

Observations of Excessive Hydrogen from Transuranic Waste Type IV Solidified Organics

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Abstract – *A series of batch heatup experiments and a limited set of continuous data studies have provided qualitative evidence that several mechanisms for hydrogen production other than simple real-time radiolysis are causing unexpectedly high hydrogen emissions from some drums of transuranic solidified organic wastes.*

I. INTRODUCTION

Elevated-temperature (i.e., 57 EC), drum-scale gas generation testing¹ of transuranic (TRU) Waste Type IV organic sludges at multiple DOE facilities has found unacceptably high hydrogen gas release rates and pressurization from some drums. These hydrogen emissions are in excess of what may be anticipated from real-time radiolysis and are in excess of room-temperature hydrogen emissions. This paper briefly highlights observations from laboratory-scale studies that provide indication of the mechanisms that may underlie these excess hydrogen emissions.

II. DRUM-SCALE TESTING

Drum-scale gas generation testing in the summer of CY01 as part of the 3100 Cubic Meter Project^a at the Idaho

National Engineering and Environmental Laboratory (INEEL) suffered a greater than 50% failure rate in attempting to qualify Type IV TRU organic sludges for the TRUPACT-II cask due to excessive hydrogen and/or overpressurization.² This low success rate forced the removal of the easily-accessible TRU organic sludges from the project candidate drum inventory with detrimental impacts on the project schedule. Drum-scale testing of TRU organic sludges at the Rocky Flats Environmental Technology Site (RFETS) has also seen unacceptably high rates of hydrogen emissions and potential pressure problems.³ The hydrogen and overpressure problems are preventing transport of TRU organic sludges from both facilities to WIPP in the TRUPACT-II cask and jeopardizing DOE's ability to meet significant waste shipment and closure milestones at both sites. These results corroborate drum-scale results from the mid-80s that also measured unusually high hydrogen emissions from Type IV drums.⁴

^a The DOE is required to move 3100 Cubic Meters of TRU waste out of Idaho by December 31, 2002 per the Settlement Agreement Between the US

Department of Energy and the Governor of the State of Idaho resolving Civil Cases 91-0035-S-EJL and 91-0054-S-EJL, October 17, 1995.

III. LABORATORY-SCALE TESTING

III.A. First Round of Simple G-value Measurements

One year before drum-scale testing was attempted, high rates of hydrogen emissions were reported by researchers at Argonne National Laboratory-West (ANL-W) performing lab-scale, elevated-temperature gas generation tests with 50-g samples of TRU organic sludges. The lab-scale gas generation tests utilized a group of Type IV samples that were leftover from chemical and radiological assay for WIPP waste stream certification.

The first round of lab-scale gas generation testing at ANL-W measured hydrogen emissions from TRU organic sludges at rates that were five times greater than that which can be explained by pure radiolysis. The high hydrogen emissions seen in these studies were not well correlated with ionizing radiation deposition rate. Corresponding G-values ranged from 1.7 to 13 over the series of elevated-temperature tests. Each sample did, however, exhibit G-values in the range of 1.2 to 2.3 at room temperature in perfect agreement with previous room-temperature studies of hydrogen generation from freshly made TRU organic sludge.⁵ Hydrogen emissions were clearly higher at elevated temperature indicating hydrogen production/release by mechanisms other than radiolysis alone.

Excessive hydrogen emissions also occurred simultaneously with increased oxygen consumption but this effect was not consistently correlated across the group of samples, i.e., oxygen consumption was also higher at elevated temperature but the ratios of oxygen consumption versus hydrogen release differed between samples. The one clear trend seen in addition to the obvious temperature effect was an apparent inverse relationship between hydrogen emissions and halogenated solvent concentrations. The inverse solvent relationship indicated that hydrogen might be scavenged into nongaseous species HCl and HF to varying degrees based on halogen presence testing.^{6,7,8}

While the oxygen consumption rates were elevated corresponding with increased hydrogen emissions, the relation was not clear enough to point exclusively to any particular type of oxygen-based reactions. The simplest explanation for excess hydrogen seemed to be chronic accumulation and elevated-temperature release. Specifically, it was hypothesized that room-temperature transport of gaseous hydrogen out of the sludge matrix might be sufficiently slow over decades of drum storage to enable accumulation of hydrogen within the sludge. The

elevated-temperature oxygen consumption would be presumed to be decoupled from the hydrogen release in this storage scenario.

Hydrogen accumulation in such a case might be through any of several mechanisms including solubility, inert particle surface capture and viscous microbubble entrapment. If this were the case, it was further speculated that the elevated temperatures of gas generation testing might have altered effective equilibrium and/or transport properties within the sludge matrix to release portions of the stored hydrogen inventory during testing. In spite of the fact that hydrogen solubility is generally considered low, the possibilities of viscous entrapment or particle surface storage seemed plausible enough to warrant further inquiry.

III.B. Batch High-Temperature Desorption Experiments to Verify and Quantify Hydrogen Storage

Expanded testing within the available inventory of 50-g TRU organic sludge samples was conducted in FY01.⁹ This work brought an additional 38 Item Description Code (IDC)^b 003 samples into the study inventory. The first observation from the second year's study was of the tremendous heterogeneity within the group. The cited FY01 year-end report contains a collection of color photos that show the heterogeneity.^c Some sludge samples were received in too dry a condition to permit safe handling in laboratory hoods. Texture of the dry samples ranged from powder to chalk-like. Other samples were quite moist and able to leave an oily film on sample jars. Coloring of most sludge samples ranged from beige to dark brown with some samples being bright yellow. All these samples had been through organics analyses at another laboratory on the INEEL before being returned to ANL-W for these gas studies. A review of the organics data for these samples found absolutely no correlation between the data and any of the color or texture properties of the samples. This heterogeneity still remains unexplored. It was noted that the dry fraction of samples received at ANL-W was about 50% which was about the same fraction of drums that easily passed drum-scale testing for hydrogen and total gas in the INEEL drum-scale tests.

^b Item Description Code is a DOE labeling system for materials. Primary members of the TRU Waste Type IV Organic Sludge group are the IDC 003 Organic Setups and the IDC 801 OASIS Sludge.

^c <http://tmfa.inel.gov/Documents/BatchE.pdf>

This second round of testing was principally intended to verify the accumulation-and-release hypothesis and bracket the ranges of stored hydrogen concentrations in the TRU waste. This testing occurred over a range of temperatures above gas generation testing temperatures up to 200 EC with batch-mode experiments in both air and inert atmospheres intended to rapidly desorb stored hydrogen and bracket the ranges of effective molality of hydrogen in the sludge. However, these rapid heatup desorption tests produced more evidence of temperature dependence and some evidence of oxygen correlation thereby reinforcing the case for reaction-based hydrogen production rather than just simple storage. The increased apparent correlation between oxygen and hydrogen seemed to be limited to temperatures below approximately 150 EC above which sample discoloration and soot formation accompanied anoxic hydrogen release from some samples.

To aid interpretation of the second year's data and consider further the potential role of oil cracking in these systems, the TRU organic sludge testing in FY01 was augmented with thermal analyses with fresh nonradioactive samples of the base hydrocarbon oil that is the principal component and source of hydrogen in these sludges, Texaco Regal R&O 32 Oil[®].^d Not surprisingly, the base oil was found to be capable of yielding considerably more hydrogen at all temperatures when oxygen was also present. It is not known how similar the modern oil is to the original oil used in metals machining operations at the former Rocky Flats Plant. Apart from fundamental oil blending modifications with unknown differences in cracking susceptibility, it may be safely presumed that the old oil in TRU sludge drums has undergone considerable change during twenty to thirty years of storage. These changes would include competing changes that should produce both larger compounds through polymerization and presumably smaller organic compounds through chronic radiation damage. The degree to which these larger (i.e., polymerized) and smaller (i.e., radiolysis product) compounds might exhibit different thermal cracking responses is unknown. The degree to which differing plutonium particle sizes in different drums might enable more chronic radiation damage versus largely being self-shielding is unknown.

Figure 1 plots the hydrogen release behavior from different samples of IDC 003 TRU Organic Setup Sludge

upon heating in air-filled sealed canisters. Also plotted are hydrogen releases from modern Texaco Regal R&O 32 Oil[®] heated in air and inert argon. All batch tests depicted in Figure 1 included 2- to 3-g samples in 80-ml test vessels with the atmosphere of choice sealed at approximately 0.84 atm at room temperature and then heated to the test temperature for hold times of 20 hours. The test vessels were then allowed to cool to room temperature and then were headspace sampled and analyzed. It must be noted that the 20-hr heatup time for samples was entirely arbitrary and that such batch-style testing has the opportunity to significantly mask quicker phenomenon.

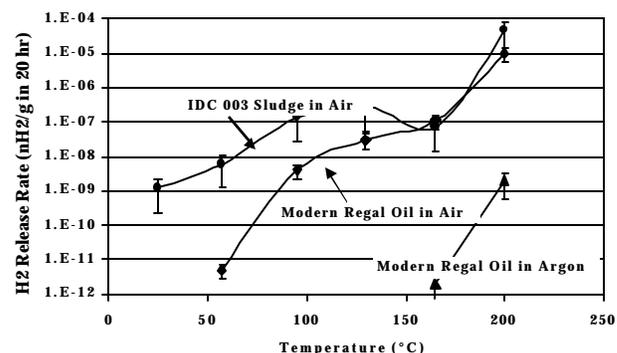


Figure 1. Comparison of rates of hydrogen release from TRU Type IV samples heated in air and modern Texaco Regal R&O 32 Oil[®] samples heated in air versus argon.

Main observations from the cumulative data shown in Figure 1 are that more hydrogen is released from TRU sludge samples than from the modern equivalent of the base oil and that all samples (i.e., TRU waste, oil in air, and oil in argon) are capable of soot-producing anoxic pyrolysis above 150 EC. Soot production below 150 EC was negligible for all samples. This 150 EC threshold has useful implications for treatment planning with TRU waste revolving around thermal desorption. Most important, however, from Figure 1 is the disparity shown between hydrogen from the TRU organic sludge versus hydrogen from modern oil below 150 EC. At 57 EC, only about 25% of the difference in hydrogen production between the TRU sludge samples and the modern oil can be explained by real time radiolysis. The fundamental question continues to be – what mechanisms are causing the excess of hydrogen from the TRU organic sludge?

Upon consideration of batch test observations and literature, the second year's studies ended with three candidate mechanisms as possible explanations for the

^d Note: Texaco Regal R&O 32 Oil[®] is the modern nearest-equivalent to Texaco Regal A[®], the principle cutting fluid used in machining operations at the former Rocky Flats Plant.

excess hydrogen. These mechanisms are

- elevated temperature release of stored hydrogen that had accumulated in the sludge via soluble storage, viscous entrapment and/or particle adhesion (this hydrogen would have been produced at normal rates by simple radiolysis over decades of storage),
- thermal cracking (with an apparent association with oxygen consumption in most data) of organic compounds other than original oil compounds that have been formed through combined effects of thermodynamic transition and chronic radiation damage (the new minor components are presumed to be susceptible to cracking at lower temperatures than original oil compounds), and
- lowered effective thermal cracking activation energies due to the presence of free radicals formed continuously by ongoing ionizing radiation.

The first two mechanisms are chronic radiation effects while the latter mechanism would be an example of ionizing radiation energy deposition providing an instantaneous catalysis effect enabling cracking reactions that otherwise would not proceed at lower temperatures. This radiocatalysis effect has been seen previously in cracking alteration of heavy oils using intense low-Linear Energy Transfer (LET) sources of radiation but to our knowledge has not been investigated in cases with high-LET radiation sources within the matrix.¹⁰ If radiocatalysis is, in fact, occurring in the TRU Type IV wastes, this may be the first observation of radiocatalysis in a high-LET system.

The second year's work also invested some time unsuccessfully investigating the apparent inverse relationship between hydrogen and carbon tetrachloride that had been observed previously. Our particular interest was in a simple predictive tool such as a room-temperature headspace speciation tool for estimation of the hydrogen release potential of a drum before drum-scale testing. The key to such a tool would have been reasonable correlation between vapor and sludge phase VOC concentrations. Our investigation of sealed sample headspaces, however, found little correlation with the sludge phase VOC concentration data thereby undermining the basis for a VOC-based predictive tool.

The arbitrary 20-hr heatup time of the batch mode of investigation was clearly a handicap to resolving the causes of excess hydrogen at drum-scale test temperatures. Fortunately, in late FY01, funding through the DOE's Alternatives to Incineration Program provided the opportunity to build a glovebox-based system able to host the necessary simultaneous thermal analysis and off-gas characterization studies that, if allowed to continue

through to completion, should finally resolve the hydrogen source question.

III.C. Limited Thermal Analysis with Continuous Off-Gas Characterization Studies

In early FY02 we began installation of a system that couples real-time Fourier Transform Infrared (FTIR) spectroscopy and gas chromatography to the off-gas stream from combined Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) instrumentation into a plutonium-handling glovebox at ANL-W. This experimental system was assembled to enable simultaneous measurement of mass changes and heat flux within TRU organic sludge samples (tools to observe effects of reactions and enthalpic transitions) while at the same time being able to measure principle off-gas components, particularly hydrogen.

Unfortunately for the topic discussed in this paper (i.e., what is causing the excess hydrogen in some drums of TRU Type IV waste?), the spring of CY02 brought major changes in emphasis relating to closure of selected DOE sites. As pertains to this project, just as the glovebox-based system installation was being completed, the funding that would be needed to undertake studies of the hydrogen production and release mechanisms, has been redirected to development of drum-scale techniques to address the hydrogen transportation problem. Those familiar with TRU waste transportation issues and all ongoing efforts in that area, including the authors of this paper, recognize that the transportation problem with TRU Type IV wastes may very well be resolvable with novel techniques under development within the DOE (e.g., VOC-resistant passive hydrogen getters) and, further, that application of alternative techniques does not necessarily require answering the mechanism question.

Nonetheless, simultaneous to turning our attention to planning drum-scale experiments, a few simple studies on the TRU Type IV sludges have been conducted with the new instrument group. The few samples that are discussed below are a very small segment of the population of samples that could be studied. And, even the limited data has shown opportunity for system improvements that will be valuable to researchers who may continue this inquiry in the future.

Several observations from these limited studies are included. The first of these observations deals with solvent concentration and solvent desorption behavior and its implication on thermal desorption treatments that might be applied TRU organic sludges. The second

observation is further confirmation of higher temperature cracking behavior seen in essentially all samples with a typical onset temperature of about 150 EC. Finally, lower-temperature hydrogen release data is plotted for several samples.

III.C.1. Solvent Desorption

Figure 2a shows the mass loss rate from a typical heated TRU sludge sample while Figure 2b plots the carbon tetrachloride (as a key VOC) off-gas concentration from the same sample as the VOCs are distilled. This particular sample had less than 4 wt% light components. The brief group of samples that were analyzed had a median VOC concentration of about 7 wt%. This is particularly noteworthy in itself as some references may indicate considerably higher solvent concentrations, in some cases up to 50 wt% of the final sludge waste.

Even though the sample being heated to produce the data of Figure 2 is only 500-mg mass and has free-breathing access to the TGA/DSC carrier gas flow of 30 ml/m standard air, there is a dramatic delay in onset of VOC volatilization relative to expectations, i.e., until temperatures above 100 EC. Such an onset in volatilization is well beyond the normal boiling points of most VOCs in these wastes (e.g., pure carbon tetrachloride boils at about 77 EC at standard pressure). We explored this behavior further with some surrogate work that compared the volatilization of pure carbon tetrachloride with the distillation of 7 wt% carbon tetrachloride in Texaco Regal R&O 32 Oil® (Figure 3).

The significant shifts in general volatility are presumably a combination of both unknown mixing behavior for these systems and an insight into diffusion rates in the oily and inert (in the case of real samples) matrix. The significant delay in volatilization has some potentially significant implications for considering thermal desorption as a drum-scale treatment at temperatures less than soot-producing pyrolytic destruction. Specifically, if small 500-mg samples bathed in a carrier gas flow had to be taken to near-pyrolytic temperatures and still required more than 30 minutes to evolve VOCs, the treatment durations to accomplish VOC extraction from full drums has the potential to be quite lengthy. This data may also have implications for interpretation of total pressure data in drum-scale testing.

III.C.2. Higher-Temperature Hydrogen Release

Figure 4 shows both the instantaneous and cumulative hydrogen release behavior for Sample 11. This sample

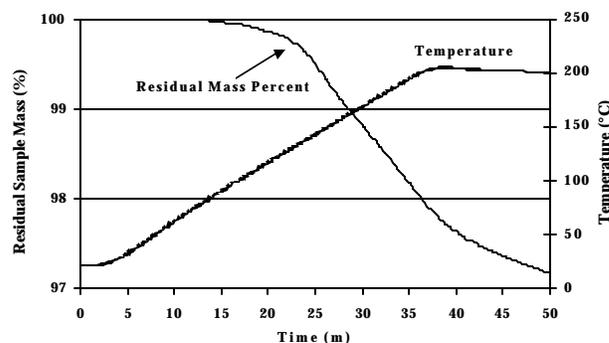


Figure 2a. Typical plot of mass loss seen by TGA due to solvent loss in air carrier gas; this plot is for 500 mg of Sample 11 heated in a 30 ml/m air flow with a 5 EC/m temperature ramp rate.

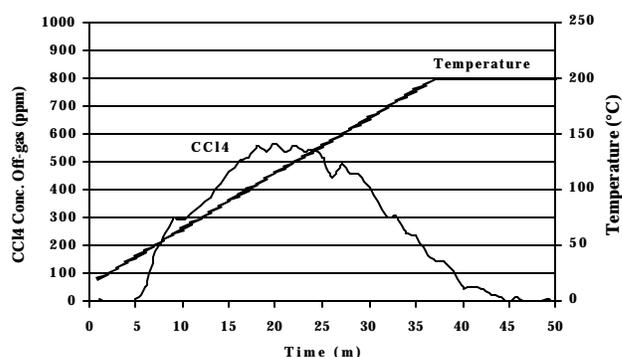


Figure 2b. Carbon tetrachloride concentration in the off-gas of the TGA/DSC run for Sample 11 shown in Figure 2a.

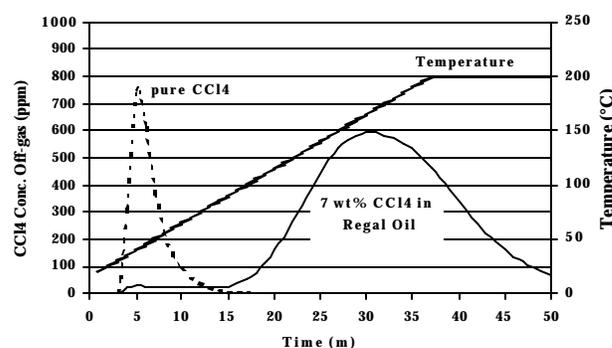


Figure 3. Comparison of rates of pure carbon tetrachloride vaporization versus 7 wt% carbon tetrachloride distillation from Regal Oil.

yielded measurable quantities of hydrogen throughout the measurement including a strong pulse of hydrogen centered at 75 EC which subsided fairly quickly. This

sample also shows the typical initiation of higher-temperature hydrogen release at about 150 EC. The most significant feature of Figure 4, however, is the burst of hydrogen centered at about 75 EC. This is certainly the type of phenomena that could not be observed in the pervious format of batch studies.

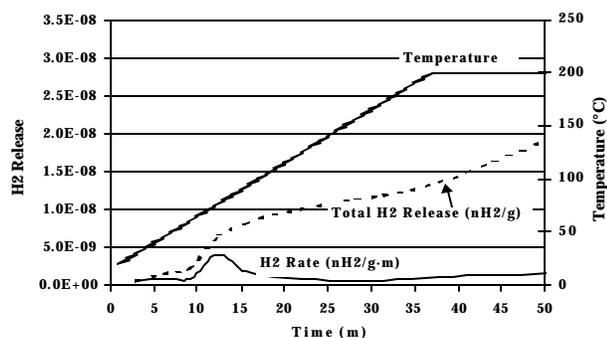


Figure 4. Time plot of instantaneous release rate of hydrogen for Sample 11 (500 mg) heated in a 30 ml/m air flow with a 5 EC/m temperature ramp rate.

III.C.3. Lower-Temperature Hydrogen Release

The behavior of particular interest to this study is the lower-temperature hydrogen release behavior from TRU Type IV sludges, such as the pulse of hydrogen at 75 EC from Sample 11. The measurable hydrogen before the pulse may be the release of stored hydrogen while the pulse itself seems indicative of some type of hydrogen-releasing reaction. Unfortunately, enthalpic heat flow associated with VOCs completely masked our ability to see reaction heat flow for this pulse. Such a reaction might be through either of the postulated reaction mechanisms listed previously or through yet another mechanism. What is clear is that the system had to reach a certain minimum temperature for the release to begin and the hydrogen release event was of limited extent, clearly ending before the onset of the typical >150 EC effects.

Diagnosing the 75 EC hydrogen pulse from Sample 11 would be aided if the same behavior were seen in other samples. Unfortunately, however, lower-temperature hydrogen behavior, to the limited extent we were able to study it, has been quite unique between samples.

Figure 5 plots the hydrogen release rate data for Sample 11 along with hydrogen release rates for three additional samples (specifically, 3, 7 and 26). In each case, sample mass and handling procedures were identical as were instrument air source and flow rates, system pressure and the TGA/DSC temperature ramp rates. Figure 5

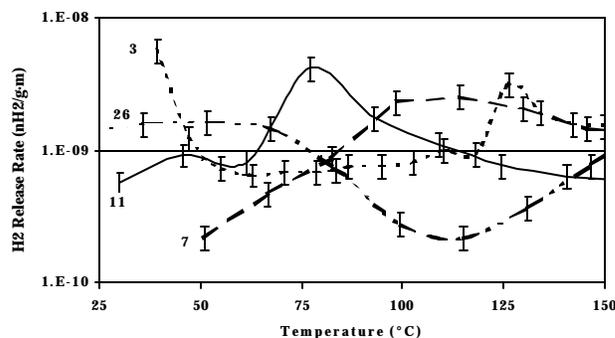


Figure 5. Comparison of rates of hydrogen release from four separate TRU Type IV samples (internal sample numbers 3, 7, 11, and 26) heated in air; air flow rates were 30 ml/m, sample sizes were 500 mg and ramp rates were 5 EC/m in each case.

represents well the range of hydrogen data we were able to see in our limited studies with the new TGA/DSC-based system.

The hydrogen release of Sample 3 deserves some comment. This sample was releasing large amounts of hydrogen during the sample preparation and handling (typically about a five minute activity). We seem to have seen the tail end of the main hydrogen release from Sample 3 during the initial moments of the experiment. Hydrogen was exiting the sample even before the TGA/DSC system heatup was initiated. We speculate that Sample 3 shows a system containing minor components that were able undergo oxygen-associated hydrogen release reactions at roomtemperature. We further speculate that the sample jar holding the 50 mg of Sample 3 had probably become completely anoxic while in sealed storage and that the hydrogen-releasing reactions began when the sample jar's lid was removed in the air-atmosphere glovebox. Unfortunately, we are not in a position to test this theory. We did not expect such behavior and, therefore, were not sampling headspaces before opening. Nor were we conducting sampling and instrument loading operations in inerted atmosphere control. Future work with these samples should incorporate these changes.

A final observation from Sample 3 is the distinct second hydrogen pulse centered at about 125 EC which is associated neither with the first hydrogen pulse nor with the subsequent onset of >150 EC cracking. Our only comments on the hydrogen release plots from Samples 7 and 26 are to note that fluctuations below 150 EC are less extreme and, if we were to see widespread indication of hydrogen storage, we would expect more hydrogen release

rate plots like that of Sample 26.

IV. CONCLUSIONS

Our only conclusion to date is that some types of reactions seem responsible for some of the excess hydrogen being seen in some cases of 57 EC drum-scale gas generation testing of TRU Type IV solidified organics. This conclusion is drawn from some highly varying observations. Too little is known to narrow the range of possible reactions. Our chief tool in identifying reactions, i.e., real-time heat flux measurements, is lost due to enthalpic heat flow supplying energy to VOCs during system heatup. We can not rule out some cases of hydrogen accumulation and release but recognize that finding evidence of storage in reacting systems is probably impossible. It is difficult to estimate varieties of sludge matrices that may presently exist after considering

- variation in original oil, inert and VOC fractions,
- variation in localized and drum-total cumulative and instantaneous ionizing radiation energy doses,
- variation in storage conditions, and
- variation in radiolysis, recombination and matrix depletion effects.

It has certainly proven difficult to isolate mechanisms for hydrogen production and release from these organic systems. The three mechanisms discussed previously, i.e., storage-and-release, cracking of radiation-produced organic compounds and radiocatalysis, as well as other causes may be at play. Several research paths including inerted sampling remain to be pursued to resolve these questions.

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