JSC-Rocknest: A large-scale Mojave Mars Simulant (MMS) based soil simulant for in-situ resource utilization water-extraction studies

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Abstract

The Johnson Space Center-Rocknest (JSC-RN) simulant was developed in response to a need by NASA's Advanced Exploration Systems (AES) In-Situ Resource Utilization (ISRU) project for a simulant to be used in component and system testing for water extraction from Mars regolith. JSC-RN was designed to be chemically and mineralogically similar to material from the aeolian sand shadow named Rocknest in Gale Crater, particularly the 1-3 wt.% low temperature (<450 ºC) water release as measured by the Sample Analysis at Mars (SAM) instrument on the *Curiosity* rover. Sodium perchlorate, goethite, pyrite, ferric sulfate, regular and high capacity granular ferric oxide, and forsterite were added to a Mojave Mars Simulant (MMS) base in order to match the mineralogy, evolved gases, and elemental chemistry of Rocknest. Mineral and rock components were sent to the United States Geological Survey (USGS) in Denver for mixing. Approximately 800 kg of JSC-RN was sent back to NASA in 5 gallon buckets, which were subsampled and characterized. All samples of the USGS-produced simulants had similar evolved gas profiles as a small prototype batch of JSC-RN made in JSC laboratories, with the exception of HCl, and were similar in terms of mineralogy and total chemistry. Also, all JSC-RN subsamples were homogenous and had similar mineralogy, total chemistry, and low-temperature evolved gas profiles as the Rocknest aeolian sand shadow examined with *Curiosity*'s instrument suite on Mars. In particular, the low temperature water releases were similar and the amount of water evolved from JSC-RN at <450 ºC was similar to the water content of Rocknest based on SAM water peak integrations. Overall, JSC-RN is ideally suited for ISRU studies of water extraction of global martian soil due to its excellent agreement with measured properties of martian soils and its proven feasibility for large-scale production.

1. Introduction

Martian soil simulants are materials that are mineralogically, chemically, and/or geotechnically similar to martian regolith, and can be used for multiple purposes such as scientific research, education, mission development, and to test and develop in-situ resource utilization (ISRU) technologies. The fidelity of a simulant depends on the application it is being used for. For example, the testing of rover wheels would require a simulant that closely matches the geotechnical properties of martian surface materials. Martian soil simulants are of particular interest to ISRU because of the abundance of soil (defined here as unconsolidated material) on the surface of Mars and the ease with which it can be excavated from the surface compared to solid rock. The most well characterized soil to date was called Rocknest and was analyzed by the Mars Science Laboratory (MSL) *Curiosity* rover's instrument suite. Rocknest is an ideal basis for a new martian soil simulant because it has been extensively characterized and has been interpreted to represent local soil and possibly global martian soil (Blake et al., 2013; Bish et al., 2013; Archer et al., 2014).

Johnson Space Center-Rocknest (JSC-RN) is a new simulant that was specifically designed to be produced in large quantities and used by the National Aeronautical and Space Administration (NASA) Advanced Exploration Systems (AES) ISRU project in component and system testing for water extraction from martian soil. Water can be extracted from unconsolidated material through heating, where adsorbed and structural water are thermally removed from regolith materials. The water can then be condensed and purified for use as drinking water or split by electrolysis into hydrogen and oxygen for use as propellant for spacecraft or as a source of breathable O_2. As such, the focus of JSC-RN was to replicate the evolved gas profiles, especially the low temperature (<450 °C) water release, detected in

Rocknest by the Sample Analysis at Mars (SAM) instrument on the *Curiosity* rover. It was essential that JSC-RN be cost-effective and composed of materials that could be purchased commercially (i.e., not synthesized in the lab) because many ISRU system and component tests require hundreds of kilograms of simulant. Here, we describe the development and characterization of JSC-RN, which is based on the evolved gases, mineralogy, and total chemistry of the Rocknest aeolian sand shadow.

1.1 Mineralogical, geochemical, and physical properties of martian soils

1.1.1 *In-situ* analysis of Rocknest

The first sample scooped by the MSL *Curiosity* rover was named Rocknest, and was collected on top of the Bradbury group, which underlies the Mount Sharp group in northern Gale Crater (Sutter et al., 2017). It was sampled from an inactive, dust-covered sand shadow that was interpreted to be deposited by northerly winds on the leeward side of an obstacle (Blake et al., 2013).

Five samples were scooped from the Rocknest sand shadow and individually delivered to the Sample Acquisition, Sample Processing and Handling–Collection and Handling for In situ Martian Rock Analysis (SA/SPaH-CHIMRA) instrument, where they were sieved to a grain size of <150 µm (Blake et al., 2013). Approximately 40-50 mg portions of scoops 3 and 4 were delivered to the Chemistry and Mineralogy (CheMin) X-ray diffractometer (XRD) and scoop 5 was delivered to both SAM and CheMin.

The <150 µm size fraction of Rocknest was delivered to the SAM oven for heating from 40 to 870 °C at a heating rate of approximately 35 °C/min (Sutter et al., 2017). As the sample was heated, volatile-bearing phases thermally decomposed and the evolved gases (e.g., O_2, H_2O, SO_2,

88 HCl) were then sent to a quadrupole mass spectrometer (QMS), tunable laser spectrometer
89 (TLS), or gas chromatograph (GC) using a helium carrier gas (~0.8 sccm) (Mahaffy et al., 2012;
90 Webster et al., 2013; Freissinet et al., 2015).

91 Alpha Proton X-ray Spectrometer (APXS) bulk chemical analysis was performed on
92 <150 μm sieved material that was delivered to the observation tray on top of the rover. APXS
93 analysis was also done on a wheel scuff in the Rocknest sand shadow called "Portage", which
94 was un-sieved. Chemical analyses of sieved and un-sieved portions of the Rocknest sand shadow
95 were largely similar (Blake et al., 2013; Bish et al., 2013).

96 1.1.2 Mineralogical properties of Rocknest and global martian soils

97 CheMin XRD analyses of Rocknest showed that it was mineralogically similar to martian
98 basalts as well as basalts found in martian meteorites (Blake et al., 2013). The crystalline
99 component contained plagioclase feldspar, olivine, and pyroxene (Table 1; Bish et al., 2013;
100 Achilles et al., 2017). The chemical composition of olivine was estimated using refined unit-cell
101 parameters in Rietveld refinements and showed it was consistent with the Mg-rich endmember
102 forsterite (Morrison et al., 2018a; 2018b; Bish et al., 2013). CheMin did not detect perchlorates,
103 halides, carbonates, phosphates, or sulfates in the crystalline portion; therefore, if these phases
104 were present, they were non-crystalline or below the CheMin detection limit of 1-2 wt.% (Bish et
105 al., 2013). Rocknest also contained a large (~35 wt. %) X-ray amorphous component consistent
106 with basaltic glass, allophane, poorly crystalline sulfate, and nanophase iron oxides such as
107 ferrihydrite (Bish et al., 2013; Sutter et al., 2017; Achilles et al., 2017). The amorphous
108 component was rich in Si, Fe, and S (Achilles et al., 2017).

Prior to MSL, observations by several landers, rovers, and orbiters categorized martian soils as either "bright dust" or "dark soil" and determined that they were mineralogically and chemically uniform across the martian surface (Yen et al., 2005). Bright dust exists as a ~1 mm thick surface layer and the particle size has not been determined with certainty due to the resolution of *in-situ* imagers (Yen et al., 2005; Ming & Morris, 2017). Dark soils are located beneath the bright dust layer and have grain sizes up to 100 μm (Yen et al., 2005). *In-situ* analyses by *Viking* I and II, Mars *Pathfinder*, the Mars Exploration Rovers (MER) *Spirit* and *Opportunity*, and *Phoenix* used instruments including the Miniature Thermal Emission Spectrometer (Mini-TES), multispectral imagers, and Mössbauer spectrometer to estimate surface and subsurface mineralogy and chemistry of martian soils (Yen et al., 2005, and references therein). Additionally, orbiter-based spectrometers provided information on the global distribution of soils and their estimated mineralogies; however, due to instrument limitations (e.g., could not distinguish between some spectrally similar phases) these data were not as definitive and robust as those from the CheMin XRD on *Curiosity*. Multispectral imagers on the MER and *Pathfinder* rovers showed that the bright soils were dominated by nanophase iron oxides and the dark soils contained altered iron-bearing minerals and ferrous iron-bearing silicates (Yen et al., 2005). Nanophase iron oxides, such as palagonite or ferrihydrite, have been detected in other spectrally bright regions of Mars including Olympus Mons and Amazonis Planitia (Morris et al., 2000). Local bright soil deposits in Gusev Crater and Meridiani Planum had Mini-TES signatures similar to Mars Global Surveyor TES signatures of global average martian dust, suggesting that bright dust is globally distributed across the martian surface (Yen et al., 2005). *In-situ* and Mars Global Surveyor TES results suggested that global dust is composed of framework silicates, olivine, pyroxene, amorphous material, hematite, and magnetite

(Hamilton et al., 2005). The iron-mineralogy and spectral characteristics of dark soils at Gusev Crater and Meridiani Planum were similar, suggesting that dark soils may also be globally distributed, or at least are derived from sources of similar composition (Yen et al., 2005).

Table 1. Quantitative mineralogy (wt.%) of MGS-1, MMS, and the USGS produced JSC-RN simulant compared to Rocknest analyzed by CheMin. Rocknest mineralogy was based on Rietveld refinement and FULLPAT analyses of CheMin data (Achilles et al., 2017). The MMS mineralogy is based on a 35 wt.% < 2 mm/65 wt.% dust mixture analyzed at JSC. The JSC-RN mineralogy was based on the average quantitative mineralogy of three subsamples from USGS prepared mixtures, shown with standard deviations. MGS-1 mineralogy is based on the recipe listed in Cannon et al., (2019). Mineralogy of JSC Mars-1 was not reported. n.d. = not detected.

Mineral	Rocknest Crystalline + Amorphous	MGS-1	MMS (measured at JSC)	JSC-RN average
Plagioclase	26.3 ± 7	27.1	60.4	42.9 ± 0.5
Olivine	13.3 ± 4	13.7	n.d.	11.7 ± 0.8
Pyroxene	19.7 ± 8.5	20.3	12.3	11.0 ± 0.5
Magnetite	1.8 ± 3	1.9	n.d.	n.d.
Anhydrite	0.9 ± 2	0.9	n.d.	n.d.
Hematite	1.0 ± 1	1.1	1.1	1.7 ± 0.4
Quartz	0.8 ± 2	n.d.	0.6	2.3 ± 2.8
Calcite	n.d.	n.d.	1.0	1.5 ± 0.3
Ilmenite	0.9 ± 3	n.d.	2.2	1.0 ± 0.2
K-feldspar	n.d.	n.d.	2.2	2.3 ± 0.6
Analcime	n.d.	n.d.	1.3	1.0 ± 0.1
Goethite	n.d.	n.d.	n.d.	1.7 ± 0.3
Pyrite	n.d.	n.d.	n.d.	0.6 ± 0.0
Ferric sulfate	n.d.	n.d.	n.d.	0.3 ± 0.1
Amorphous	35 ± 15	35	3.1	-
Amorphous + smectite	-	-	18.7	20.4 ± 1.3

1.1.3 Geochemical properties of Rocknest and martian soils

APXS analyses of the Rocknest sand shadow revealed basaltic chemistry dominated by SiO_2 and FeO_{total} (Table 2), and was similar to soils analyzed across Mars (Bish et al., 2013; Blake et al., 2013; Yen et al., 2005). The bulk chemistry of Rocknest as detected by APXS was within two standard deviations of MER APXS analyses of basaltic soils at the Gusev Crater and Meridiani Planum landing sites (Blake et al., 2013). Rocknest contained slightly lower SiO_2 (42.97 wt.%) than Gusev Crater (46.1 wt.%) and Meridiani Planum (45.7 wt.%). Rocknest also contained slightly higher iron (19.18 wt.%) than Gusev Crater (16.3 wt.%) and Meridiani Planum (18.8 wt. %) (Blake et al., 2013). The general similarity of the chemical compositions between Rocknest and bright soils in Gusev Crater and Meridiani Planum indicates that martian soils possess a dust component that is globally distributed across Mars as well as a local component that is similar across many regions on Mars (Blake et al., 2013).

Table 2. Alpha Proton X-ray Spectrometer (APXS) chemical composition data from Rocknest bulk material measured from disturbed soil (Achilles et al., 2017) compared to JSC-RN and other martian simulants. The chemistry of JSC-RN is based on the average of 21 subsamples of large-scale batches of JSC-RN mixed by the USGS, and is shown with standard deviations.

Oxide	Rocknest bulk, wt. %	JSC Mars-1[1]	MGS-1[2]	MMS[3]	JSC-RN (small prototype), wt.%	JSC-RN (USGS, averaged), wt.%
SiO_2	42.97	43.5	47.2	49.8	45.96	45.82 ± 0.18
TiO_2	1.19	3.8	0.4	1.1	1.07	1.06 ± 0.02
Al_2O_3	9.37	23.3	11.6	17.2	13.73	13.66 ± 0.09
FeO_T	19.18	15.6	17.5	11.0	17.76	17.71 ± 0.19
MnO	0.42	0.3	0.1	0.2	0.18	0.18 ± 0.01
MgO	8.69	3.4	9.9	6.1	9.38	9.51 ± 0.06
CaO	7.26	6.2	5.6	10.5	7.61	7.97 ± 0.03
Na_2O	2.70	2.4	2.8	3.3	3.06	3.05 ± 0.02
K_2O	0.49	0.6	0.5	0.5	0.54	0.54 ± 0.01
P_2O_5	0.95	0.9	0.1	0.2	0.16	0.16 ± 0.00
Cr_2O_3	0.49	-	0.1	0.1	0.05	0.06 ± 0.00
Cl	0.69	-	-	-	0.24	0.43 ± 0.13
$\%SO_3$	5.47	-	4.3	0.1	1.00	1.77 ± 0.27
Total	99.87	100.0	100	100	99.45	99.65 ± 0.21

1.1.4 Volatile properties of Rocknest and martian soils

H_2O evolved during the heating of the Rocknest soil sample was attributed to phases in both the crystalline and amorphous components, and was similar to the water content of other martian soils (Archer et al., 2014; Sutter et al., 2017). Most (~80 %) of the water in Rocknest was evolved <450 °C and was characterized by a broad release that peaked around 280 °C and tapered off around 450 °C (Figure 1; Archer et al., 2014). The broad low temperature water release likely had contributions from multiple sources, including adsorbed water from high surface area nanophase iron oxides in the amorphous component (Archer et al., 2014; Achilles et

[1] Allen et al., 1998
[2] Cannon et al., 2019
[3] Peters et al., 2008

177 al., 2017). Structural H_2O, structural OH, or water inclusions could also have contributed to the
178 observed water release (Archer et al., 2014). Evolved water content in the Rocknest soil sample
179 (2.0 ± 1.3 wt.%; Archer et al., 2013; Table 3) was similar to water content in soils analyzed in
180 Chryse Planitia and Utopia Planitia by the *Viking* landers (~1 %; Biemann et al., 1977).

181 Evolved O_2 from Rocknest peaked ~380 °C and was likely caused by the thermal
182 decomposition of an oxychlorine (i.e., perchlorate or chlorate) (Figure 1; Archer et al., 2014;
183 Sutter et al., 2017; Hogancamp et al., 2018). The presence of oxychlorines was supported by the
184 simultaneous release of mid temperature O_2 and chlorinated hydrocarbons (Archer et al., 2014).
185 Thermal decomposition of perchlorates or chlorates (with the exception of Mg and Fe
186 oxychlorines) produced chlorides, which then reacted with water and other minerals (e.g.,
187 sulfates) in the sample to evolve high temperature (>600 °C) HCl (Sutter et al., 2017; Clark et
188 al., 2020). The HCl release from Rocknest started at ~475 °C and steadily increased with a peak
189 at ~750 °C (Figure 1; Archer et al., 2014; Sutter et al., 2017), which is characteristic of
190 perchlorate/water-producing phase mixtures run in the laboratory under SAM-like conditions
191 (Clark et al., 2020). Oxychlorines have also been detected at 0.4-0.6 % by the Thermal and
192 Evolved Gas Analyzer (TEGA) instrument and the Wet Chemistry Lab (WCL) on the *Phoenix*
193 lander and have been suggested to be globally distributed in martian regolith (Hecht et al., 2009).

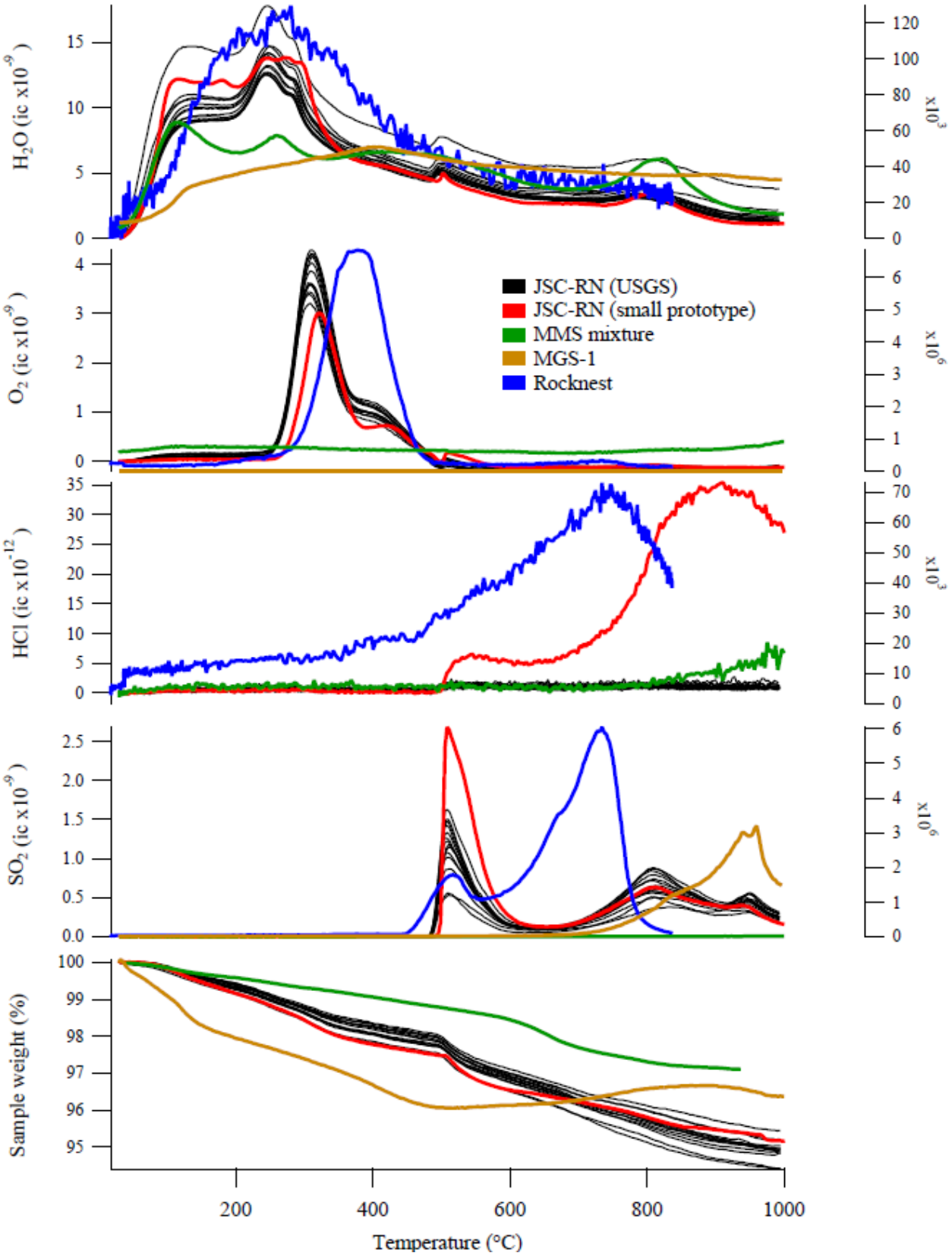
194 Evolved SO_2 peaks at ~515 °C and ~730 °C in Rocknest were attributed to the presence
195 of sulfates, sulfites, and/or sulfides (McAdam et al., 2014). The SO_2 peak at ~515 °C was
196 attributed to the oxidation of a sulfide such as pyrite or pyrrhotite because an increase in evolved
197 SO_2 coincided with a decrease in O_2 (Figure 1; McAdam et al., 2014). The SO_2 peak at ~730 °C
198 could be caused by the thermal decomposition of calcium sulfite, which can form by the reaction
199 of $CaCl_2$, SO_2, and H_2O (McAdam et al., 2014). It could also be caused by the thermal

200 decomposition of iron sulfate or from SO_4^{2-} adsorbed on high surface area particles (McAdam et
201 al., 2014). Sulfates are believed to be globally distributed across Mars but have not been detected
202 in soils by evolved gas analysis prior to the Rocknest soil sample. Sulfates were likely present at
203 the *Phoenix* landing site because they are globally distributed and S and Cl correlate in martian
204 global dust and soils (Golden et al., 2009). SO_2 peaks <1000 °C were not detected by TEGA at
205 the *Phoenix* landing site, suggesting that Mg- and Fe sulfates were not present (Golden et al.,
206 2009). If sulfates were present at the *Phoenix* landing site, they may have been in the form of Ca-
207 or Na sulfate because these phases thermally decompose above the temperature range of TEGA
208 and both cations were detected by the WCL (Golden et al., 2009).

209

210 Table 3. Weight percentages of major and some minor volatiles, pertinent to this work, that were
211 released from the Rocknest soil sample during heating to ~870 °C. SO_3 and ClO_4 abundances
212 were calculated from SAM SO_2 and O_2 releases, respectively. Ranges are based on the average
213 values from four SAM analyses of Rocknest. (Archer et al., 2014)

Volatile	Abundance (wt.%)
H_2O	1.6-2.4
SO_3	0.5-3.5
ClO_4	0.3-0.5
CO_2	0.7-1.0


H2O (ic x10-9)
O2 (ic x10-9)
HCl (ic x10-12)
SO2 (ic x10-9)
Sample weight (%)
x10^3
x10^6
x10^3
x10^6
JSC-RN (USGS)
JSC-RN (small prototype)
MMS mixture
MGS-1
Rocknest
Temperature (°C)

214

Figure 1. Evolved H_2O, O_2, HCl, and SO_2 from laboratory analyses of a small prototype mixture of JSC-RN prepared in the JSC laboratory, 13 subsamples of JSC-RN mixed in large-scale quantities at the USGS, a 35 wt.% <2 mm/65 wt.% dust MMS mixture, MGS-1, and Rocknest analyzed by SAM on the *Curiosity* rover. Laboratory data are shown on the primary y-axis and SAM data are shown on the secondary y-axis. Thermal gravimetric (TG) data are shown for the small-scale and large-scale versions of JSC-RN, MMS, and MGS-1. EGA data were not available for JSC Mars-1 and HCl data were not available for MGS-1.

1.2 Previous martian soil simulants

Several martian soil simulants exist, including Johnson Space Center Mars-1 (JSC Mars-1), Mojave Mars Simulant (MMS), and Mars Global Simulant (MGS-1). JSC Mars-1 consists of weathered volcanic ash that was spectrally similar to bright dust on the martian surface, and was developed primarily for use in science research, engineering studies, and education. JSC Mars-1 was sourced from meteorically altered basaltic material from late a Pleistocene cinder cone on the flank of Mauna Kea volcano in Hawaii (Allen et al., 1998). Meteoric weathering of this volcanic material produced a suite of minerals similar to the bright regions of Mars based on orbital spectral data (Evans and Adams, 1979; Morris et al., 1993; Allen et al., 1998). JSC Mars-1 primarily consists of "finely crystallized and glassy particles of a volcanic rock known as 'hawaiite' (Allen et al., 1998, pp.406). The bulk quantitative mineralogy of JSC Mars-1 contains calcium feldspar, minor magnetite, and a large amorphous component rich in ferric oxide (Allen et al., 1998). The total chemistry of JSC Mars-1 is dominated by SiO_2, Al_2O_3, and FeO_{total} (Allen et al., 1998; Table 2). JSC Mars-1 does not replicate the volatile properties of well-characterized martian soils; it lost 7.8 wt.% and 21.1 wt.% when heated to 100 °C and 600 °C, respectively,

238 primarily due to water adsorbed on mineral surfaces and contained within glass particles (Allen
239 et al., 1998). The water content of JSC Mars-1 is far greater than water content of martian soils
240 measured *in-situ* by TEGA on the *Phoenix* lander or the SAM instrument on the *Curiosity* rover
241 (Leshin et al., 2013; Smith et al., 2009).

242 MMS is mineralogically and chemically similar to igneous rocks on Mars and their
243 weathering products, and was developed based on newly acquired physical and chemical data
244 from martian soils. While JSC Mars-1 relied upon orbital observations, MMS was developed
245 using data from *in-situ* analyses by the *Viking* landers, Mars *Pathfinder*, and MER *Spirit* in
246 addition to orbital data (Peters et al., 2008). MMS was sourced by the Jet Propulsion Laboratory
247 (JPL) for testing instruments and sampling systems for the *Phoenix* and MSL missions. MMS is
248 crushed Saddleback Basalt sieved to >2 mm granules, <2 mm sand, and dust (Peters et al., 2008).
249 The Saddleback Basalt was sourced from an early Miocene outcrop in the western Mojave
250 Desert near Boron, California and was commercially mined by Carlton Global Resources (CGR)
251 (Peters et al., 2008). Peters et al. (2008) reported that the mineralogy of MMS was dominated by
252 plagioclase feldspar, pyroxene, olivine, and magnetite and was chemically similar to martian
253 basalts. The bulk mineralogy of MMS sent to JSC from JPL did not contain olivine or magnetite,
254 as reported in Peters et al., (2008). Additionally, Peters et al. (2008) did not report any
255 phyllosilicates or calcite, which were detected at about 15.6 wt.% and 1.0 wt.%, respectively, in
256 the MMS mixture sent to JSC. It is possible that the batches of MMS sent to JSC were sourced
257 from a chemically altered area of the Saddleback Basalt, explaining the presence of
258 phyllosilicates and calcite. Although MMS broadly mimics the mineralogy and chemistry of
259 martian regolith, it does not replicate the evolved gases (e.g., O_2, H_2O, SO_2, HCl) from martian

soils analyzed by either TEGA or SAM (Figure 1). Specifically, MMS lost ~1 wt.% water at 450 °C (Figure 1), whereas Rocknest contained 2.0 ± 1.3 wt.% water (Archer et al., 2014).

The University of Central Florida developed the Mars Global Simulant-1 (MGS-1) in order to more precisely replicate martian global basaltic regolith based on newly available physical and chemical data from the Rocknest soil sample analyzed by the *Curiosity* rover (Cannon et al., 2019). MGS-1 was developed as a mineralogical standard for basaltic soils on Mars and consists of 13 components (Cannon et al., 2019; Table 1). Mineral-based simulants like MGS-1 are created by physically mixing individual minerals rather than crushing a rock or sourcing a natural soil. Mineral-based simulants are ideal for experiments where mineralogical fidelity to martian soil is of upmost importance, such as mineral alteration studies. Crushed rock-based simulants are preferred for geotechnical tests (e.g., rover wheel testing) over mineral-based simulants because they more closely approximate the physical properties of natural soils (Peters et al., 2008). Additionally, MGS-1 does not accurately capture the low temperature evolved gases of the Rocknest soil sample, particularly the low temperature water. MGS-1 lost ~3.7 wt.% water <450 °C with a water release peak ~400 °C, whereas Rocknest contained 2.0 ± 1.3 wt.% (Archer et al., 2014) and evolved a water release peak at ~280 °C (Figure 1).

Here, we describe the development and characterization of a new crushed rock-based martian soil simulant, Johnson Space Center-Rocknest (JSC-RN), which was specifically designed to be produced in large quantities and used by the NASA AES ISRU project in component and system testing for water extraction from martian soil. JSC-RN uses MMS as a base but contains additives in order to better approximate the chemical, mineralogical, and volatile properties of martian soils. Unlike previous simulants, the primary focus of JSC-RN was to simulate the low

temperature evolved gases, particularly the 1-3 wt.% low temperature (<450 ºC) water release as measured by the SAM instrument on the *Curiosity* rover (Leshin et al., 2013).

2. Methods

2.1 Thermal and evolved gas analysis

Powdered samples (e.g., individual minerals, simulant mixtures) were analyzed on a Setaram Labsys EVO simultaneous thermal gravimeter (TG)/differential scanning calorimeter (DSC) connected to a ThermoStar quadrupole mass spectrometer for evolved gas analysis (EGA). This technique matches the EGA capability of the SAM instrument on the *Curiosity* rover, adding TG and DSC capabilities to provide a more complete understanding of reactions and phase transitions in the laboratory samples. TG measures sample weight loss as a sample is heated, and was used to determine the amount of water evolved from the sample at low temperatures (<450 °C). DSC measures exothermic and endothermic phase transitions and chemical reactions as a sample is heated. EGA is used to measure and quantify the gases released from the sample during pyrolysis. Samples (~10-50 mg) were loaded into an alumina ceramic crucible and placed inside the Labsys furnace alongside an identical empty reference crucible. The system was purged with He carrier gas at a flow rate of 10 sccm and pressure of 30 mbar, similar to the carrier gas and pressure conditions on the SAM instrument. The sample crucible and the empty crucible were heated from room temperature to 1000 °C at a heating rate of 35 °C/min.

2.2 X-ray diffraction

Powdered samples were individually analyzed for qualitative mineralogy using a PANalytical X'Pert Pro MPD X-ray diffraction instrument with an X'celerator detector and Co Kα radiation. Data were collected under ambient conditions at a step size of 0.02° per minute from 2° to 80° 2θ at 40 mA and 45kV. Minerals were identified using HighScore software equipped with the International Center for Diffraction Data (ICDD) database and the Crystallography Open Database (COD).

Select samples were analyzed for quantitative mineralogy using the above methods and Reitvield refinement in HighScore and MDI JADE software. The select samples were spiked with a National Institute of Standards and Technology (NIST) corundum (Al_2O_3) standard in order to quantify mineral and X-ray amorphous abundances (Bish and Howard, 1988). Novaculite and NIST lanthanum hexaboride standards were used to characterize the instrument's 2θ alignment and line broadening function, respectively.

2.3 X-ray fluorescence

Powdered samples were analyzed for bulk chemistry using a Malvern PANalytical Zetium X-ray Fluorescence (XRF) vacuum spectrometer. ~1 gram of each sample was placed in a muffle furnace at 950 °C for 1.5 hours. 0.4000 g of each post-loss on ignition (LOI) sample was mixed with 3.6000 g of 4-9s pure lithium tetraborate, placed in a platinum crucible, and heated with a meeker burner until completely melted. The melt was mixed three times during the heating stage, transferred to a platinum casting dish, and quenched to form a glass disk for XRF analysis including SiO_2, TiO_2, Al_2O_3, Fe_2O_3 total, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5. Geochemical

rock standards BHVO-2 and NBS-688 were prepared using the same methods described above. The amount of Fe^{2+} was measured on unheated samples using the Reichen and Fahey (1962) procedure modified by including a titration of NBS-688 geochemical standard rock and multiplying titrated sample FeO concentrations by the ratio of the titrated NBS-688 value to its standard value (7.64 wt.% FeO; Govindaraju, K., 1994). The measurements and calculation account for slight differences in acid concentrations and other vagaries in the technique. Concentrations of Fe^{3+} were calculated using the XRF Fe_2O_{3total}, %LOI data, and the measured Fe^{2+} values.

Samples were prepared and analyzed for trace elements using XRF. 7.0000 grams of each sample were mixed with 1.4000 grams of high purity Copolywax powder and mixed for 10 minutes. The mixture was pressed into a briquette using a 50,000 psi press. Five dozen geochemical rock standards were prepared using the above methods and were used to assemble working curves for each element.

3. Results and Discussion:

3.1 Development of JSC-RN and final recipe

The base of JSC-RN was a mixture of two different size fractions of MMS that approximated the <150 µm size fraction of Rocknest analyzed by both SAM and CheMin. Two size fractions of MMS (dust and <2 mm) were mixed in various ratios and subsequently analyzed for mean particle size using a Microtrac BlueWave laser particle size analyzer. A 65 wt.% dust/35 wt.% < 2 mm MMS mixture was determined to have a particle size of approximately 90 % < 150 µm, which matches the particle size distribution of the Rocknest sample (Archer et al. 2014).

The MMS base (65 % dust, 35 % <2 mm) was augmented by adding phases to more closely approximate the known mineralogy, evolved gases, and chemistry of Rocknest. The highest priority was to replicate the 2.0 ± 1.3 wt. % (Archer et al., 2014) low temperature water release (<450 °C) observed in the Rocknest soil sample. All potential additives and mixtures were analyzed individually for their mineralogy and thermal and evolved gas profiles. Select mixtures were analyzed for total chemistry using XRF.

Fifteen iterations of trial mixtures of MMS (65 % dust, 35 % <2 mm) and additives led to the final recipe shown in Table 4, which most closely matched the evolved gases, water content, total chemistry, and mineralogy of the Rocknest soil sample. Additives that were cost-effective, pre-powdered, and available in large quantities were preferred. Each component, the reasoning for adding it to the MMS base, and any processing steps prior to simulant mixing are described below and in Table 4.

Sodium perchlorate.

Sodium perchlorate was added to the MMS base because it fairly closely reproduced the mid temperature (~380 °C; Figure 1) O_2 release observed in SAM data from the Rocknest soil sample. Although Na-, K-, and Ca perchlorate all evolve mid temperature O_2 without the coevolution of HCl, Na perchlorate is less hygroscopic than other perchlorates and therefore more feasible for large-scale production. Sodium perchlorate was added at 1 wt.% to approximate the ClO_4 detected in Rocknest based on SAM mid temperature O_2 peak integrations. Although ClO_4 was only detected at ~0.4 wt.% in Rocknest (Table 3), the actual amount of perchlorate could be higher due to reactions with Fe-bearing phases and due to the oxidation of reduced sulfur, both of which decrease the amount of evolved O_2 from perchlorate (Archer et al.,

2014). The sodium perchlorate arrived in granular form and was powdered with a ball mill prior to mixing with the other simulant components.

Sulfide and sulfate.

Pyrite and ferric sulfate were added at 1 wt.% each to replicate the ~515 °C and 730 °C SO_2 releases observed in Rocknest, respectively. As mentioned above, previous laboratory SAM-like EGA experiments by McAdam et al. (2014) also supported the presence of iron sulfide and sulfate in Rocknest. SO_3 abundances from SAM ranged from 0.5 ± 0.1 to 3.5 ± 0.7 wt.% in the four runs of the Rocknest sample (Archer et al., 2014; Table 3), making 2 wt.% sulfur species in JSC-RN a reasonable approximation. Pyrite was chosen as the reduced sulfide because, although pyrrhotite is more likely to be present in martian samples (e.g., Lorand et al., 2005; Vaniman et al., 2014), it oxidizes much more quickly than pyrite. Therefore, pyrite is more suitable for this simulant because it is more stable over time. The pyrite arrived in hand-sample form and had to be crushed and then powdered with a ball mill. The ferric sulfate was pre-powdered and no additional processing steps were required prior to mixing with the other components.

Granular ferric oxides.

As stated previously, the Rocknest water release profile was broad enough that there were likely multiple sources of water that contributed to the peak. Therefore, we selected multiple materials that produced water release peaks spanning the temperature range of the Rocknest water release. High capacity granular ferric oxide (GFO) was added because it evolved a broad low temperature water release similar to what was observed in the Rocknest soil sample, and to simulate the amorphous component in Rocknest. GFO's (both high and regular capacity) are used in water filtration and large amounts can be purchased commercially at a relatively low

cost. Additionally, GFO's are pre-granulated, minimizing the steps for final simulant mixing and homogenizing at the USGS. XRD of the high capacity GFO revealed two broad "humps" similar to 2-line ferrihydrite with contributions from hematite (Supplementary figure 1). The high capacity GFO simulated the nanophase iron oxides present in the amorphous component of Rocknest (~35 wt.%; Table 1). Ferrihydrite is otherwise time-consuming to synthesize in the lab, especially in the large-scale quantities necessary for ISRU experiments. The high capacity GFO produced a water release peak (190 ºC) lower than the Rocknest sample (280 ºC), therefore it could not be the only source of water in Rocknest.

Regular capacity GFO was added to the MMS base primarily because it produced a water release peak at 245 ºC, which was similar to the water release peak in the Rocknest soil sample (280 ºC). Regular capacity GFO was identified as goethite by XRD (Supplementary figure 2). Goethite was not detected by CheMin in the Rocknest sample, but it can not be excluded because it may have been present at or below the detection limit of the instrument (~1-2 wt. %) and/or particle sizes were too small to coherently diffract X-rays. Both GFO's arrived as soft granules and were powdered with a ball mill prior to mixing with the other simulant components.

Goethite.

Another goethite sample was added because it evolved a water peak at ~300 °C due to dehydroxlation, which was slightly higher than the regular capacity GFO goethite (~245 °C) and closer to the water release peak observed in Rocknest (280 ºC). The addition of this goethite served to broaden the overall H_2O release profile, making it more similar to what was observed in Rocknest. Finely powdered goethite was sourced from a pottery pigment company (Table 4), and also acted as an orange/yellow pigment for the final mixture. This goethite was pre-

414 powdered and no additional milling was required prior to mixing with the other simulant
415 components.

416 *Forsterite.*

417 Forsterite, the Mg-rich endmember of olivine, was added to increase the total Mg and Si
418 in the mixture. Forsterite did not produce any evolved gases within the SAM temperature range.
419 Olivine was detected at 13.3 ± 4 wt.% in Rocknest, therefore the 10 wt.% added to JSC-RN was
420 a reasonable approximation. The foresterite arrived in granular form and was powdered using a
421 ball mill prior to mixing with other simulant components.

422

423 Table 4. Components of JSC-RN, their sources, the initial form they arrived in, and processing
424 steps prior to mixing with other the components

Component	Wt.%	Source	Initial Form	Processing Steps
$NaClO_4$	1	Synthetic, Sigma Aldrich	granules	Milling
Goethite	1.5	Laguna Clay Company	powder	None
Pyrite	1	Natural, Ward's	hand samples	Crushing, milling
Ferric Sulfate	1	Synthetic, Sigma Aldrich	powder	None
High Capacity GFO (ferrihydrite)	5	Kolar Filtration	granules	Milling
Regular capacity GFO (goethite)	2.5	Bayoxide	granules	Milling
Forsterite	10	Nature's Footprint	granules	Milling
Mojave Mars Simulant (65 % dust, 35 % <2 mm)	78	Jet Propulsion Laboratory	sand/dust	None

425

426

3.2 JSC-RN mixed by the USGS

The final recipe included the types and amounts of each additive and how to prepare (i.e., mill and mix) each additive (Table 4). This recipe, along with MMS dust, MMS <2 mm, and the additives were sent to the Geology, Geophysics, and Geochemistry Science Center at the USGS in Denver, CO for crushing, milling, and mixing. At the USGS, consolidated materials were ground to fine powders using a 30 gallon ceramic lined ball mill with corundum grinding balls. Consolidated materials were ground in ~50 kg aliquots for a total grinding time of 30 minutes. All simulant components were mixed together in a 10 ft^3 V-blender to ensure homogeneity.

Approximately 800 kg of JSC-RN were sent back to JSC from the USGS in 5-gallon buckets (21 buckets total). Thirteen buckets of JSC-RN were randomly sampled and analyzed on the TG/DSC/EGA instrument (described in section 2.1) and three of those samples were analyzed with XRD (section 2.2). All 21 buckets of JSC-RN were subsampled and analyzed for total chemistry using XRF (section 2.3). The results were analyzed for homogeneity between the buckets and for any differences from the small prototype of JSC-RN made in the laboratory. The results were also compared to Rocknest data from CheMin, SAM, and APXS. Images of JSC-RN mixed by the USGS and the Rocknest sand shadow are shown in Figure 2.

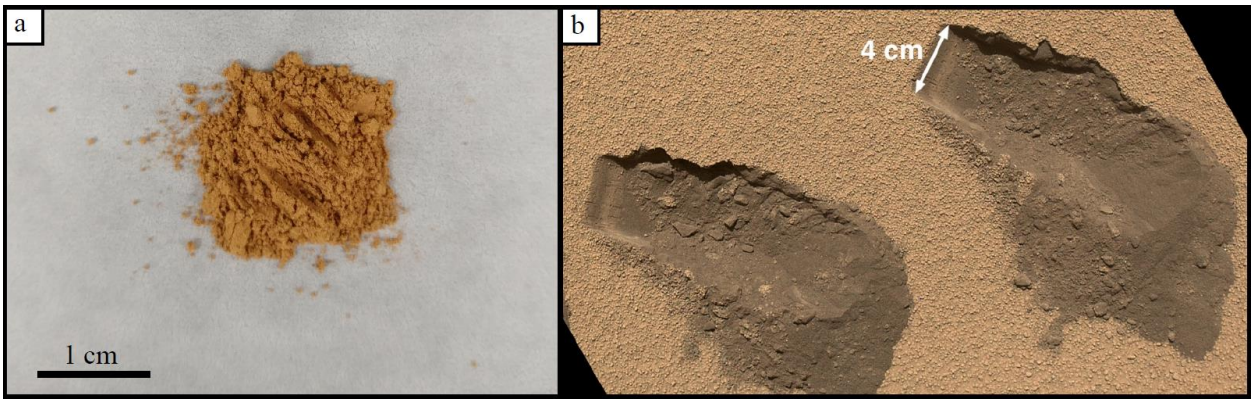


Figure 2. a) JSC-RN simulant mixed by the USGS. b) Scoop trenches in the Rocknest sand shadow, which were analyzed by instruments on the *Curiosity* rover.

3.3 Mineralogy and total chemistry of JSC-RN

The average quantitative mineralogy of three subsamples of JSC-RN mixed by the USGS were mineralogically homogenous and better approximated the mineralogy of the Rocknest soil sample compared to MMS (Table 1). The largest mineralogical differences between JSC-RN and Rocknest analyzed by CheMin were pyroxene and the phyllosilicates, which were discrepancies introduced by the MMS base (Table 1). JSC-RN better approximated the olivine abundance in Rocknest compared to MMS alone (Table 1). JSC-RN was primarily developed to match the low temperature evolved gases and the number of additives was minimized in order to make large-scale production simpler and more cost-effective. Therefore, some differences in mineralogy between JSC-RN and Rocknest analyzed by CheMin were expected.

The total chemistry of subsamples of JSC-RN prepared by the USGS indicated that they were chemically homogenous and similar to Rocknest drill-fines that were analyzed by APXS (Table 2). All oxides were similar between JSC-RN and Rocknest except for Al_2O_3, which was

higher in JSC-RN due to the MMS base (13.7 wt.% in JSC-RN compared to 9.37 wt.% in Rocknest; Table 2). This was expected because terrestrial basalts are known to contain more Al than martian basalts (e.g., Wänke & Dreibus, 1988; McSween et al., 2009). Overall, JSC-RN was a better chemical match to Rocknest analyzed by APXS compared to MMS alone.

3.4 Thermal and evolved gas analysis of JSC-RN

Evolved gas analysis of the 13 subsamples of JSC-RN mixed by the USGS demonstrated that they were homogenous and matched low temperature (<450 °C) gas evolutions detected by SAM in Rocknest (Figure 1). Low temperature (<450 °C) weight loss due to evolved water in the JSC-RN subsamples was consistently ~2 wt.% (Figure 1), which was similar to H_2O abundances from Rocknest as detected by SAM (2.0 ± 1.3 wt. %; Archer et al., 2014; Table 3). JSC-RN evolved minor amounts of water >450 °C due to phyllosilicate dehydroxylation, which was not consistent with results from SAM. The O_2 release peak from JSC-RN was slightly lower (312 °C) than that of Rocknest (380 °C), possibly due to differences in the type of oxychlorine and/or effects of Fe-bearing minerals in the sample. The lower temperature SO_2 release in JSC-RN was the same as Rocknest analyzed by SAM (both ~515 °C). However, the second SO_2 peak in Rocknest (~730 °C) was lower than that of JSC-RN (~810 °C). The discrepancy in the second SO_2 release could be caused by differences in the cation-type of sulfate and/or effects of other phases in the sample on sulfate decomposition temperature. The high temperature (>600 ºC) HCl release present in the small-batch prototype of JSC-RN prepared in the laboratory and in Rocknest analyzed by SAM was not present in the JSC-RN subsamples mixed by the USGS (Figure 1). It is currently unknown what caused the discrepancy in the high temperature HCl evolutions between the USGS-prepared and small lab-prepared prototype of JSC-RN, but high-temperature HCl was not a priority for testing the ISRU water-extraction equipment. Overall,

JSC-RN broadly matched the SO_2, O_2, and H_2O gas evolutions detected by SAM in the Rocknest soil sample and was a much better match than the MMS mixture without additives (Figure 1). Specifically, JSC-RN matched the low temperature water profiles and abundances as detected by SAM in the Rocknest soil sample.

3.5 Water re-adsorption in JSC-RN

JSC-RN mixed by the USGS was analyzed for its ability to re-adsorb atmospheric water after being heated in order to determine if previously heated samples could be reused for water extraction purposes. Nine sub-sample of JSC-RN were heated to 1000 °C in a Labsys EVO DSC/TG/mass spectrometer using the methods described in section 2.1 and allowed to cool to room temperature. The samples were left exposed to laboratory air for 2 days, 8 days, and 2 weeks (3 of each). The same samples were then re-heated to 1000 °C on the Labsys EVO. TG weight loss data from the first heat and second heat analyses were compared in order to determine how much water was re-adsorbed by the post-heat sample when left exposed to laboratory air.

Results from the water re-adsorption experiments demonstrated that JSC-RN did not re-adsorb water after being heated to 1000 °C and then exposed to laboratory air for 2 days, 5 days, and 2 weeks. When heated to 1000 °C for the first time, JSC-RN had a TG weight-loss of ~2 wt.%, most of which was due to water (Figure 3). When the same sample was reheated to 1000 °C after being exposed to laboratory air for 2 days-2 weeks, it had a TG weight-loss of <0.1 wt.% at 450 °C (Figure 3). The low amount of water re-adsorption indicates that JSC-RN cannot be reused for water-extraction purposes after it is heated. This was expected because the low temperature water release in JSC-RN was not solely due to adsorbed water; it also had

contributions from structural water and hydroxylated phases (e.g., goethite) that decomposed during thermal analysis.

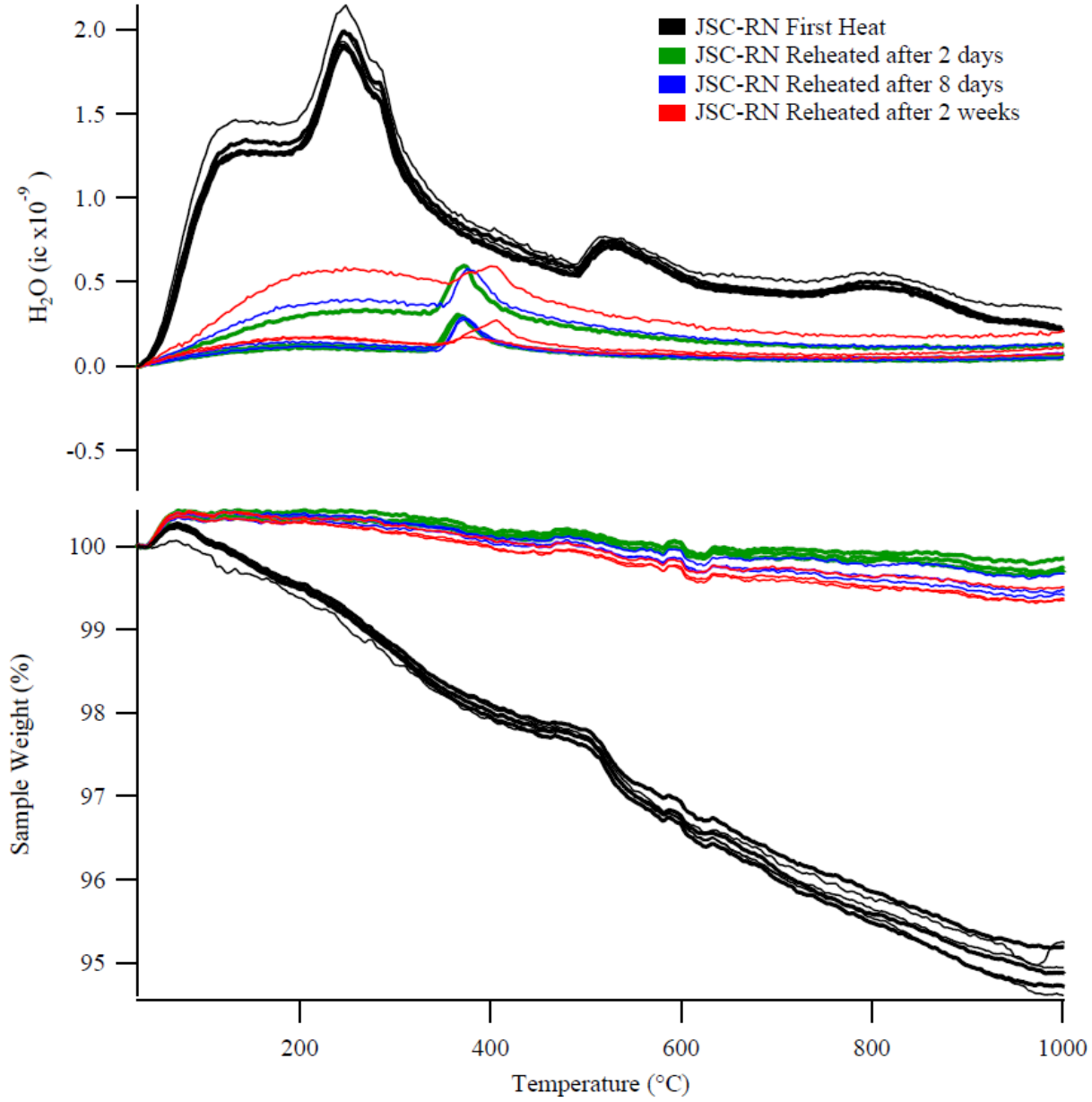


Figure 3. H_2O and sample weight loss from JSC-RN produced by the USGS after being heated to 1000 °C (first heat), and then reheated to 1000 °C after the sample was exposed to laboratory air for 2 days, 8 days, and 2 weeks.

3.6 Applications of JSC-RN

JSC-RN is ideal for large-scale experiments and device testing where volatile content is the primary focus. This includes the testing of equipment meant to evolve gases through heating for uses such as liquid H_2O for human consumption, breathable O_2, or rocket propellant. JSC-RN is the highest fidelity martian soil simulant available in terms of evolved O_2, SO_2, and particularly the low temperature (<450 °C) H_2O.

JSC-RN is suitable for most other experiments and equipment testing where large quantities of martian soil simulant are necessary. JSC-RN is feasible and cost-effective to make in large quantities because it uses commercially available additives, most of which are pre-granulated or powdered. Large-scale applications for JSC-RN include ISRU systems and component testing, ISRU plant growth studies, and ISRU habitat studies.

JSC-RN can also be used for geophysical applications where a crushed-rock based simulant is preferred. Crushed-rock simulants are ideal for testing ISRU technologies where geophysical properties are important (e.g., rover wheel testing) (Peters et al., 2008). Although both JSC-RN and the original MMS simulant are crushed-rock based simulants, JSC-RN is a closer match to Rocknest in terms of mineralogy, chemistry, and evolved gases. Mineral-based simulants such as MGS-1 are more applicable for studies that require mineralogy that precisely matches the quantified mineralogy of martian soils. Applications that may require a mineral-based simulant include science research that focuses on mineralogy, such as mineral alteration experiments.

3.7 Future development of JSC-RN

JSC-RN will be further developed by changing the base from MMS to a crushed rock that better simulates martian soil mineralogy. The mineralogy of MMS reported by Peters et al. (2008) and the mineralogy of MMS sent to JSC were different. One of the major differences was that the batches of MMS sent to JSC contained phyllosilicates (Table 1). The presence of phyllosilicates in MMS caused high temperature (>450 °C) water releases in JSC-RN, which were not observed in Rocknest (Figure 1). Additionally, MMS dust and MMS <2 mm did not contain olivine as reported in Peters et al. (2008). Several active basalt quarries are currently being evaluated for their potential to be mined for large quantities of crushed rock-based martian soil simulant which better matches the mineralogy of Rocknest.

It is important to note that the future development of JSC-RN is highly dependent on the user's application and therefore, what properties (e.g., mineralogy, chemistry) are important. For example, if JSC-RN were to be used for mineral alteration studies, it should be modified to more closely match the mineralogy of Rocknest. If the high temperature (>450 °C) evolved gases (e.g., SO_2, HCl) are important for the simulant application, it should be modified to more closely match the high temperature evolved gases from Rocknest. Overall, future development of JSC-RN will reflect the needs of the simulant-using community.

Conclusions

JSC-RN was designed to mimic the evolved gases, mineralogy, and total chemistry of the well-characterized martian soil sample, Rocknest, which was analyzed by the *Curiosity* rover in Gale Crater, Mars. JSC-RN was specifically developed for use in large-scale ISRU systems and

component testing of a water-extraction device where the low temperature (<450 °C) evolved gases were of primary importance. JSC-RN was homogenous and similar to Rocknest in terms of mineralogy, total chemistry, and low temperature evolved gases. Specifically, the water content of JSC-RN was ~2 wt. %, which was similar to H_2O abundances from Rocknest as detected by SAM. JSC-RN is an ideal martian soil simulant for use in studies that require large quantities of low-cost martian soil simulant, in particular studies where volatile content is of primary importance. However, we stress that further modifications to the JSC-RN will depend on the user's application (e.g., water extraction, geotechnical tests).

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Data statement:

Data published in this paper are publicly available on the Harvard Dataverse data repository: https://doi.org/10.7910/DVN/7BH7NL

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