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Methane spikes, background seasonality and non-detections on Mars: A geological perspective

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ABSTRACT

The story of methane (CH_4) on Mars continues to grow. A long series of CH_4 detections (spikes, plumes, seasonal variations) and non-detections in the martian atmosphere suggest that CH_4 is occasionally released from subsurface rocks, but also that an unknown process of rapid CH_4 removal in the atmosphere must exist. The observations can be interpreted integrating concepts of subsurface geological gas source variability (CH_4 seepage flux patterns), atmospheric chemistry (CH_4 removal processes), and atmospheric circulation (CH_4 transport and dilution). While the last two are widely studied, potential gas seepage patterns on Mars have never been discussed. In this work, we use the factors controlling gas seepage flux patterns observed on Earth to address key questions about the significance of the martian detections and non-detections. As on Earth, CH_4 seepage on Mars must occur mainly through advection (non-diffusion) mechanisms, driven by pressure gradients and permeability, typically related to faults and fracture networks, which control release patterns, in terms of intensity, duration and variability. CH_4 release may occur, therefore, whenever gas pressure and/or rock permeability increase (e.g., via destabilization of storage bodies such as clathrates or zeolites; breaching of seals such as permafrost; planetary stresses, impacts, or gas pressure build-up along faults). Rapid atmospheric pressure changes, due to storms and winds, may also play a role. All these forcings can lead to local, episodic, irregular or seasonal gas releases, which may explain the observations acquired so far if relatively rapid (month or day time-scales) mechanisms of CH_4 removal exist in the lower atmosphere or near-surface. The release patterns cannot reveal whether CH_4 is biologic or abiotic. If CH_4 sensors operate discontinuously and only in one site or over limited regions, then, non-detections will be the rule and detections will be relatively rare. The chances of CH_4 detection may increase if the observations are focused and repeated on specific, potential areas of gas release determined by geological analysis.

1. Introduction

On Earth, most of the methane (CH_4) in the atmosphere is a result of biochemical processes, and the possibility that methane in the atmosphere of Mars, so far detected only episodically, might reflect martian microbial life has been a subject of great interest. Since 2003, there have been multiple reports of methane in the martian atmosphere, with detections from orbit around Mars (Formisano et al., 2004; Fonti and Marzo, 2010), from terrestrial telescopes (Krasnopolsky et al., 2004; Mumma et al., 2009) and ground-based measurements in Gale crater (by the Tunable Laser Spectrometer, TLS, on the *Curiosity* rover; Webster et al., 2015, 2018). In particular, *Curiosity* observed methane spikes (up to ~ 9 ppbv; Webster et al., 2015; Roos-Serote et al., 2016) and apparently seasonal CH_4 changes (~0.2–0.7 ppbv; Webster et al., 2018). Telescopic measurements detected up to ~45 ppbv, equivalent to plumes of 19,000 metric tons of CH_4; Mumma et al. (2009). There is a continuing debate on the validity of such detections (Zahnle et al., 2011; Villanueva et al., 2013; Webster et al., 2015), as CH_4 signals have been attributed to erroneous retrieval processes or contamination. However, non-detections have also been reported from ground-based observations by *Curiosity* (Webster et al., 2013), from telescopic follow-ups by Villanueva et al. (2013) to the earlier detections of methane plumes over Mars (Mumma et al., 2009), and from more recent analyses using the Echelon-Cross-Echelle Spectrograph onboard the Stratospheric

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Observatory for Infrared Astronomy (Aoki et al., 2018). Martian atmospheric chemistry predicts that methane is destroyed by excited oxygen atoms, $O(^1D)$, and OH, resulting in a methane lifetime of about 300 years (Atreya et al., 2007), but this is not rapid enough to explain the CH_4 variations observed so far. Faster removal processes could be related to CH_4 adsorption onto quartz grains (Knak-Jensen et al., 2014), interactions with zeolites in atmospheric dust (Holmes et al., 2015) or oxidation by hydrogen peroxide in the regolith, with a resulting shorter lifetime of 200 days or even a few hours near the surface (Lefèvre and Forget, 2009). O_2 depletions temporally correlated with CH_4 would support this latter model (McConnochie et al., 2014). This is a subject of continuing research. Concerning the source of methane, most of authors agree that CH_4 observed in the martian atmosphere is produced in the subsurface, within rocks (e.g., Max et al., 2013; Blamey et al., 2015; Viscardy et al., 2016; Oehler and Etiope, 2017; Webster et al., 2018), and not in the atmosphere by exogenous processes, as suggested, for example, by hypotheses of meteor showers (Fries et al., 2016), electrical discharge (Robledo-Martinez et al., 2012) and ultraviolet irradiation of organics (Keppler et al., 2012).

The CH_4-observation history for Mars includes non-detections, variable background concentrations with apparently seasonal oscillations, and episodic spikes. What does all this mean? Methane that is observable in the atmosphere must be a result of a competition between CH_4 source and atmospheric destruction/consumption, modulated by atmospheric transport and dilution. Assuming that martian methane is produced in the subsurface, the variability of the observations can be interpreted only by integrating three types of study: (a) CH_4 release modeling (i.e., geological seepage patterns, in terms of flux intensity, duration, and variability), (b) atmospheric CH_4 sinks (i.e., methane consumption), and (c) atmospheric circulation modeling (CH_4 transport and dilution). Items (b) and (c) have widely been addressed in previous studies (e.g., Atreya et al., 2007; Lefèvre and Forget, 2009; Holmes et al., 2015; Viscardy et al., 2016; Pla-Garcia et al., 2018; Neary and Daerden, 2018, and references therein). In this work we focus on item (a), answering the question whether the variability of methane in the martian atmosphere is compatible with geological seepage mechanisms. Specifically, we use factors controlling gas seepage patterns observed on Earth to address two key questions: are the variable and episodic detections on Mars, as well as the non-detections, compatible with geological mechanisms of gas release from subsurface rocks? Can the release variability (seasonality, in particular) provide insight into the origin (microbial, thermogenic or abiotic) of methane?

Subsurface CH_4 generation and seepage phenomena on Earth, and potentially on Mars, were reviewed in Oehler and Etiope (2017). Here, we complete the discussion of possible gas seepage patterns, in the light of the several types of martian CH_4 observations, including the recent report of seasonal variations (Webster et al., 2018). A basic descriptive model of seepage variability is also proposed, which can help in developing new models of the fate of CH_4 in the martian atmosphere. Our analysis will show that all CH_4 observations reported so far, including the non-detections, are compatible with geological gas seepage processes that may occur on Mars, regardless of the CH_4 origin and providing that a mechanism exists for rapid removal of CH_4 from the atmosphere.

2. Key concepts of geological CH_4 seepage on earth

An extensive discussion of potential methane seepage on Mars is reported in Oehler and Etiope (2017), and we refer the reader to that work also for definitions and terminology on gas origin and seepage (e.g., microbial, thermogenic, biotic, abiotic, macro-seeps, mud volcanoes, microseepage). Here, we review concepts of methane seepage on Earth that are critical for discussion of potential seepage patterns on Mars and interpretation of the atmospheric CH_4 data acquired so far. Specifically, advection (driven by pressure gradients and rock permeability) as the main mechanism of gas motion from subsurface rocks to the surface (Section 2.1), the geological controls on pressure gradients (Section 2.2), controls on permeability (i.e., faults and fractures; Section 2.3) and the resulting seepage flux patterns in terms of intensity duration and variability (Section 2.4). The application of these processes to Mars is discussed in Section 3.

2.1. *Mechanism of CH_4 seepage: advection or diffusion?*

A key point in the discussion on methane source variability on Mars is the recognition that the major gas migration mechanism in subsurface rocks is not diffusion, as often assumed, but advection. This is well known on Earth. Diffusion, the gas motion driven by concentrations gradients, is important only at small spatial scales and over long times in low-permeability, low-porosity rocks (Etiope and Martinelli, 2002). Modeling work has indicated that diffusion cannot be a key mechanism for methane release on Mars and cannot explain the plumes and concentration variations (Stevens et al., 2015, 2017). In contrast, advection is driven by permeability and gas pressure gradients; it is the mechanism leading to relatively fast and long-distance gas migration, including gas seepage to the surface, either as focused emissions (macro-seeps, including gas vents and mud volcanoes) or as weak, diffuse exhalations (microseepage) (Malmqvist and Kristiansson, 1985; Brown, 2000; Etiope and Martinelli, 2002; Etiope, 2015 and references therein).

In geological formulations, advection in a one-dimensional form, along the z axis is expressed as

$$v = k\ \Delta P/(\mu Z) \tag{1}$$

Where v is the gas velocity (m sec^{-1}), k is the intrinsic permeability (m^2), μ is the dynamic gas viscosity (kg m^{-1} sec^{-1}) and ΔP is the pressure difference (kg m^{-1} sec^{-2}) between two points spaced at a distance Z (m). Estimates of gas velocity through faults and fracture systems may be obtained applying the "planar fissure" and "cubic law" relationships, where k can be expressed as $b^2/12$ (with b the fissure width) and $b^3/6d$ (where d is the mean distance between intersecting fissures), respectively (Etiope, 2015 and references therein). The relationship between gas seepage and faults, and related geological conditions, is discussed in Section 2.2.

The gas flux (F) can then be derived knowing the gas concentration C (kg m^{-3}):

$$F = C\ v \tag{2}$$

Gas advection fluxes can be quite variable over time and can explain the rapid changes observed in surface seeps on Earth, whereas such changes are not compatible with diffusion mechanisms. Importantly, gas advection increases the potential for seepage of gas generated in deep geological sources. It has been considered, for example, that serpentinization on Mars, likely located several kilometers below the surface, could not produce localized gas pulses by diffusion to the surface (Yung and Chen, 2015). But on Earth, methane generated in deep serpentinized rocks clearly reaches the surface through advection along faults (e.g., Etiope et al., 2011, 2016). To be rigorous, then, serpentinization produces H_2, and CH_4 is produced by subsequent reactions of that H_2 with CO_2 (CO_2 hydrogenation); thus, CH_4 production may occur in rocks that are shallower than those where serpentinization occurs (e.g., Oehler and Etiope, 2017; Etiope et al., 2018).

2.2. *Controls on pressure gradients*

For gas seepage, the pressure gradient in Eq (1) is the key factor that can change over short-time intervals (from instantaneously to a few days or months) and is responsible for seepage variability discussed in Section 2.4. Pressure gradients and their changes can be induced by both endogenous (geological) and exogenous (atmospheric) factors.

2.2.1. *Geological controls*

Endogenous, geological factors refer to tectonic stresses, variations in lithostatic loading, rock fracturing, localized gas generation, recharge and discharge of aquifers or fluid reservoirs. Sedimentary basins and their constituent rocks, in particular, are subject to basin loading, compaction, extensional and compressional stresses that change the gas pressure gradients. In the presence of water-saturated rocks, gas can migrate to the surface if its pressure (P_G) is above the sum of hydrostatic pressure (P_w), given by the height of the piezometric surface, plus capillary pressure (P_C) controlled by the interfacial tension of water and pore size. The gas can also fracture the rock if its pressure, P_G, overcomes the lithostatic pressure, P_L (Etiope and Martinelli, 2002). Gas seepage is then the result of an interplay between P_G and P_L, and $P_w + P_C$ in presence of aquifers. The build-up of P_G, the main requisite for gas seepage, implies gas accumulation, and this is the reason why methane seeps are generally linked to subsurface pressurised reservoirs. Earthquakes, through the passage of seismic waves, can then suddenly modify the gas pressure confinement and therefore may trigger advective gas pulses (Mazzini and Etiope, 2017).

2.2.2. Atmospheric controls

Methane emission from microseepage (the slow, weak, areal exhalation of gas from the soil, without evident morphological features or fluid manifestations) can be significantly controlled by exogenous (atmospheric) factors, such as barometric pressure and wind intensity. Rapid changes of atmospheric pressure as well as wind velocity and direction are known to affect the release of gases stored in the soil and subsoil, down to depths of several meters. As barometric pressure decreases, gases are drawn upward out of the ground, and when pressure increases, gases are pushed downward, a phenomenon known as “atmospheric pumping” (e.g., Nilson et al., 1991; Massmann and Farrier, 1992). Changes in atmospheric pressure at a site may produce vertical pressure gradients in subsurface gases (Massmann and Farrier, 1992). Barometric changes of 1000–2000 Pa over a period of 1–2 days may produce advective velocities of the order of 10^{-4} cm/sec within a soil with permeability of 10^{-12} m^2 (Clements and Wilkening, 1974). A wind gust can trigger a pulse of gas release via the Bernoulli effect, creating a low-pressure event above the ground (e.g. Reimer and Bowles, 1979; Klusman, 1993). Winds may however also suppress gas release by modifying pressure gradients in the ground in a way that retards vertical gas flow to the surface (Lewicki et al., 2007).

2.3. Geological controls on permeability: the role of faults and fracture networks

On Earth, gas seepage is always related to tectonic faults and fracture networks. It occurs especially in fault intersections, regardless of tectonic regime, fault activity and seismicity (Macgregor, 1993; Bonini, 2013; Etiope, 2015; Mazzini and Etiope, 2017). In other words, methane can be released to the surface even in tectonically non-active regions and areas far from seismic zones. Tectonic regimes can be characterized by compressional (reverse and thrust faults), extensional (normal faults), uplift (radial faults) or shear (strike-slip faults) stress. The literature reports numerous examples of methane seepage in different types of faults and tectonic settings on Earth. For example, gas seepage along normal faults occurs in the Katakolo Bay in Greece (Etiope et al., 2013b) and in the Tiber Delta in Italy (Ciotoli et al., 2016); seepages along thrust faults are those typical (but not exclusive) of mud volcanoes worldwide (Bonini, 2013; Mazzini and Etiope, 2017). The Giswil seep (Switzerland) is an example of gas exhalation along a strike-slip fault (Etiope et al., 2010). And gas migration studies demonstrate that non-active, ancient faults in stable terrains (e.g., in granites, within cratons) can be gas-bearing (e.g., Malmqvist and Kristiansson, 1984, 1985). In fact, while compressional and extensional stresses may play a role in controlling water and oil migration (i.e. hydraulic conductivity), they do not significantly affect the gas-bearing property of faults, as a fault that is impermeable to water can be permeable to gas, as happens in argillaceous rocks and granites (e.g., Etiope and Lombardi, 1995; Horseman et al., 1999; Ciotoli et al., 2005; Etiope and Martinelli, 2002). And as discussed above, gas pressure is the main factor driving seepage even in poorly permeable and non-active (and non-seismic) fracture networks related to faults (Bonini, 2013; Etiope, 2015).

However, seismic events and fault activity may enhance seepage, leading to more intense and episodic emissions. Numerous examples are known of degassing events or variations related to earthquakes, either in mud volcanoes (e.g., Mellors et al., 2007; Kopf et al., 2009; Mazzini and Etiope, 2017 and references therein) or other types of surface seeps (Heinicke and Koch, 2000; Yang et al., 2006). In addition to a modification of gas pressure confinement due to the passage of seismic waves (discussed in Section 2.2), earthquakes can also increase rock permeability through fracturing (Mazzini and Etiope, 2017). This will result in sudden events of degassing.

2.4. CH_4 seepage flux patterns: intensity and variability

2.4.1. Methane seepage flux intensity

On Earth, the intensity of methane emission (flux) may span a wide range of values, depending on the type of the seeping structure (gas-oil seep, mud volcano, microseepage from the soil) and the gas pressure and spatial extent (area) of the seep (e.g., Etiope, 2015). Methane release from single emission points (macro-seeps) is typically in the order of 10^{-1} and 10^4 tonnes $year^{-1}$ (the flux from gas vents with a diameter <1 m is typically between 10^{-1} and 10^2 tonnes $year^{-1}$). Individual release events from single macro-seeps may emit orders of grams to several kg of gas in a few minutes (e.g., Etiope et al., 2011; Etiope et al., 2013b). Mud volcanoes can release several tonnes of gas in a few hours (e.g., Mazzini and Etiope, 2017). Diffuse exhalations from the ground (microseepage, over km^2 scale areas) is generally expressed in terms of grams per m^2 per day (typically mg m^{-2} d^{-1}) and is frequently in the range 10^0–10^3 mg m^{-2} d^{-1} (equivalent to orders of 10^{-1}-10^2 tonnes km^{-2} $year^{-1}$; e.g., Etiope and Klusman, 2010). These fluxes have been measured for both biotic (thermogenic or microbial) methane in sedimentary basins and abiotic methane in igneous (mafic-ultramafic) rocks. Therefore, significant pressure gradients, and thus gas accumulations (as discussed in section 2.2), can occur in all types of rocks, especially when they are fractured.

2.4.2. Methane seepage flux variability

Methane emission in active gas-oil seeps and mud volcanoes (bubbling pools, gas vents) may significantly change over a wide range of time scales, from minutes to days and years, depending on variations in subsurface gas pressure, which may be cyclic or irregular, and often induced by seismic activity (e.g., Delisle et al., 2010; Yang et al., 2006).

Microbial methanotrophic activity in the soil, modulated by soil temperature, humidity and organic content, determines seasonal variation of methane microseepage, which is higher in dry-winter periods, and lower in wet-summer periods (Etiope and Klusman, 2010). In permafrost regions, where methane of biological or geological origin can accumulate within or below the permafrost layer, seasonal ice-thawing produces summer increases of methane flux (e.g., Christensen, et al., 2004; Portnov et al., 2013; Wang et al., 2014). On the basis of numerous observations on macro-seeps and microseepage, the patterns of gas emissions from the ground can be characterized by three main types: continuous, intermittent and episodic, as depicted in Fig. 1.

(a) continuous emission over long-term (years to geological time scales), with hourly, daily and seasonal weak oscillations; the emission can be one of either
  - high flux, continuous venting (e.g., macro-seeps of hydrocarbons, active mud volcanoes, hydrothermal-volcanic vents, mofettes, fumaroles; e.g., Chiodini et al., 2010; Etiope et al., 2013b) or
  - low flux diffuse microseepage, with weak exhalations over wide areas and with low oscillations (e.g., Klusman et al., 2000; Etiope and Klusman, 2010).

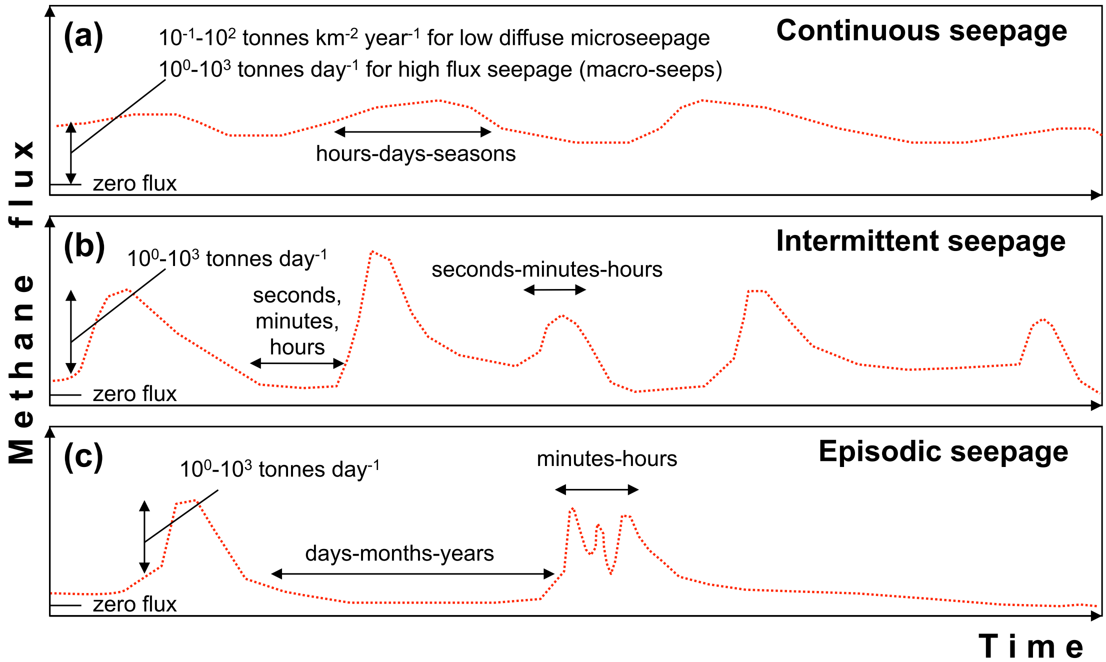

Fig. 1. Main methane emission patterns observed in seepage processes on Earth. The patterns are illustrative, summarized from numerous observations reported in the literature (e.g., Klusman et al., 2000; Yang et al., 2006; Chiodini et al., 2010; Delisle et al., 2010; Etiope and Klusman, 2010; Etiope et al., 2013b; Mazzini and Etiope, 2017; Krabbenhöft et al., 2010; Embriaco et al., 2014).

(b) intermittent emission over a long-term, with stronger and sudden, short-term (seconds, minutes, hours), variations (e.g., repeated gas eruptions, irregular venting in mud volcanoes and gas seeps, geysers; e.g., Delisle et al., 2010; Mazzini and Etiope, 2017). A continuous, background exhalation always accompanies this type of emission.

(c) episodic emission, with low or strong exhalations, spaced out by periods of days, months, or years with very low or nil emission between the episodes. This pattern is typical of expulsion of gas pockets in shallow subsoil, driven by seismic activity or the Bernoulli effect induced by episodic strong winds and storms, or episodic migration of gas slugs along faults driven by seismic activity, overpressure pulses, and the so-called "fault burps" (e.g., Haney et al., 2005; Krabbenhöft et al., 2010; Embriaco et al., 2014). The events can be singular (one pulse) or multiple (sequence of sub-events), both lasting minutes or hours; a weak continuous, background (quiescent) exhalation may persist.

Patterns (a) and (b) generally imply large and active gas sources (with highly pressurised reservoir rocks). Pattern (c) is more typical of nearly drained seepage systems (generally characterized by old and dying seeps). We consider this pattern as the most likely for Mars, and in the next section, we show that Mars has geological features compatible with an episodic type of seepage.

3. Potential seepage intensity and variability on mars

Oehler and Etiope (2017) described in detail the relevant geology on Mars that could affect abiotic methane generation, conduits for gas migration, storage of methane in the subsurface, and triggers for methane release. To summarize, methane generated by any process in the martian subsurface will migrate along permeable conduits, most often provided by fault and fracture systems. That methane will either be released to the atmosphere or stored in clathrates, zeolites, or conventional stratigraphic/structural traps, where it will accumulate. Conventional traps consist of reservoir rocks with effective methane seals, such as shales, evaporites (salt or anhydrite) or permafrost (Oehler and Etiope, 2017). Anything that destabilizes the clathrates, breaks down the zeolites, or breaches the seals of conventional methane traps, has the potential to contribute to episodic releases. Regions on Mars identified as potential sites for methane seepage in Oehler and Etiope (2017) are summarized in Table 1 of that paper. Of those sites, the mud-volcano-like mounds in deep basins of the lowlands and the faulted and serpentinized areas with mafic-ultramafic rocks (e.g., Nili Fossae) were highlighted as key locations for potential methane release.

Seepage intensity is controlled by the entire generation, accumulation and migration system. In areas where little methane has been generated or accumulated, seepage intensity would be low. In other areas, where methane has accumulated and faults to the surface provide conduits for release, methane seepage may be episodic and of moderate to high intensity when tectonism or atmospheric processes (described in Section 2.2.2) create conditions that enhance seepage. It is also important to note that, since gas accumulations would be expected to be more or less long-lasting in a specific site, a site that may have episodically seeped methane to the martian atmosphere would be expected to repeat that type of release through time. This would apply particularly to sites with visible, macro-seepage phenomena that have modified the ground morphology, such as the mud-volcano-like mounds in the northern lowlands (e.g., Skinner and Mazzini, 2009; Oehler and Allen, 2010; Ivanov et al., 2014). Sites like these could be major release locations suitable for potential follow-up studies.

Below we focus on geological and atmospheric factors that, through rock permeability and gas pressure gradients, would control intensity and variability of gas seepage on Mars. Fig. 2 summarizes these factors. We additionally discuss implications of the lower gravity on Mars (compared to Earth) on fracture density and openness as well as the effects of Mars' comparatively low atmospheric pressure on the abundance of recent impactors that could contribute to episodic pulses of methane.

3.1. *Potential methane accumulation and release mechanisms*

Once generated by biotic or abiotic processes, methane can migrate

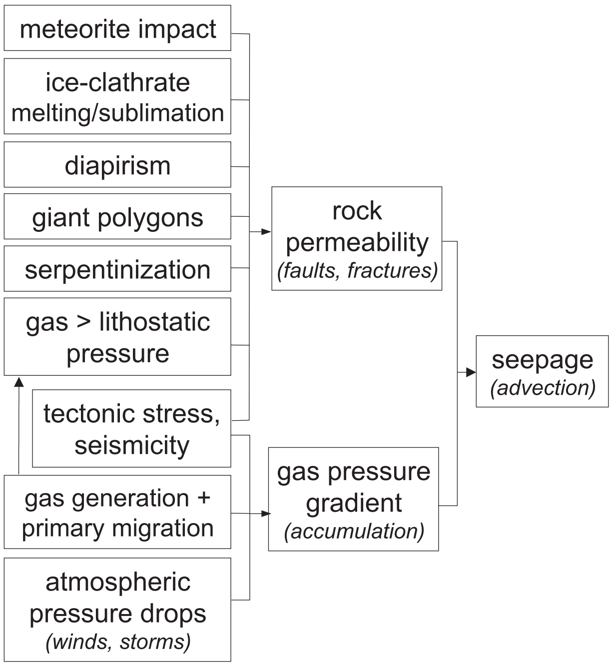

Fig. 2. Factors that can control the variability of gas seepage on Mars through rock permeability and gas pressure gradients. Gas generation and primary migration in source rocks, in addition to pressure gradients, can influence rock permeability through the opening of fractures when gas pressure overcomes lithostatic pressure (see text). All factors can lead to episodic and "pulse"-like gas release to the atmosphere.

and accumulate in permeable rocks. Max et al. (2013) discussed potential formation and destabilization of methane clathrates (hydrates) on Mars in detail. In regions of permafrost on Earth, it is well known that the gas-hydrate-stability-zone (GHSZ) is determined by local mean surface temperature, geothermal gradient, pore water geochemistry, and confining pressure (which increases with depth). Methane hydrates will destabilize and release free methane gas if the pressure drops below the GHSZ or the temperature increases above the GHSZ. For Mars, using an average martian surface temperature of 200 K, Max et al. (2013) state that methane hydrate would not be stable at confining pressures less than ~ 140 kPa (1.4 Bar), which would correspond to depths of ~15 m. This would be the top of the GHSZ, though at colder temperatures (generally at latitudes > 60°), the top of the GHSZ would be at shallower depths (Chastain and Chevrier, 2007). So shallow depressurization, such as might occur in areas of erosion, ice sublimation, recent impacts or faulting, could destabilize shallow clathrates and episodically release the gas to the surface. Similarly, temperature increases can destabilize clathrates and such increases might be associated with magmatic intrusion, venting of gas from depth that may also convey heat (Max et al., 2013), or possibly seasonal or obliquity-related changes.

Methane stored in zeolites has also been suggested to be a potential source of sporadic atmospheric releases on Mars, with destabilizing events such as impacts, seismic activity or erosion being a cause of the temporal variability (Mousis et al., 2016). And methane could be stored in lithologic traps, as, for example, those formed in fault blocks associated with complex craters (Oehler and Etiope, 2017). The seals for these types of traps can be breached by fault movements (e.g., Fig. 3), pressure changes, and, in the case of a permafrost seal, also by sublimation or melting of the permafrost. Since salt can be mobile in the subsurface and permafrost can re-form, releases due to faulting in salt or permafrost may be episodic, partly because breached seals in ice or salt can heal themselves with time.

Gas pressure changes can then be driven by processes similar to those occurring on Earth, as discussed in Section 2.2, where seismic events can lead to methane emission pulses.

3.2. The role of faults

Mars has extensive fault systems developed during formation of the dichotomy and uplift of the Tharsis volcanic edifice (e.g., Anderson et al., 2001; Mège et al., 2003; Knapmeyer et al., 2006; Hauber et al., 2010; also summarized in Golombek and Phillips, 2009) that may function as major permeability routes for gas migration in the subsurface. The dichotomy encircles the planet and includes many regions with apparent concentrations of extensional faults (Knapmeyer et al., 2006; Golombek and Phillips, 2009). Tharsis-related faults extend over nearly 1/3 of the planet and include radial extensional faults and concentric compressional

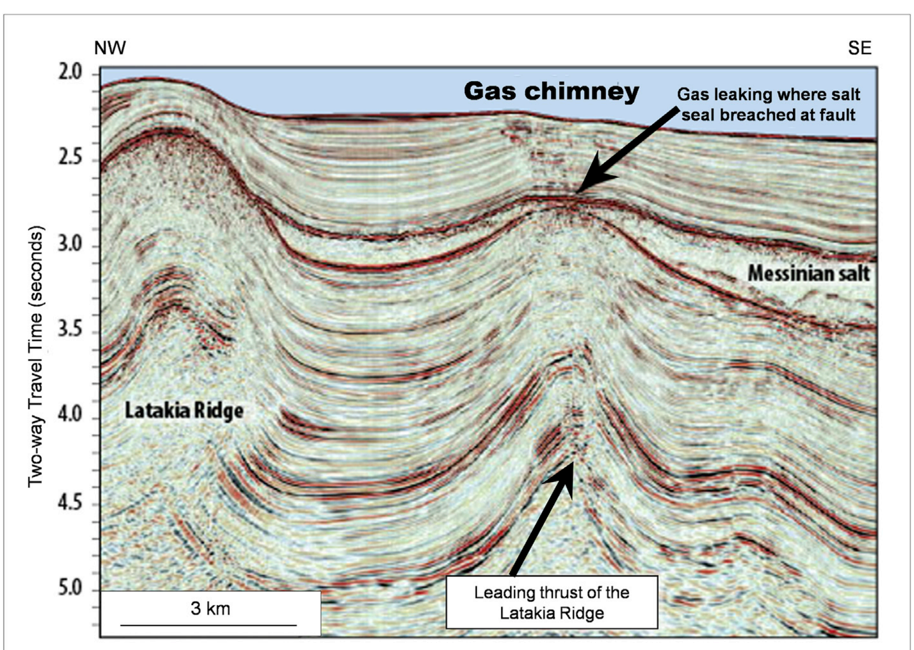

Fig. 3. Seismic reflection section showing an example of gas seepage from reservoirs. The image illustrates a natural gas system in offshore Syria, where a salt seal has been breached by faulting. At the point of the leak (top arrow), methane seeps to the surface, forming a "gas chimney" in subsurface sediments. While Mars does not have similar tectonic settings, this image is shown only to illustrate the importance of seals for gas and how they can be breached. Gas chimneys are identified in seismic data as disturbances in rock layering (caused by the low seismic velocity of gas which results in poor data quality or apparent "push-downs" of stratal layers). Seeping methane associated with gas chimneys has also been identified by gas sampling and chromatographic/spectroscopic analyses of gas on the sea floor (e.g., Ruppel and Kessler, 2017; Thornton et al., 2016). In other examples of similar leakage, multiple gas pockets (reservoirs) can be developed along fault systems. Image adapted from Bowman (2011), with seismic data courtesy of CGG, and permission to use this figure provided by Gulf PetroLink, the publisher of GeoArabia.

faults that form wrinkle ridges, which may overlie thrust faults (discussed in detail in Golombek and Phillips, 2009).

Impacts add to these fault systems, as does fracturing from processes such as giant polygon-formation in the northern plains (Oehler and Allen, 2012; Allen et al., 2013), serpentinization of olivine-rich rocks (e.g., Ehlmann et al., 2010), which may enhance gas accumulation in igneous rocks whose primary permeability would otherwise be quite low (Etiope et al., 2013a), and sedimentary diapirism, which can produce structures on Mars that resemble terrestrial mud volcanoes (Oehler and Allen, 2010) as well as both sedimentary dykes (Grotzinger et al., 2014) and pipes (Rubin et al., 2016). In addition, it is important to note that the lower gravity of Mars induces lower lithostatic pressure than on Earth, resulting in higher fracture density, at any depth (Heap et al., 2017). The lower gravity may also result in greater depth of fault-penetration and may enhance formation of dilational pit crater chains, some of which may even be forming today (Ferrill et al., 2004; Smart et al., 2011). Therefore, even igneous rocks (mafic and ultramafic) can be more fractured than those on Earth, forming excellent reservoir rocks. Taken together, these processes have created a martian subsurface that is heavily fractured (e.g., Rodríguez et al., 2005) and thus likely to provide numerous conduits for gas migration and release to the atmosphere (e.g., De Toffoli et al., 2018).

Faults from the dichotomy-forming event, the build-up of Tharsis, and major impacts would penetrate deep into the subsurface, providing conduits for methane generated and accumulated at great depth. Although most of these faults would have developed early in Mars' history, they are likely to have been reactivated many times by continuing tectonic stresses, with subsequent, episodic methane releases associated with such reactivations (e.g., Plaza-Faverola et al., 2015). On late Mars, tectonic stresses may be due to planetary cooling, evolution of the dichotomy, basin subsidence, ice sublimation, volcanism, sedimentary diapirism, and continuing impacts. This type of reactivation could keep the older deeper faults open, particularly in cases where they have been cemented (e.g., as in the many faults with cement fills in Gale crater; Siebach et al., 2015; Yen et al., 2017; Kronyak et al., 2018).

It is fault movement and pressure changes associated with the most recent planetary stresses that could contribute to current episodic emissions, accounting for both temporal and spatial variability in methane releases. Data expected from the upcoming Mars InSight Lander should provide new insights to current seismicity and tectonism on Mars.

3.3. The role of meteorite impacts in shallow gas release

On Mars, episodic gas releases may be induced by recent/current meteoritic impacts. The loss of atmosphere on Mars particularly enhances the abundance of small and recent impactors hitting the martian surface. These not only could contribute to fault-mediated seepage of methane from the subsurface, but their associated seismic waves could change gas pressures, triggering advective pulses of methane.

To understand the frequency of recent impactors, Daubar et al. (2013) evaluated 248 impact sites formed within the last few decades using images from the Context Camera (CTX) and High Resolution Imaging Science Experiment (HiRISE) on NASA's Mars Reconnaissance Orbiter by comparing the most recent images with previous images taken of the same sites. From these observations, they calculate that meter-to decameter-sized craters are forming on Mars at a rate of 1.65×10^{-6} craters/km^2/yr, for craters with effective diameters ≥ 3.9 m, which amounts to > 200 of these meteorite strikes per year.

However, most recent impact craters are small. Forty-four craters were highgraded by Daubar et al. (2013), as those had both before- and after-impact images of the impact sites. These craters range from ~2 to 34 m in diameter and all but one are < 15 m in diameter. Accordingly, the depths of penetration of most of the recent craters would be expected to be from < 1 m to ~8 m (Daubar et al., 2014).

So the question is: can these recent impacts penetrate subsurface clathrates or ice (that may seal methane reservoirs), thereby accounting for episodic methane releases? First, various lines of evidence show that permafrost/ice is present in the near surface of mid to high latitudes of Mars. The Phoenix mission, which landed in the northern plains, at 68.2°N, 234.3°E, showed patches of water ice below the lander (mean depth of 4.6 cm), which had been exposed by the spacecraft thrusters during landing (Mellon et al., 2009; Smith et al., 2009), and permanent water ice has been detected by the High Resolution Stereo Camera (HRSC) on the European Space Agency (ESA) Mars Express spacecraft on the floor of a 35 km crater at ~70.5°N, 103°E (https://mars.nasa.gov/resources/5266/mars-crater-ice/). At mid-latitudes, HiRISE image data have shown several examples of small, recent craters that expose water ice, which fades over a few months, presumably from sublimation (Byrne et al., 2009), and potentially extensive ice is suggested by Dundas et al. (2018) in their report of deposits of ice exposed in cliffs at ~ 55°S and 55°N. Those deposits, which can be > 100 m thick, extend downwards from depths of 1–2 m. And, finally, there is the possibility of equatorial ice (Wilson et al., 2018) in the uppermost meter or so of the Medusae Fossae Formation, along the dichotomy. So shallow ice in parts of the mid and higher latitudes (and possibly equatorially) could seal methane trapped in shallow lithologic reservoirs. If a recent impactor hits one of these ice seals, it could breach that seal, accounting for a pulse of methane released to the atmosphere.

In contrast, as noted, methane clathrates may be restricted to depths greater than 15 m in equatorial latitudes (Max et al., 2013) though they are likely to exist at shallower depths at latitudes > 60° (Chastain and Chevrier, 2007). So clathrates at latitudes > 60° may well be destabilized by physical disruption caused by shallow recent impacts. Deeper clathrates, at lower latitudes, would be more difficult to destabilize by small impactors and might only be affected by some of the largest of the recent impacts.

3.4. The role of atmospheric pressure and temperature

Atmospheric factors (described in Section 2.2) can be quite important for subsurface methane release. Mars is a windy and stormy environment, with wind speeds up to around 30 m per second (e.g., Cantor, 2007). Winds and pressure changes, also related to the strong daily thermal variations, may therefore be important contributors to episodic release of methane that may have reached near-surface horizons, as observed on Earth. The same processes inducing martian dust uplift, such as thermal creep airflow or "dust devils", characterized by a pressure drop in their center (e.g., de Beule et al., 2014; Küpper and Wurm, 2015) could produce gas exhalation "pulses". And, in a dry, water-free (and thus presumably microbial-free) subsurface, possible seasonal (cyclic) variations of microseepage can be related to seasonal variations of atmospheric temperature, pressure, and winds.

Atmospheric processes may additionally overprint on any methane releases that occur from subsurface geological processes. For example, in a preliminary study, Pla-Garcia et al. (2018) suggest that variable background methane detections at Gale crater might be a result of changes in local ground temperatures caused by atmospheric circulation. They suggest that during the period on Mars of Ls (solar longitude) 225–315, which correlates with low background methane abundances (Webster et al., 2018), airflow would originate from the cold northern hemisphere, whereas in other seasons, the airflow into Gale crater would be from more tropical areas, closer to Gale and consequently warmer. If this were the case, then warmer temperatures in Gale crater beyond the Ls 225–315 period might affect clathrate releases in the region.

Thermal oscillations, caused by the variation of the obliquity or by seasons, can destabilize clathrates at relatively large depths (several hundred meters) depending on latitude and thermal conductivity of the ground (Gloesener et al., 2018) or cause melting of permafrost seals for conventionally trapped methane. The same temperature changes may control microbial activity, if any, as observed on Earth, so that warmer periods may induce higher methane consumption by methanotrophs and thus lower surface seepage rates (Etiope and Klusman, 2010). This possibility, though hypothetical, is clearly an area of continuing research and these types of mechanisms deserve additional experimental and modeling work assuming different scenarios of near-surface methane occurrence, as well as seasonal changes in martian circulation processes.

4. Can seepage variability provide insight into biotic vs abiotic methane origin?

The answer is no. Based on what has been discussed above, gas flux intensity and variability at the ground-atmosphere interface are solely determined by physical factors (permeability and pressure gradient), which operate on any type of subsurface methane, regardless its origin. The variability of gas release to the atmosphere is more linked to variability of factors affecting gas accumulations (especially those shallow), rather than to variability of gas production in a deep source rock. Both microbial and abiotic methane can accumulate in gas pockets, in clathrates, in zeolites, or in conventional reservoirs trapped below ice, after migration from a source rock. Different from diffusion, where CH_4 isotopic composition affects the diffusion coefficient and thus CH_4 migration, in seepage, which is mostly driven by advection (see Section 2), CH_4 isotopic composition, and thus its origin, has no influence on gas flow rates or responses to pressure stress.

Even seasonal variations of atmospheric methane on Mars (e.g., Webster et al., 2018) cannot be attributed to biotic or abiotic origins. On Earth, microbes (methanotrophs) in the soil determine microseepage seasonality, by consuming more methane in summer and wetter seasons, so that fluxes are higher in winter and dry seasons (Etiope and Klusman, 2010). However, on Mars, potential methane-consuming and/or generating bacteria could only reside in the subsurface, in the presence of liquid water, in endolithic ecosystems within pore spaces of rocks and in ice and permafrost (Oehler and Etiope, 2017 and references therein). Although seasonal temperature variations in these systems could control such hypothetical microbial activity (and thus methane fluxes at the surface), as discussed above, CH_4 seasonal variations on Mars can also be due to atmospheric changes (winds and storms), melting/sublimation of permafrost and ice, and destabilization of shallower clathrates, all of which could operate on non-microbial methane, as well. Therefore, CH_4 seasonality on Mars is not diagnostic of methane origin.

5. Summary model and concluding remarks

By analogy with gas seepage on Earth, subsurface gas pressure gradients on Mars (induced by gas accumulations and permeability of fracture/fault networks) represent the main determinant of methane seepage occurrence, intensity and variability. Mars has a brittle and potentially highly fractured and faulted lithosphere, which may widely host gas accumulations and gas migration routes for seepage to the surface. Episodic, occasional or recurrent, methane releases will occur when specific geological and atmospheric processes induce sudden or progressive changes of pressure and permeability. It is the sum of generation location, subsurface accumulation points, conduits for release to the atmosphere, and triggers for release that control the sites of methane release on the surface, accounting for spatial variability. Atmospheric processes (e.g., barometric pressure drops related to winds and storms) will overprint on the spatial variability and may contribute to seasonal variations. Fig. 4 summarizes the entire system.

Although it might still be argued that some of the methane detections on Mars may not be real, the methane observations acquired so far, including the spikes, seasonal oscillations and non-detections (see references in the Introduction), appear compatible with geological seepage dynamics. In addition, the very existence of methane seepage appears logical and expected given the abundance of methane-generating mechanisms and the great potential for gas storage and migration to the surface (Oehler and Etiope, 2017). Obviously, the variability of

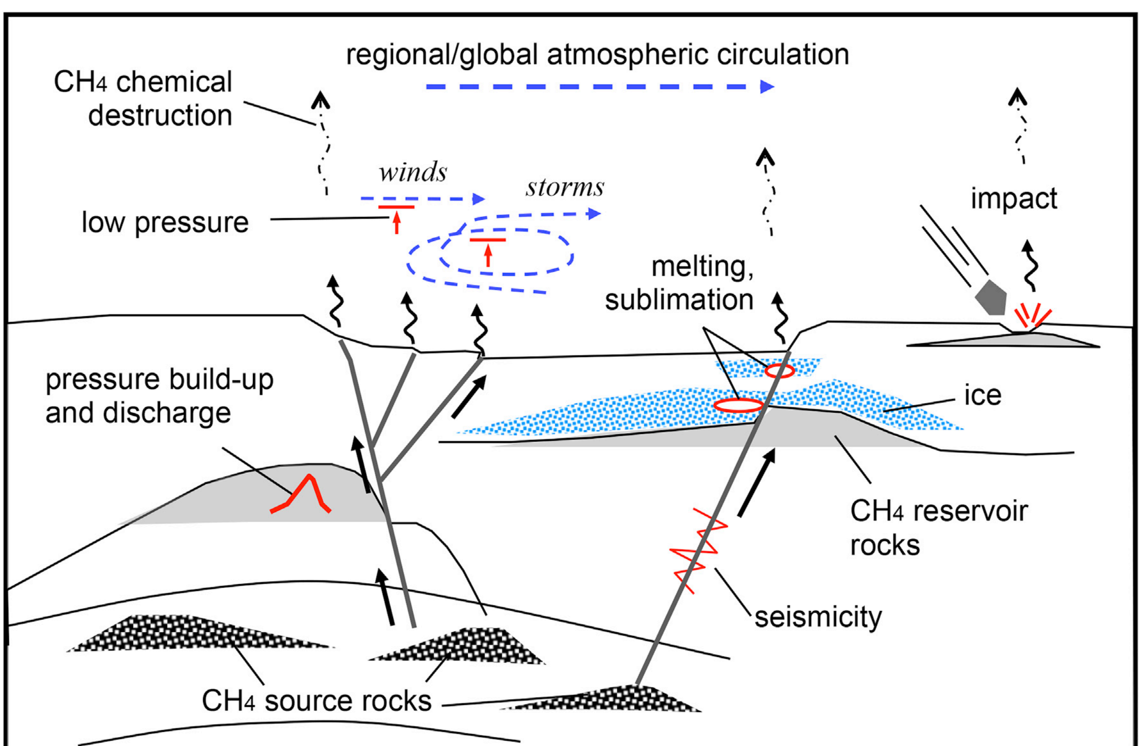

Fig. 4. Summary sketch of endogenous (geological, subsurface) and exogenous (atmospheric) processes (all marked in red) that can produce episodic (irregular or seasonal) release of methane on Mars. Gas seepage spikes may result from rapid changes in the gas pressure gradient (reservoir and atmospheric pumping) or sudden increase of rock permeability (opening of pathways due to seismicity, impact, ice melting/sublimation, or local tectonism). Squiggly arrows: methane release; thin blue dashed arrows = near-ground air circulation (winds, storms, “dust devils”) inducing low pressure above the ground (Bernoulli effect). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

methane seepage discussed in this work needs to be integrated in a unifying model with simulations of atmospheric circulation and proposed, additional processes of rapid atmospheric methane removal (e.g., Lefèvre and Forget, 2009; Knak-Jensen et al., 2014; Holmes et al., 2015), which can be tested against all methane observations acquired so far.

Given the very low (ppbv) amounts of methane only episodically detected in the martian atmosphere, net of the atmospheric removal process, the average level of seepage on Mars is likely orders of magnitude lower than that on Earth. This fact coupled with the known variability of seepage on Earth, argue that the source locations for the methane detected in the martian atmosphere may be restricted to specific regions with relatively high potential for methane generation and seepage (see detailed discussion of potential seepage sites in Oehler and Etiope, 2017). And weak, localized, sporadic seepage fluxes (as in the seepage pattern "c" discussed in Section 2.4.2) could result into very low global average CH_4 concentrations, eventually below detection limits or not requiring very fast removal processes. However, it is important to take into account that the "lifetime" of a seepage site is generally quite long or perennial, at least lasting centuries. Therefore, a site that may have episodically released methane on Mars is expected to repeat the release sooner or later.

Allowing for the oscillating character of methane seepage and the potential for additional atmospheric removal processes (as referenced above), non-detections can be more frequent than detections. Thus, if methane sensors operate discontinuously and only in one site or over a limited number of regions, then non-detections will be the rule and detections will be relatively rare. The chances of methane detection may increase if the observations are focused and repeated on specific, high-graded areas of gas release determined by geological analysis (Oehler and Etiope, 2017). Seepage variability, including seasonality, being controlled mainly by physical migration factors, is not related to methane origin. Thus, although methane of biologic origin is conceivable, to date there is no definitive evidence for past or present life on Mars, and the methane data are not sufficient, in themselves, to conjecture about any relevance to life on Mars.

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