

Binding of methane to activated mineral surfaces – a methane sink on Mars?

S. J. Knak Jensen (1), J. Skibsted (1), H. J. Jakobsen (1), I. L. ten Kate (2), H. P. Gunnlaugsson (3), J. P. Merrison (4), K. Finster (5), Ebbe Bak (5), J. J. Iversen (4), J. C. Kondrup (1), **P. Nørnberg** (5)
(1) Instrument Center for Solid-State NMR Spectroscopy, Department of Chemistry, Center (iNANO), Aarhus University, Denmark, (2) Department of Earth Sciences, Utrecht University, The Netherlands. (3) CERN, PH Div, CH-1211 Geneva 23, Switzerland and KU-Leuven, Instituut voor Kern- en Stralingsfysica, Celestijnenlaan 200d, B-3001 Leuven, Belgium (4) Department of Physics and Aarhus University, Denmark. (5) Department of Bioscience, Aarhus University, Denmark.

Abstract

Tumbling experiments that simulate 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-CH₃ bonds, which stay intact for temperatures up to at least 250° C. These findings offer a model for a methane sink that might explain the fast disappearance of methane on Mars.

1. Introduction

Recently methane (CH₄) has been observed in the Martian atmosphere from a satellite orbiting the planet [1] as well as from Earth based telescopes [2]. A significant feature of methane concentrations is that they show a substantial time and spatial variation. Detailed snapshots measurements by MSL have shown that the concentration of methane is very low, i.e., 0.18 ± 0.67 ppbv and considered unlikely related to microbial activity [3]. However, the most recent results from Curiosity at Gale crater (7.2 ± 2.1 ppbv) indicate episodically methane production [4]. To reconcile these findings a fast destruction mechanism is required. 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 [5].

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 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.

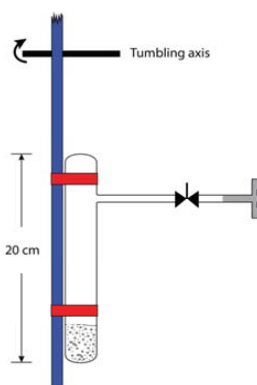


Figure 1: Schematic drawing of the tumbling apparatus.

3. Results and discussion

The reaction of ^{13}C -enriched methane with surface sites of highly active quartz particles is unambiguously demonstrated by the $^{13}\text{C}\{^1\text{H}\}$ CP/MAS and $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectra, of which the latter spectra are shown in Fig. 2. 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. An un-tumbled quartz/methane flask was stored and used as a control for the activation effect.

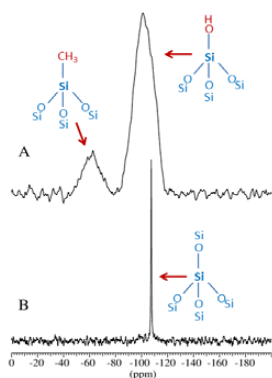


Figure 2: ^{29}Si MAS and CP/MAS NMR spectra

The standard one-pulse ^{29}Si MAS NMR spectrum of the methane-quartz sample in Fig. 2B exhibits a narrow resonance (FWHM = 0.11 ppm) at $\delta(^{29}\text{Si}) = -107.5$ ppm, i.e., the well-known ^{29}Si chemical shift for α -quartz [6] and [7], 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 $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR spectrum (Fig. 2A), 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 $\text{SiO}_2/^{13}\text{CH}_4$ sample. Most interestingly, from previous investigations of modified silica surfaces, HPLC materials, and heterogeneous catalysts [8] and [9] it is known that methyl groups directly bonded to a Si atom on a silica surface give ^{29}Si resonances in distinct regions of the ^{29}Si chemical shift scale according to the number of attached methyl groups. For example, for a $(\text{CH}_3)_2\text{Si}(\text{OSi})_2$ species: $\delta(^{29}\text{Si}) = -14$ to -20 ppm, while for $\text{CH}_3\text{Si}(\text{OSi})_3$ species: $\delta(^{29}\text{Si}) = -53$ to -65 ppm. Thus, the observed resonance at -61 ppm can be assigned to a $(\text{SiO})_3\text{Si}-\text{CH}_3$ site. This result and the absence of the resonance at -61 ppm for the tumbled sample of pure quartz present an unambiguous and direct proof that agitation of quartz in a methane atmosphere results in a methyl group being directly bonded to a Si atom.

In addition to the $\text{SiO}_2/^{13}\text{CH}_4$ experiments we also tumbled a sample of olivine (from the Spanish island of Lanzarote) in ordinary CH_4 (with an isotope distribution of about $^{12}\text{C} = 99\%$ and $^{13}\text{C} = 1\%$). The rate of pressure change for olivine is lower than that for quartz, but not more than a factor of two.

4. Summary and Conclusions

Our laboratory studies show that a wind mediated erosion process of ordinary quartz crystals can produce activated quartz grains, which sequester methane by forming covalent Si-C bonds. If this process is operational on Mars, which our recent preliminary studies on olivine indicate could be the case then it can explain the observed fast destruction of methane.

Acknowledgements

This research was supported by Villum Kann Rasmussen Foundation, the Danish National Research Council, the Danish Council for Independent Research, Natural Sciences and the Carlsberg Foundation. The authors wish to thank Dr. Morten Bo Madsen, University of Copenhagen, for useful discussions.

References

- [1] Formisano, V. et al.: Science 2004, 306, 1758-1761.
- [2] Krasnopolsky, V. et al.: Icarus 2004, 172, 537-547.
- [3] Webster, C.R. et al.: Science 2013, 342, 355-356.
- [4] Webster, C.R. et al.: Science 2015, 347, 415-417.
- [5] Jensen, S.K.J. et al.: Icarus 2014, 236, 24-27.
- [6] Lippmaa, E. et al.: J. Am. Chem. Soc. 1980, 102, 4889-4893.
- [7] Smith, J.V. and Blackwell, C.S.: Nature 1983, 303, 223-225.
- [8] Albert, K. and Bayer, E. J.: Chromatogr. 1991, 544, 345-370.
- [9] Kellberg, L. et al.: J. Catal. 1993, 143, 45-51.