

**PRODUCTION OF CHLORINATED HYDROCARBONS DURING THE THERMAL DECOMPOSITION OF METAL CARBONATES AND PERCHLORATE SALTS.** R. C. Quinn<sup>1</sup> and D. J. Pacheco<sup>2</sup>, <sup>1</sup>SETI Institute, NASA Ames Research Center, Moffett Field, CA 94035 (email: Richard.C.Quinn@nasa.gov), <sup>2</sup>San Jose State University, San Jose, CA 95076.

**Introduction:** The first report of the *in situ* detection of organic compounds of martian origin was based on the results of the Viking Carbon Assimilation experiment, also referred to as the Pyrolytic Release (PR) experiment [1]. Following the discovery of perchlorates in martian soil [2], the generation of chloromethane ( $\text{CH}_3\text{Cl}$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) during sample analysis in the Viking gas chromatograph-mass spectrometer (GCMS) [3] was attributed to the thermally induced reaction of soil organics with perchlorate [4]. More recently,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$  were detected during thermal analysis of martian soils using the Sample Analysis at Mars (SAM) instrument suite on the Curiosity rover [5].

We have reexamined the Viking GCMS and PR results to establish mechanisms that may result in the formation of chlorinated hydrocarbons during the thermal analysis of martian soils. We show, using Viking protocols, that the thermal decomposition of carbonates in the presence of metal catalysts can, in some cases, result in methane formation and, when perchlorate is present, in the formation of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ . We hypothesize that the origin of the organics detected in the Viking PR experiment was not due to the fixation of atmospheric carbon into organic carbon as presumed [1], but instead may have been due the formation and subsequent thermal decomposition of inorganic carbonates. Although terrestrial organic contamination may have provided the dominant carbon source for the production of chlorinated hydrocarbons during the Viking GCMS analyses, based on our results, it appears that a contribution from inorganic carbonates is also possible.

**Experimental:** A custom built system was used to replicate key aspects of the Viking GCMS [3]. Thermally evolved gases were separated using a poly-metaphenylene oxide coated 2,6-diphenyl-para-phenylene oxide (Tenax, 2m, 60/80 mesh) GC column. In experiments that used  $\text{H}_2$  carrier gas, as was done in the Viking GCMS, a palladium/silver  $\text{H}_2$  separation tube was used to remove the carrier prior to sample product elution into the MS. Experiments were also carried out using helium as the carrier gas. A Pyroprobe 2000 with a 1500 GC interface (CDS Analytical Inc.) was used to heat samples held in a 50 micro liter quartz tube and to introduce the evolved volatiles into the GC column. Thermal analyses were performed using three different

sample headspace gases:  $^{13}\text{CO}_2$ ,  $\text{H}_2$  (the gases used in the Viking GCMS), and He.

$\text{NiCa}(\text{CO}_3)_2$  and  $\text{FeCa}(\text{CO}_3)_2$  were synthesized to test nickel and iron as catalysts for the production of hydrocarbons during the thermal decomposition of carbonates [6]. Thermal analyses were performed using the mixed metal carbonates alone and with different combinations of magnetite, hematite, magnesium perchlorate and/or acetone.

**Results and Discussion:** Acetone contamination at ppb levels was detected during the Viking lander 2 (VL2) GCMS analyses [3]. We show that, as expected, when perchlorate is combusted in the presence of acetone,  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  are produced (fig. 1). During sample analysis on Mars, the VL1 GCMS detected the presence of  $\text{CH}_3\text{Cl}$  while the VL2 GCMS detected  $\text{CH}_2\text{Cl}_2$ . We believe that differences in sensitivity caused by the effluent divider, which split variable amounts of carrier gas from the Viking MS, can account for the fact that each of the VL1 and VL2 instruments did not detect both  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ . Our results indicate that the volatilization of acetone and perchlorate produces small amounts of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$ , and that this may explain the VL2 GCMS results. However, we note that although  $\text{CH}_3\text{Cl}$  was observed using the VL1 GCMS, acetone was not. This

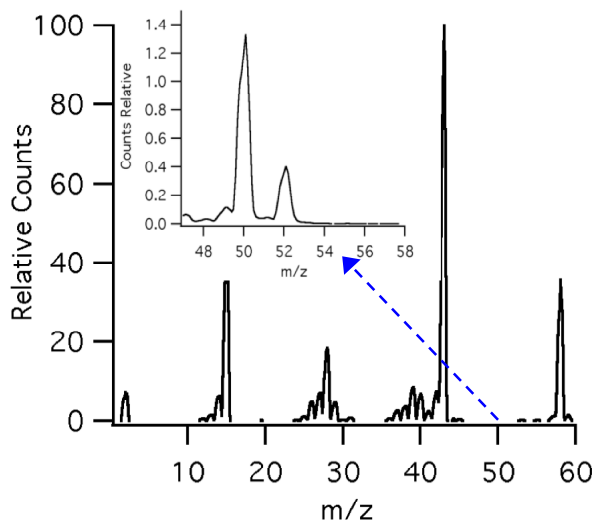


Fig. 1. Mass spectrum of acetone eluted after volatilization in the presence of perchlorate using Viking GCMS protocols.  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  also elute with different retention times (inset).

fact, in combination with the PR results, may suggest that during the thermal analysis of martian soils, other chlorinated hydrocarbon production mechanisms that do not involve organic contamination or soil organics may be possible.

**Carbonate Decomposition.** When thermal decomposition of the metal carbonates is carried out in the presence of  $H_2$  (the Viking carrier gas), methane is produced. In general, to mimic the Viking protocols samples were sequentially heated for 30 seconds at 200°, 350°, or 500°C. Although, in some experiments, extended heating durations were performed. We find that the quantity of methane produced depends on the metal catalysis, thermal volatilization time and temperature. When thermal analysis of the metal carbonates is performed in the presence of perchlorate,  $CH_3Cl$  and  $CH_2Cl_2$  are detected (fig. 2).

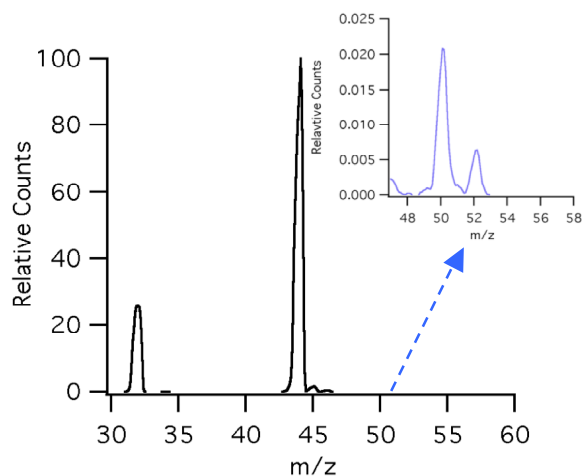


Fig. 2. Mass spectrum of  $O_2$  and  $CO_2$  produced after heating  $NiCa(CO_3)_2$  to 350°C using Viking GCMS protocols.  $CH_3Cl$  is also eluted with a later retention time (inset).

**Viking PR experiments.** In the Viking PR experiment, martian soils were incubated for 120 hours in a test cell containing an added mixture of  $^{14}CO_2$  and  $^{14}CO$  (92:8 by volume; partial pressure 2.2 mbar). After incubation, the soil was pyrolyzed at 625°C and volatile products were trapped. After trapping, volatiles were desorbed and measured as two separate fractions, residual  $^{14}CO$  and  $^{14}CO_2$ , and trapped  $^{14}C$ -labeled organics. Picomolar levels of labeled organic products were detected from 0.25 cc samples that were incubated either in the dark or exposed to UV light [1]. In contrast to the assumption that labeled organics formed in the soils, we propose the possibility that labeled-carbonates were formed by  $^{14}CO_2$  adsorption onto basic-pH Viking soils [7]. Possible carbonate formation mechanisms, at PR incubation temperatures, include

the reaction of  $^{14}CO_2$  with soil superoxides or other soil oxidants. Under some conditions using He head-space and carrier gas, we have detected the production of trace levels of  $CH_3Cl$  and  $CH_2Cl_2$  during the thermal volatilization of metal carbonates and hydrated perchlorate mixed with magnetite and hematite. We report on additional experiments designed to confirm this observation and to determine relevant mechanisms.

**References:** [1] Horowitz N. H. et al. (1977) *JGR*, 82, 4659–4662. [2] Hecht, M. H. et al. (2009) *Science* 325, 64–67. [3] Biemann K. et al. (1977) *JGR* 82, 4641–4657. [4] Navarro-González R. et al. (2010) *JGR* 115, E12010. [5] Mahaffy P. R. et al. (2010) *Press Conference* 45th AGU Meeting, San Francisco CA. [6] Jagadeesan D. et al. (2009) *ChemSusChem* 2, 878–882. [7] Quinn R. and Orenberg J. (1993) *Geochim. Cosmochim. Acta* 57, 4611–4618.

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