

WILL MSR SAMPLES CACHED ON THE MARTIAN SURFACE EXPERIENCE SIGNIFICANTLY GREATER THERMAL DEGRADATION THAN SAMPLES RETAINED IN THE ROVER? M. Fries¹,
¹NASA Astromaterials Acquisition and Curation Office, Johnson Space Center, Houston TX 77058. Email: marc.d.fries@nasa.gov

Introduction: Since the first Mars Sample Return (MSR)-related report published by the Jet Propulsion Laboratory (JPL) in 1974 [1], a series of panels, reports, and white papers have recognized the importance of sample temperature in meeting mission goals and defined a sample maximum temperature (henceforth SMT) limit. The Mars Sample Handling and Requirements Panel (MSHARP, 1999) flatly stated that “[t]he main issue in sample preservation is temperature” [2]. The Mars Exploration Program Analysis Group (MEPAG)’s “Science Priorities for Mars Sample Return” report (2008), declared that “[s]ignificant loss, particularly to biological studies, occurs if samples reach +50°C for three hours” whereby “scientific objectives related to life goals could be seriously compromised” [3]. Overall, a total of seven panels, white papers, and conference reports adopted a SMT of $-40\pm 17^\circ\text{C}$ to preserve samples sufficiently to confidently achieve success in studies of past or present martian life (see more detail in [5]). In contrast, the Mars 2020 rover (M2020) mission adopted a SMT of $+60^\circ\text{C}$ for samples stored on the martian surface and $+50^\circ\text{C}$ for samples retained inside the rover, as stated in a conference poster presented by Beaty et al., 2016 [4].

M2020 is currently collecting samples for MSR in tubes. Half of those tubes will be retained within the M2020 rover body (hereafter rover samples, or RS) and half will be deposited on the martian surface (cached samples or CS), with a currently undetermined number of each collected up to ten years later for return to Earth. CS samples can be expected to experience significantly higher temperatures than RS samples based on their exposed location in sunlight. This work will explore differences in deleterious chemical reaction rates due to thermal environment of both tube types. The findings

here should be debated openly and considered when deciding which samples to return to Earth.

Temperatures: Temperatures are modeled in [6] and [7] with respect to worst-case cold (WCC) and worst-case hot (WCH), signifying annual minima and maxima over the course of a martian year. Ground temperatures at Jezero Crater feature WCH of 14°C at solar longitude (L_S) of 179° and WCC of -103°C at L_S of 91° . M2020 does not record temperatures in the sample tubes so only [6] exists for estimating sample temperatures.

Rover Samples (RS): Temperatures in the “Adaptive Caching Assembly” (ACA) sample tube storage rack on board the rover are not included in Novak et al (2022) rover thermal behavior model, so temperatures from the nearest hardware (the “linear stage”) are used as a proxy. Additionally, all values given in Novak et al (2019) were calculated using environmental factors for Holden Crater. To the best of the author’s knowledge no data on ACA temperatures are available for the Jezero Crater landing site, so we use an estimate based on linear interpolation of Holden annual ground temperatures to the same data for Jezero Crater. Holden Crater experiences a maximum ground temperature at WCH of 32°C and a minimum at WCC of -103°C , and Jezero sees 14°C and -90°C for the same parameters [ibid]. The values for WCC max/min for Holden are $-86/-107^\circ\text{C}$ [6, Fig 10], and WCH max/min are $-8/-55^\circ\text{C}$ [6, Fig 12]. Jezero values are estimated by adjusting the linear stage temperatures in linear relation to the Holden and Jezero ground temperatures. The delta between WCH and WCC ground temperatures is 134°C for Holden and 104°C for Jezero, so the temperature span of Jezero is 0.776 that of Holden. This factor is multiplied by the delta for high and low values for WCH and WCC at Holden, reducing WCH values by 14°C and increasing WCC values by 10°C . The resulting WCH max/min values for Jezero are -22 and -69°C . WCC max/min values are -76 and -97°C (Table 1).

Cached Samples (CS): CS samples are ejected from the rover and lie on the martian surface for possible later retrieval. Modeling in Novak et al (2022) was performed assuming the tubes were not in physical contact with the surface, but estimate that 5°C cooling will occur in the WCH case for “sandy” and 10°C for “rocky” ground. We apply a 5°C decrease to the WCH maximum of 47.8°C [7]: $47.8 - 5 = 42.8^\circ\text{C}$. Novak et al (2022) does not quote a low temperature in the nominal

	Ground Temperature		RS		CS
	Jezero	Holden	Holden	Jezero (calc)	Jezero
WCH Max	288	306	266	252	317
WCH Min	n.a.	n.a.	219	205	190
WCC Max	n.a.	n.a.	188	198	263
WCC Min	184	171	167	177	175

n.a.: Not available

Table 1: Temperature values ($^\circ\text{K}$) used in this study, from [6,7]. RS values are estimated from a linear interpolation using ground temperatures at Jezero and Holden Craters. CS and RS samples temperatures are the last two columns on the right. (n.a.: not available in [6,7]).

design case for WCH, but the similar, worst-case scenario gives a low value of -84°C. We will use that value here. For WCC, temperatures range from -11 °C to -99C [from 7, Fig. 17] (Table 1).

Chemical Reaction Rates: A set of chemical reactions was examined to explore expected changes within the stored samples. Calculated values for k are shown in Table 2. Reaction rates (k) vary with temperature according to the Arrhenius equation ($k = A \exp(-\frac{E_a}{RT})$). A is the pre-exponential factor, E_a is the activation energy, T is temperature in Kelvin, and R is the universal gas constant. Reaction rate information (Table 2) was obtained from literature and the NIST Kinetics Database [8] using data recorded as near to MSR sample temperatures as possible. These values are from literature studies performed at 1 atm, but studies were chosen where the temperature ranges at least approximate those for MSR samples.

Reaction 1: Dehydration of calcium sulfate[10]. $\{CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4(s) + 2H_2O(g)\}$ This reaction is important because water will likely alter minerals and mobilize perchlorates to degrade organics, among other deleterious effects. This reaction is a multi-step process with multiple k/T slope regimes. k is sharply dependent on temperature with dramatic changes in k for CS samples compared to RS. (Table 2). At temperature minima the difference between the two is slight, but the higher temperatures seen by CS samples can drive dehydration by 10^3 - 10^5 -fold, with k values reaching into the $1e^{-5}$ range.

Reaction 2: Oxidation of a light alkane via oxygen radical. [11]. $\{C_3H_8 + O \cdot \rightarrow 2 \cdot C_3H_7 + \cdot OH\}$ This reaction proceeds rapidly at MSR tube temperatures, and the rate is 2.4x greater for CS tubes than RS at WCH maximum ($k_{CS} = 8.54e-2$) and 3.8x faster at WCC maximum ($k_{CS} = 4.3e-2$).

Reaction 3: Benzene decomposition via oxygen radical [12]. $\{C_6H_6 + O \cdot \rightarrow Products\}$ These data were measured as a combustion product whereas in MSR tubes the oxygen radical would be produced via ambient ionizing radiation. The reaction rate is 5.6x greater for CS tubes than RS at WCH maximum ($k_{CS} = 3e-14$) and 14.2x faster at WCC maximum ($k_{CS} = 7.7e-15$). Aromatics will preferentially survive both the tube conditions and the martian surface.

Reaction 4: Perchlorate decomposition via chlorine radical reaction. [13] $\{ClO_4 + \cdot Cl \rightarrow ClO_3 + ClO\}$ This reaction is sluggish at MSR tube temperatures despite

RXN 1: Sulfate dehydration		
k_{RS}	k_{CS}	k_{CS}/k_{RS}
8.1E-09	2.1E-05	2651
1.2E-12	2.8E-14	0.02
2.2E-13	4.1E-08	183347
6.6E-16	3.5E-16	0.5
RXN 2: Alkane oxidation		
3.6E-02	8.5E-02	2.4
1.4E-02	9.0E-03	0.7
1.1E-02	4.3E-02	3.8
5.9E-03	5.5E-03	0.9
RXN 3: Benzene oxidation		
5.4E-15	3.0E-14	5.6
7.8E-16	3.4E-16	0.4
5.4E-16	7.7E-15	14.2
1.5E-16	1.3E-16	0.9
RXN 4: Perchlorate reaction		
1.6E-10	1.7E-10	1.0
1.6E-10	1.5E-10	1.0
1.5E-10	1.6E-10	1.1
1.5E-10	1.5E-10	1.0

Table 2: Reaction constant k values for rover samples (k_{RS}) and cached samples (k_{CS}) for the reactions discussed in text. The ratio of the two is an expression of how much faster reactions progress in CS samples relative to RS samples.

its low activation energy, although ionizing radiation should increase the activity of this reaction. The reaction rate is comparable between CS tubes and RS at WCH maximum ($k_{CS} = 1.7e-10$) and only 1.1x faster at WCC maximum ($k_{CS} = 1.6e-10$).

Discussion: The reactions shown here are illustrative and are not the complete suite of deleterious reactions that will occur. For life detection investigations where ppbV or lower concentrations of compounds are important, slower reactions will be

important. Also, MSR sample tubes will be cached for up to ten years, causing lower k values to be significant. In three of the four reactions (Table 1) reaction rates proceed significantly faster for cached samples than those stored in the rover body. CS samples experience 2.4-fold increase in alkane oxidation at WCH with a substantial k of $8.5e-2$. Dehydration of sulfates is especially concerning because of the broad suite of deleterious secondary reactions caused, and the k differences between CS and RS samples are dramatic. Based on these considerations, return to Earth of the RS samples is favored over the CS samples.

References: [1] Jaffe, L.D., et al 1974. *JPL Internal Rept.*, (760-101). [2] Carr, M.H., et al 1999. *NASA Tech. Memo, 209145(47)*, p.1999. [3] Borg L., Des Marais D., Beaty D., 2008. *Astrobiology* (8,3) 489-535. [4] Beaty, D.W., et al, 2016. *47th LPSC*, Abstract 2662. [5] Fries, M. and Calaway, M., 2018. *42nd COSPAR Scientific Assembly*, 42, pp.B4-2.[6] Novak, K., et al 2019. 49th Int'l Conf on Env Syst. [7] Novak, K., et al 2022. 51st Int'l Conf on Env Syst. [8] NIST Kinetics Database: Online resource <https://kinetics.nist.gov/kinetics/index.jsp> [9] Elprince, A.M., et al., 1982. *Soil Sci. Soc. of America J.*, 46(3), pp.530-535. [10] Iwasaki, S. and Koga, N., 2020. *Phys. Chem. Chem. Phys.*, 22(39), pp.22436-22450. [11] Sauer Jr, M.C. and Mani, I., 1970. *J. Phys. Chem.*, 74(1), pp.59-63.[12] Cvetanović, R.J., 1987. *J. Phys. Chem. Ref. Data*, 16(2), pp.261-326. [13] Xu, Z.F. and Lin, M.C., 2003. *J. Chem. Phys.* 119(17), pp.8897-8904.