Icarus 236 (2014) 24–27

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

A sink for methane on Mars? The answer is blowing in the wind

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ARTICLE INFO

Article history:
Received 11 September 2013
Revised 5 March 2014
Accepted 15 March 2014
Available online 31 March 2014

Keywords:
Mars, atmosphere
Aeolian processes
Atmospheres, chemistry

ABSTRACT

Tumbling experiments that mimic the wind erosion of quartz grains in an atmosphere of ^{13}C-enriched methane are reported. The eroded grains are analyzed by ^{13}C and ^{29}Si solid-state NMR techniques after several months of tumbling. The analysis shows that methane has reacted with the eroded surface to form covalent Si–CH_3 bonds, which stay intact for temperatures up to at least 250 °C. The NMR findings offer an explanation for the fast disappearance of methane on Mars.

1. Introduction

Recently methane (CH_4) has been observed in the martian atmosphere from a satellite orbiting the planet (Formisano et al., 2004) as well as from Earth based telescopes (Krasnopolsky et al., 2004). These observations are exciting as methane may be a fingerprint of past or present life on Mars. Currently, the Curiosity rover on Mars is exploring various issues related to methane. However, so far the source of methane has not been identified. Potential sources could be biological in origin, like methanogenesis in extreme environments (Reid et al., 2006) or geochemical processes, like serpentinisation (Oze and Sharma, 2005) or volcanism (Etiope et al., 2007) or methane release from clathrates (Chastain and Chevrier, 2007). Release of methane from such processes could occur as episoidic events.

Likewise, the fate of methane is a mystery. Observations indicate that methane disappears within a few years after a plume eruption (Mumma et al., 2009; Lefèvre and Forget, 2009), while the photochemical processes that operate on Earth predict a lifetime in the range of several hundred years (Mumma et al., 2009). Various mechanisms proposed for the disappearance of methane have difficulties reproducing its short residence time (ten Kate, 2010). Reported concentrations of methane are in the range of tens of ppbv. A significant feature of methane concentrations is that they show a substantial time and spatial variation (Geminale et al., 2008, 2011; Mumma et al., 2009; Lefèvre and Forget, 2009; Krasnopolsky, 2012). Here we show, using solid-state ^{13}C and ^{29}Si magic-angle spinning NMR spectroscopies, that wind driven erosion produces highly reactive sites on mineral grain surfaces that sequester methane by forming covalent bonds with methyl groups and propose that this mechanism can be the hitherto undiscovered methane sink on Mars. The mechanism is supported by experiments where quartz (SiO_2) grains are exposed to gentle mechanical agitation in a methane atmosphere, using a specially designed experimental setup, that mimics mineral grain transport created by a typical martian wind. The predicted lifetime of methane agrees well with the one experimentally observed. We anticipate that the designed agitation process can be useful in studies of surface erosion and surface chemistry. After this paper was submitted, in situ measurements by the Curiosity team found very little evidence, if any, for methane in the Gale crater on Mars (Webster et al., 2013). These findings are discussed in relation to our findings in Section 4.

2. Materials and methods

The wind driven erosion of surface material is simulated using the specially designed apparatus depicted in Fig. 1. Commercially available quartz (Merck, 1.07536) was chosen as an analogue for

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http://dx.doi.org/10.1016/j.icarus.2014.03.036
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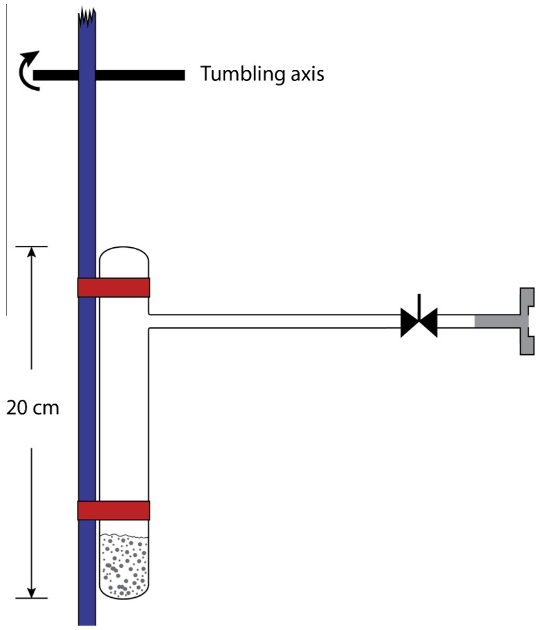

Fig. 1. Schematic drawing of the tumbling apparatus. The flask (borosilicate, Simax 3.3) contains about 10 g of SiO_2 grains, which have been sieved to extract the fraction between 125 and 1000 μm. This fraction was ultrasonic treated and washed several times to remove all attached finer particles. The gas in the flask is ^{13}C-enriched CH_4 at a pressure of approximately 600 mbar. The tumbling rate is 30 RPM. The whole tumbling apparatus is enclosed in a box to avoid any potential interference from photochemistry.

surface material because of its simple chemical composition. The quartz was placed in a borosilicate flask with ^{13}C-methane (Sigma–Aldrich, 490229, 99% enriched) to facilitate NMR investigations. The basic purity of the ^{13}C-methane gas was confirmed by ^{13}C NMR experiments on the gas loaded in a glass tube. The flask with quartz and ^{13}C-methane was sealed and mounted in a carousel where it was tumbled end-over-end at 30 RPM. The collision speed of the quartz grains as they tumble is about 1 m/s, which is a typical saltation collision speed close to threshold (Holstein-Rathlou et al., 2010; Merrison et al., 2010; Merrison, 2012). After several months of tumbling the quartz material was analyzed by solid-state NMR techniques (details of the NMR experiments are given in the Supplementary information).

3. Results and discussion

The reaction of ^{13}C-enriched methane with surface sites of highly active quartz particles is unambiguously demonstrated by the $^{13}C\{^1H\}$ CP/MAS and $^{29}Si\{^1H\}$ CP/MAS NMR spectra shown in Figs. 2 and 3, respectively. In these spectra the cross-polarization (CP) NMR technique transfers ^1H magnetization to either the ^{13}C or ^{29}Si spins *via* heteronuclear dipolar couplings and thereby acts as a filter for detecting only ^{13}C and ^{29}Si spin nuclei within a distance less than 3–5 Å to nearby ^1H nuclei. The $^{13}C\{^1H\}$ CP/MAS NMR spectrum of the quartz grains agitated in an atmosphere of methane, and stored under standard atmospheric and temperature conditions (Fig. 2A), exhibits a resonance at $\delta(^{13}C) = -1.7$ ppm, *i.e.*, very similar to the ^{13}C chemical shift reported for $Si–CH_3$ groups; for example, $\delta(^{13}C) = 0.0$ ppm for $Si(CH_3)_4$ (TMS). In addition to the ^{13}C CP/MAS NMR spectrum, we note that several other ^{13}C MAS NMR experiments for the sample (*e.g.*, inversion-recovery $T_1(^{13}C)$ measurements and $^{13}C\{^1H\}$ cross-polarization–depolarization experiments) reveal restricted rotation for the methyl group around the $Si–CH_3$ bond. Samples from the methane–quartz batch have been exposed to heat-treatment at 250 and 550 °C for 1 h. The $^{13}C\{^1H\}$ CP/MAS NMR spectrum of the 250 °C sample (Fig. 2B) shows intact $Si–CH_3$ groups while no ^{13}C signal could be detected for the 550 °C sample. The line width of the resonance for the 250 °C sample (Fig. 2B) is slightly more narrow (FWHM = 5.5 ppm) compared to that shown in Fig. 2A for the original sample (FWHM = 7.7 ppm). The observed line-narrowing may be ascribed to annealing processes and/or to elimination of water dehydroxylated from the quartz surface. A second flask with quartz and ^{13}C-methane, prepared under identical conditions as used for the sample described above, was not exposed to tumbling and kept stationary for the same period of time. $^{13}C\{^1H\}$ CP/MAS NMR spectra of this sample show no ^{13}C NMR resonances at all, which demonstrate that the reaction of methane with quartz requires activation of the quartz grains by the tumbling process.

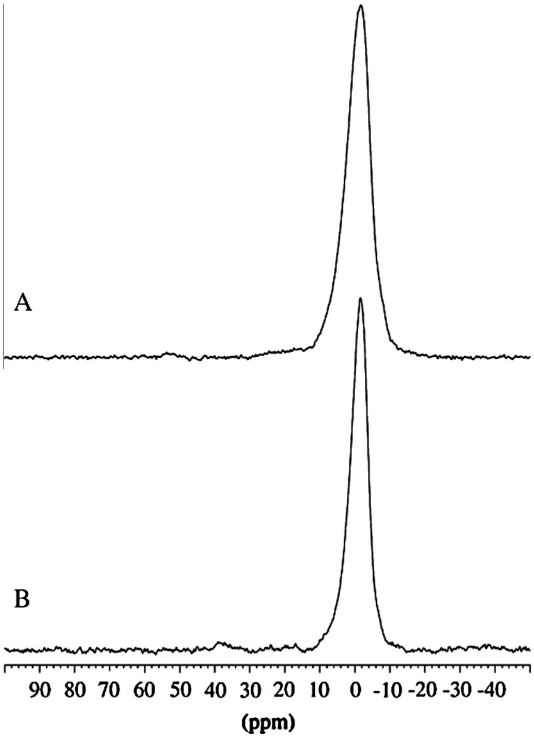

Fig. 2. $^{13}C\{^1H\}$ CP/MAS NMR spectra. Spectra of the quartz sample, agitated in an atmosphere of 99% ^{13}C-enriched CH_4 for 115 days at room temperature. The spectra are acquired at room temperature and at 7.05 T using a CP contact time τ_{CP} = 3.0 ms. (A) Spectrum of the original sample using a spinning frequency ν_R = 10.0 kHz and acquisition of 18,944 scans. (B) Spectrum of the original sample, after heat-treatment at 250 °C for 1 h, using a spinning frequency ν_R = 3.0 kHz and acquisition of 1024 scans.

The standard one-pulse ^{29}Si MAS NMR spectrum of the methane–quartz sample in Fig. 3B exhibits a narrow resonance (FWHM = 0.11 ppm) at $\delta(^{29}Si) = -107.5$ ppm, *i.e.*, the well-known ^{29}Si chemical shift for α-quartz (Lippmaa et al., 1980; Smith and Blackwell, 1983), and thus is assigned to the bulk SiO_2 structure of the sample. More importantly, the ^{29}Si surface sites of the sample are selectively detected in the $^{29}Si\{^1H\}$ CP/MAS NMR spectrum (Fig. 3A), which reveals two broadened resonances at −61 and −101 ppm. The high-intensity resonance at −101 ppm originates from ^{29}Si sites associated with hydroxyl groups, following earlier ^{29}Si CP/MAS NMR studies of silica gels. More importantly, only this resonance at −101 ppm is observed in a similar spectrum of pure quartz exposed to tumbling in ambient air under the same conditions as used for the $SiO_2/^{13}CH_4$ sample. Most interestingly, from previous investigations of modified silica surfaces, HPLC materials, and heterogeneous catalysts (Albert and Bayer, 1991; Kellberg