PERCHLORATE AND VOLATILES IN BRINES OF LAKE VIDA (ANTARCTICA): IMPLICATION FOR THE ANALYSIS OF MARS SEDIMENTS. F. Kenig[1], L. Chou[1], W.A. Jackson[2], C.P. McKay[3], P.T. Doran[1,4], A.E. Murray[5] and C.H. Fritsen[5].
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Introduction: A cold (-13.4 ˚C), saline (188 psu) evaporative brine is encapsulated in the thick (> 27 m) ice of Lake Vida (McMurdo Dry Valleys, Antarctica)[1]. This Lake Vida brine (LVBr), which contains abundant dissolved organic carbon (48.2 $mmol \cdot L^{-1}$), support an active but slow microbial community [1].

LVBr contains oxichlorines with 50 $\mu g \cdot L^{-1}$ of perchlorate (ClO_4^-) and 11 $\mu g \cdot L^{-1}$ of chlorate (ClO_3^-). We report here on the artifacts created by oxychlorines upon analysis of volatiles and volatile organic compounds (VOCs) of LVBr by solid phase micro extraction (SPME) gas chromatography-mass spectrometry (GCMS). We compare analytical blanks to a standard containing 50 $\mu g \cdot L^{-1}$ of perchlorate and to actual LVBr sample runs. The similarities and differences between our results and those obtained by the Sample Analysis at Mars instruments of the rover Curiosity are discussed.

Results and discussion: The volatiles evolved from LVBr upon analysis with SPME GCMS are dominated by CO_2, dichloromethane, HCl, and volatile organic sulfur compounds (VOSCs). Here, CO_2 is derived from the combustion of organic compounds by the oxygen released from oxichlorines in the 300 ˚C split/splitless injector of the GC. As helium was used as a carrier gas, the source of H in HCl can only be the organic matter from the sample and the organic phases used on the SPME fiber as well as the capillary column. HCl is present in blanks containing perchlorates.

The volatiles evolved from LVBr upon SPME GCMS can be divided in five groups: Chlorinated compounds, VOSCs, aromatics, oxygenated compounds, and hydrocarbons.

Chlorinated organic compounds. DCM was observed in all samples including blanks with perchlorate, suggesting that DCM is exclusively an artifact of the reaction of Cl with organic carbon in the injector.

Methyl chloride (MeCl) and trichloromethane (TCM) were not detected in the blanks but were detected in LVBr samples when using a SPME fiber made of Carboxen™/polydimethylsiloxane (PDMS). This does not mean that MeCl amd TCM are original to the brine. It more likely means that the abundance of MeCl and TCM (as well as DCM) depends on the availability of carbon in the injector and that DCM formation is favored.

Oxygenated compounds. Most of the oxygenated compounds observed in LVBr run were also observed in perchlorate blanks, but were absent from analytical blanks. These compounds include acetic acid, tetrahydrofuran, ethylacetate, and ketones such as 2-butanone. It is unlikely that any of the oxygenated compounds observed derives from LVBr; they most likely derive from reaction of the oxygen released upon perchlorate decomposition in the injector with available carbon.

Aromatic compounds. Benzene, toluene, and styrene were observed in LVBr samples, but styrene was exclusively present in samples analyzed with a SPME fiber made of PDMS/divinylbezene. Benzene, toluene and styrene may derive from the degradation of the divinylbenzene of the SPME fiber. In addition, benzene may be derived from the diphenyl moiety of the capillary column, which is coated with PDMS (95%) and polydiphenylsiloxane (5%; PDPS).

VOSCs. Dimethylsulfide (DMS) and dimethyldisulfide (DMDS) were observed in all LVBr samples analyzed and were absent from both analytical and perchlorate blanks. Thus, DMS and DMDS are most likely derived from the brine itself and, thus, are able to withstand oxidation from decomposing oxichlorines. DMS derives from the photosynthate dimethylsulfoniopropionate [2] and can be used as a biomarker.

Hydrocarbons. 3- and 2-methylpentane, *n*-hexane, and methylcyclopentane were exclusively observed in LVBr samples when analyzed with a Carboxen™/PDMS SPME fiber. These compounds are absent from blanks and there are no sources for such compounds in the in the SPME fibers and column coating. Thus, these compounds may possibly derive from the brine, having survived perchlorate degradation.

Conclusions: Most compounds are artifacts resulting from oxichlorine decomposition, but some, such as VOSCs and LMW hydrocarbons, are able to resist during analysis if sufficient organic carbon is present to uptake Cl and O derived from the perchlorates.

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