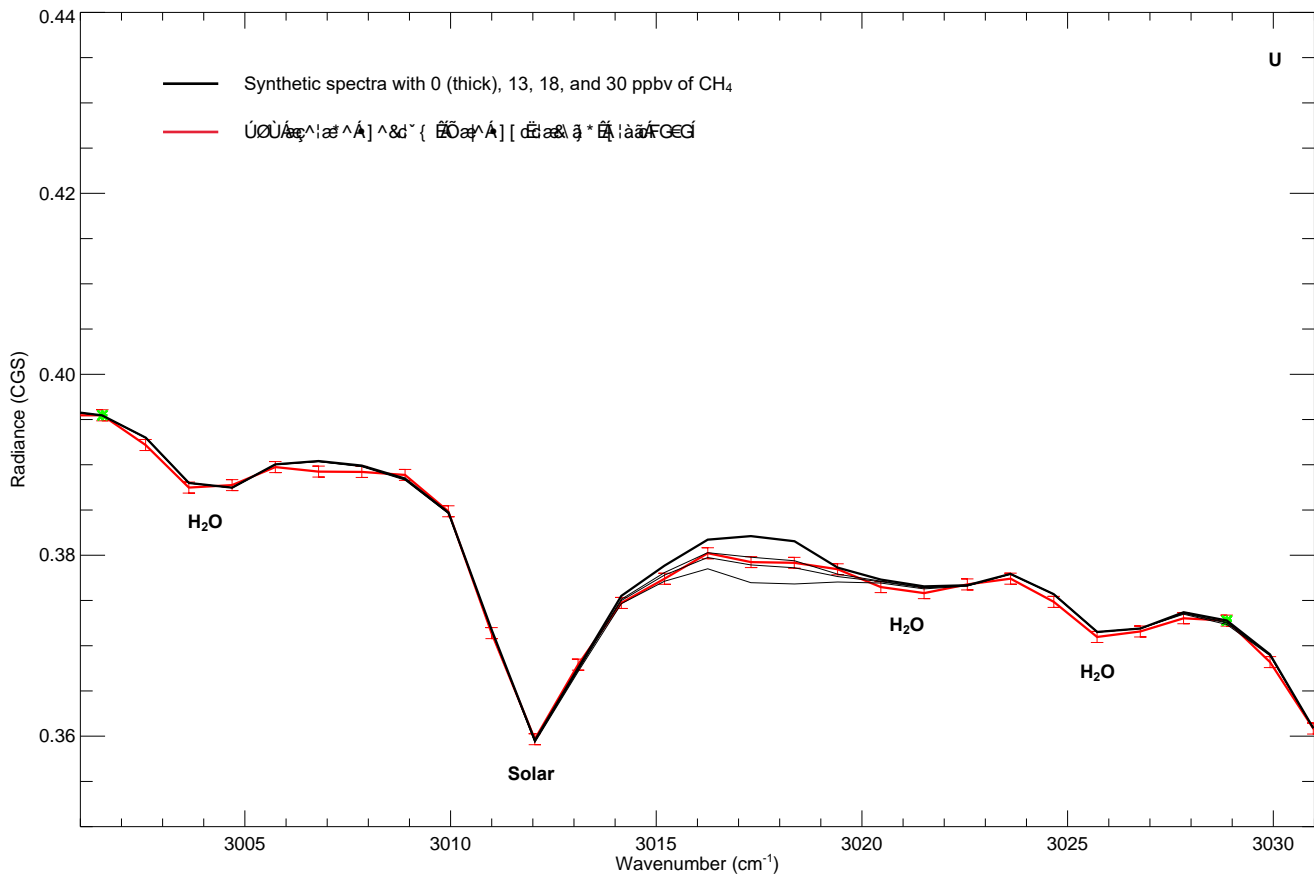
665

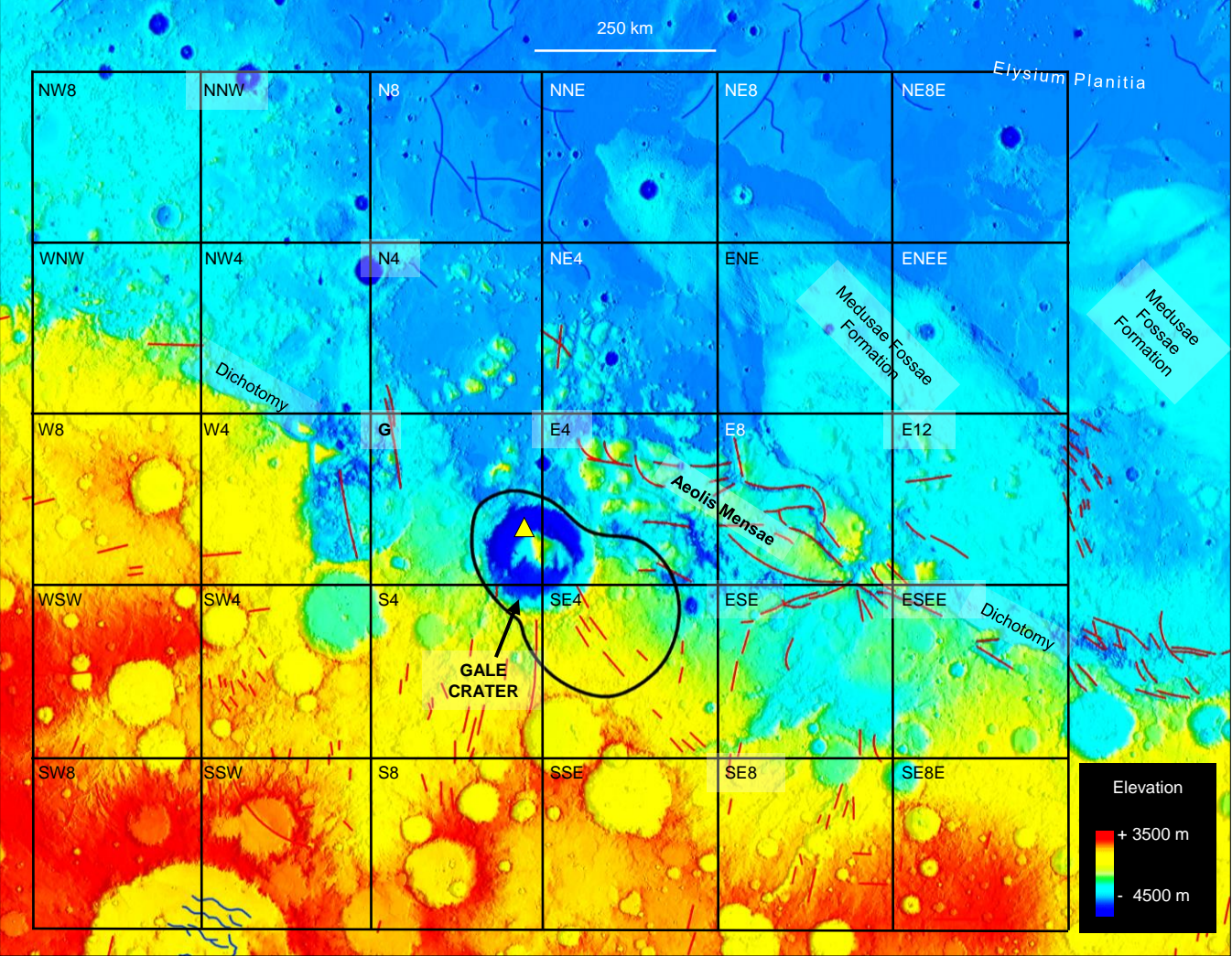
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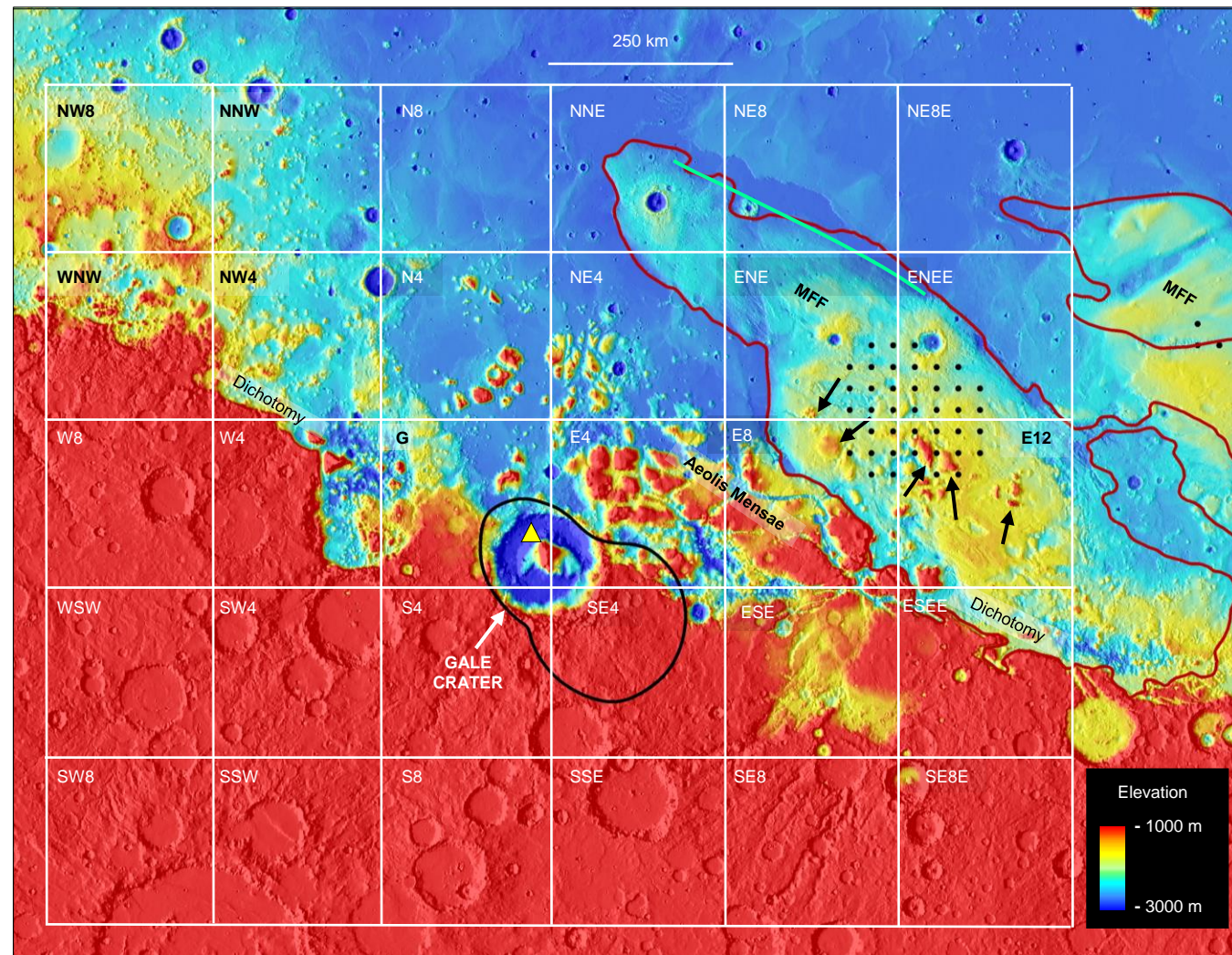
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**Table 1. List of observational constraints.** The first column provides the number of sols before (negative values) or after the TLS-SAM measurements on sol 305. The positive detections are in bold. Upper limits are provided (1- $\sigma$  uncertainty) when no CH<sub>4</sub> band is observed in PFS spectra.

<b>Sols</b>	<b>Date<sup>a</sup></b>	<b>Time</b>	<b>MEx Orbit<sup>e</sup></b>	<b>Value (ppbv)</b>	<b>Instrument</b>
-1	Sol 304	~9:45 <sup>b</sup> (LTST <sup>d</sup> )	12018	≤ 3 ppbv	PFS
<b>0</b>	<b>Sol 305</b>	<b>13:00<sup>c</sup> (LTST)</b> <b>ingestion: 20'</b>	<b>N/A</b>	<b>5.78 ± 2.27</b>	<b>TLS-SAM</b>
<b>1</b>	<b>Sol 306</b>	<b>9:41<sup>c</sup> (LTST):</b> <b>meas. duration: 43'</b>	<b>12025<sup>f</sup></b>	<b>15.5 ± 2.5</b>	<b>PFS</b>
<b>8</b>	<b>Sol 313</b>	<b>N/A</b>	<b>N/A</b>	<b>2.13 ± 2.02</b>	<b>TLS-SAM</b>
11	Sol 316	~9:24 <sup>b</sup> (LTST)	12060	≤ 5	PFS
13	Sol 318	~9:19 <sup>b</sup> (LTST)	12067	≤ 5	PFS

<sup>a</sup> Sols since MSL landing, Sol 305 = June 15, 2013. <sup>b</sup> Average time of orbit. <sup>c</sup> Starting time of observation. <sup>d</sup> Local

True Solar Time. <sup>e</sup> Orbit tracks and PFS footprints are shown in **Fig. S12a**. <sup>f</sup> Spot-tracking observation.

