**Free-Radical Intermediates from Experiments which Mimic the Winds on Planet Mars**

Jakobsen, H.J.; Jensen, S.K. (Aarhus U., Denmark, Chemistry); Gan, Z. and Song, L. (NHMFL, FSU)

**Introduction**

Recently, some of us reported that SiO2 grains tumbled end-over-end in a cylindrical Pyrex-glass tube filled with CH4 (methane) gas resulted in a gas-solid reaction with the quartz grains [1]. The tumbling frequency of this reaction flask corresponds to the grains having a speed similar to the winds on Mars. Characterization of the solid product, using 29Si and 13C CP/MAS NMR, revealed the presence of CH3–Si≡ and Si–OH groups in an otherwise unknown silicate structure [1]. Identical results have recently been observed using Al2O3 (corundum) grains, which show that SiO2 & Al2O3 act as an abrasive on the Pyrex tube. To obtain further insight on the reaction mechanism and structure this study reports preliminary EPR results on some intermediates and products of our experiments.

**Experimental**

 Solid-state EPR spectra were collected from selected samples (opened at STP or in a glove-box Ar atmosphere) packed & sealed in 0.3 or 0.4 mm outer diameter EPR sample tubes. EPR spectra were recorded at X-band frequency of 9.84 GHz on a Bruker E680 spectrometer using a high sensitivity cavity (ER 4119HS).

**Results and Discussion**

 The EPR spectra of the material (sample 0, un-sieved) obtained from the reaction between CH4 and SiO2 grains [1] are shown in **Fig. 1** using two different levels of microwave power (40 mW and 0.2 mW). Clearly, the spectra appear as an overlap of the signals from two different radicals. To be noted, the broadened spectrum at 40 mW is similar to the published spectra [2] observed following *γ*-irradiation of Pyrex, except that the concentration of the radicals producing the narrow spectral peak is much higher in our sample.



**Fig.1**. EPR spectra of sample 0 (un-sieved) at 40 and 0.2 mW, and for its sieved (< 100 μm) sample 1 at 0.2 mW (far right).

The broadened spectra of sample 0 observed at high microwave power is ascribed to the well-known boron-oxygen hole center (BOHC) [2]. It has been proposed that the electron traps which generate the narrow g = 2.0006 signal arise from a sub-microscopic silica glass structure [2]. After sieving (< 100 μm sieve) the crude 10 gram of material for sample 0 [1], the EPR spectrum for this fraction (sample 1) is also shown in **Fig. 1** for comparison with the un-sieved sample 0. A dramatic decrease in the intensity for the narrow g= 2.0006 signal was observed for the sieved sample. Moreover, a huge increase in the S/N ratios, by a factor of 20-25, was observed for both the 29Si and 13C CP/MAS NMR spectra for the sample 1 sieved fraction.

**Conclusions**

 Combined NMR & EPR results provide insight into the structure and mechanisms of a sink for CH4 on Mars.

**Acknowledgements**

 We acknowledge the NHMFL, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. We acknowledge the NMR and Mars facilities at Aarhus University.

**References**

[1] Jensen, S.J.K., *et al*., Icarus, **236**, 24-27 (2014).

[2] Brown, G., J. Mater. Science, **10**, 1841-1848 (1975).