



# Article Metal and Oxide Sublimation from Lunar Regolith: A Kinetics Study

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Abstract: When considering the extraction of metals from lunar regolith for use in space, one reductive method of interest is vacuum thermal dissociation. Given the high vacuum environment on the Moon, the sub-liquidus operation of such a process, i.e., sublimation, warrants investigation. In the current work, the kinetics of the vacuum sublimation of the more volatile major oxides found in the lunar regolith, Na<sub>2</sub>O, K<sub>2</sub>O, and FeO, are evaluated. Two distinct factors are accounted for in the current work: the change in the evaporation flux due to temperature; and the reduction in available surface area for evaporation due to sintering of the feedstock. Surface area change due to the sintering of compressed LMS-1 regolith simulant pellets was quantified via a Brunauer-Emmett-Teller analysis. The surface area of the samples was measured to vary from  $3.29 \text{ m}^2/\text{g}$  in the unsintered sample, to 1.04 m<sup>2</sup>/g in the samples sintered at 800  $^{\circ}$ C, and down to 0.09 m<sup>2</sup>/g in the sample sintered at 1150 °C. Evaporation flux was calculated using the Hertz-Knudsen-Langmuir equation using saturated vapor pressures predicted from the FactSage thermochemical package and verified against Knudsen Effusion Mass Spectroscopy data from tests conducted on lunar regolith sample #12022. The combination of these studies resulted in the conclusion that no local maxima in evaporation rate below the melting point was found for the current system, as such the highest rate of sublimation was determined to be 1200 °C for all species, at temperatures of 1200 °C and above, partial melting of the material occurs. The predicted maximum rate of sublimation for the species Fe, Na, and K at 1200 °C was 0.08, 1.38, and 1.02 g/h/g of regolith, respectively. It is noted that significant variation was seen between FactSage predictions of saturated vapor pressures and the measured values. Future work generating detailed thermochemical databases to predict the behavior of complex systems similar in composition to lunar regolith would benefit the accuracy of similar kinetic studies in the future.

Keywords: ISRU; astrometallurgy; sublimation; evaporation; SRU

## 1. Introduction

In the field of astrometallurgy, the extraction of metals from off-Earth resources, the ability to use the naturally occurring conditions in space, such as the vacuum and increased access to sunlight, are beneficial. The development of novel extraction processes that use these conditions is important for understanding the potential advantages these conditions pose to the challenge of space resource processing.

In the context of the processing of lunar regolith, one metal production variant that actively uses the extremely low pressures present on the Moon, as well as the prevalent access to increased solar flux, is thermal decomposition or pyrolysis. This process involves the heating of an oxide feedstock to a temperature at which some or all elements within that feedstock transition from the condensed to gas phase, i.e., sublimate or evaporate.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The sublimation of metals and oxides from complex silicate feedstocks under high vacuum conditions is a phenomenon that has the potential for application in off-Earth resource extraction processes. Unlike on Earth, the ultra-high vacuum present on the surface of the Moon, measured at  $3 \times 10^{-15}$  atm at night [1], results in the sub-liquidus evaporation, or sublimation, of oxides becoming thermodynamically favorable at moderate temperatures. Oxide evaporation for the extraction of oxygen has been investigated historically [2–9]. This work has predominantly included the demonstration of such processes using varying apparatus, and, in some cases, a basic thermodynamic analysis of the process. For kinetic reasons, these studies have targeted temperatures above the liquidus of the lunar regolith. A thorough study of the kinetics of the sublimation of metals from lunar regolith has not been conducted to date.

The current work will evaluate the predicted rate of metal sublimation from lunar regolith. This will include thermodynamic modelling for the prediction of evaporation flux at varying temperatures, as well as an analysis of the surface area change due to the sintering of a solid feedstock at high sub-liquidus temperatures. The aim of the current work is to evaluate the expected evaporation rate of different metal species from lunar regolith and to determine if the surface area change due to sintering will create a local maxima in evaporation rate at a temperature below the melting point of the feedstock.

Given that access to real lunar regolith for laboratory testing is limited, a regolith simulant material, LMS-1, has been used for the sintering and subsequent surface area analysis in the current work. LMS-1 is an all-purpose simulant synthetically produced by Exolith Lab [10]. It is acknowledged that, while regolith simulants are regularly used in such research to loosely predict the behavior of real lunar regolith, the accuracy of the simulant when considering surface area reduction during sintering is unknown. The determination of surface area reduction due to sintering of real lunar regolith will be a beneficial study when such a material becomes more readily available for research purposes.

Thermodynamic equilibrium modelling of a sublimation process acting under ultrahigh vacuum conditions (3 × 10<sup>-15</sup> atm) predicted that for Fe sublimation, a minimum temperature of 800 °C was required [11]. In the current work, partial melting of the regolith simulant material was observed at 1200 °C. As such, for the investigation of the sublimation kinetics of regolith material presented in the current work, the temperature range from 800 °C to 1200 °C was considered.

#### 2. Materials and Methods

#### 2.1. Lunar Simulant Sintering

Sintering experiments were conducted in the Robert Simpson High Temperature Processing facility located in the Advanced Technologies Centre at the Swinburne University of Technology. Tests were completed using a Carbolite GERO HTRH 100–600/18 furnace with six MoSi<sub>2</sub> heating elements in a vertical hanging position. The furnace was controlled with a model E3508P10 programmer.

For the sintering test work, 2.6 g samples of LMS-1 lunar regolith simulant were placed in a steel die assembly with a 13 mm diameter. The die was compressed using a manual hydraulic press for 5 min at 80 kN of pressure. Three pellets were prepared for each test. Samples were placed into an alumina (99.8%) boat on a layer of nickel foil separating the samples from the boat. This was to prevent the samples from sintering to the boat.

Samples were placed into the furnace which was then sealed and evacuated with an Edwards E2M1.5 Rotary Vane Vacuum Pump. Internal pressure was measured with a mechanical pressure gauge. A constant pressure of below  $10^{-3}$  atm was required for the system to be considered sufficiently sealed. A heating duration of six hours was used for all tests. Samples were heated to the reaction temperature and held for two hours before being allowed to cool naturally.

### 2.2. Surface Area Reduction

Brunauer–Emmett–Teller (BET) analysis [12] of the sintered LMS-1 samples was completed to determine the surface area change of the samples for different sintering temperatures. Sintered samples were fractured into quarters and inserted into a standard 1/2 in. glass sample tube. Any loose material displaced during sample fragmentation was also added to the sample tube to ensure that the mass of each analyzed sample was approximately the same. A Micromeritics Smart VacPrep machine was used for sample preparation. Sample tubes were evacuated via a rotary vacuum pump and dried at 300 °C for 12 h.

A Micromeritics TriStar II PLUS analysis machine was used for BET analysis. Polyvinyl chloride thermal jackets were placed on sample tubes prior to loading into the TriStar analysis machine. Analysis was completed in liquid nitrogen at ~77 K. A full sweep consisting of 160 points was completed between a  $P/P_0$  of 0 and 1 using nitrogen gas. The analysis presented in the current work will cover the BET range from 0.05 to 0.35  $P/P_0$ . As per ASTM standard C1274-12 [13], an R<sup>2</sup> value for the linear fit between a  $P/P_0$  of 0.05 and 0.35 was calculated and, as per C1274-12, samples with an R<sup>2</sup> lower than 0.9999 were to be rejected. No samples were rejected in the current work. For BET calculations a sample density of 3.03 g/cm<sup>3</sup> was used as per LMS-1 simulant specifications [10]. For the reporting of surface areas in the current work, an error range of 5% was added to plots; this error range was observed between multiple laboratories. This error is predominantly attributed to the accuracy of the sample mass measurements.

## 2.3. Evaporation Flux

Evaporation flux calculations were completed using saturated vapor pressures as predicted by the FactSage thermochemical package. Saturated vapor pressures were compared to measured Knudsen Effusion Mass Spectroscopy (KEMS) data from the Apollo #12022 regolith sample as reported by De Maria et al. [15]. Evaporation flux was then calculated using the Hertz–Knudsen–Langmuir (HKL) equation [16–18].

#### 2.3.1. Saturated Vapor Pressure

The FactSage 8.2 thermochemical modelling program was used to generate data that predict the output of a KEMS experiment. FactSage operates by evaluating detailed databases containing thermodynamic and phase equilibrium data for a given system in order to determine the Gibbs free energy for the transformation of all potential phases within that system as functions of temperature, pressure, and composition [19–22]. The FactSage databases used for the current work were: FactPS (for pure substances), FToxid (for oxides), and FSstel (for iron alloys and other metals). Detailed documentation about the FactSage thermochemical modelling software and the databases and solution models used in the program can be found elsewhere [19–22].

The FactSage program was run using a fixed-volume method to obtain predicted metal and oxide saturated vapor pressure values at varying temperatures. All predictions in the current work used a solid feed mass of 100 g and a volume of one liter. It is noted that this method of saturated vapor pressure prediction is only valid if the predicted final system composition still contains solid material.

The oxide composition of the Apollo #12022 material, as reported by Snyder et al. [23], that was used in the FactSage modelling is shown in Table 1. The FactSage calculation results were compared to the published KEMS data from the Apollo #12022 sample reported by De Maria et al. [15].

| SiO <sub>2</sub> | FeO   | MgO   | Al <sub>2</sub> O <sub>3</sub> | CaO  | TiO <sub>2</sub> | Cr <sub>2</sub> O <sub>3</sub> | MnO  | Na <sub>2</sub> O | K <sub>2</sub> O |
|------------------|-------|-------|--------------------------------|------|------------------|--------------------------------|------|-------------------|------------------|
| 43.22            | 21.45 | 10.44 | 9.04                           | 9.56 | 5.16             | 0.33                           | 0.25 | 0.47              | 0.07             |

**Table 1.** Apollo #12022 composition used in the calculation of saturated vapor pressures, data from

 Snyder et. al. [23]. Values adjusted to 100% omitting trace elements.

Discrepancies between the calculated and measured results will be discussed below. In the event that the calculated saturated vapor pressures significantly varied as compared to the published data, the KEMS results were instead compared to calculated saturated vapor pressures over pure oxide, binary, and ternary oxide systems. In this case, these predictions were compared to the KEMS results and a least-squares fit was used to determine the system/feed composition with the closest correlation to the measured results.

Given the computationally heavy nature of evaluating all the combinations of binary and ternary oxide systems, focus was placed on the evaluation of Fe, Na, and K, these being the most volatile oxides in the feed composition [11].

The approach taken does not give a perfect fit for some vapor species and instead equates to a loose 'best fit' approach; the use of these data is more accurate than using the FactSage predictions based on the full silicate system and allows for a more usable extrapolation beyond the temperature ranges measured by De Maria et al. [15].

## 2.3.2. Evaporation Flux Calculation

Saturated vapor pressure can be used to calculate an evaporation flux using the HKL equation. The HKL equation is shown in Equation (1), where  $dn_i/dt$  is the flux of particles hitting the surface in mol/s, A is the surface area,  $a_e$  and  $a_c$  are the coefficients of evaporation and condensation,  $p_{i,sat}$  is the saturated vapor pressure of element i,  $p_i$  is the actual partial pressure at the surface, R is the universal gas constant, T is the temperature in Kelvin, and  $M_i$  is the molar mass of the element. A detailed description and derivation of this equation can be found in [24]:

$$\frac{dn_i}{dt} = -A \frac{a_e p_{i,sat} - a_c p_i}{\sqrt{2\pi R M_i T}}$$
(1)

To determine the evaporation flux in pure vacuum, the second half of the numerator  $(-a_c p_i)$  can be removed. It is important to note that this only applies at pressures significantly below the saturated vapor pressures being evaluated. In these circumstances, this second half of the numerator can be ignored because there will be negligible condensation. A system where this is true is said to be undergoing "Langmuir evaporation" [25]. For the purposes of the current work, the area (*A*) will be included later.

In the calculations presented here the value of the evaporation coefficient ( $a_e$ ) was assumed to be unity. This was in part due to a lack of literature available evaluating the  $a_e$  of similar systems to that being modelled. From a theoretical perspective, it is important to note that the HKL equation assumes thermal equilibrium between the evaporating substance and the vapor phase [24]. Low temperature studies that have not made the assumption of thermal equilibrium, and instead accounted for the temperature difference, concluded that when accounted for, the  $a_e$  approaches unity [26]. Sossi et al. postulate that as the temperature of reaction increases, and thus the heat of reaction as a ratio of system heat decreases, the  $a_e$  of any system increases [25]. Given that the evaporation coefficient only significantly influences the results if they are very small compared to unity [24], the assumption that  $a_e = 1$  in the current work is reasonable. This does however result in the calculated evaporation rates presented here equating to a 'best case scenario'.

#### 2.3.3. Evaporation Rate Calculation

The predicted evaporation flux per unit area was multiplied by the surface area per gram of regolith determined via the BET analysis of sintered LMS-1 pellets. The calculation of predicted evaporation rate of Na, K, and Fe was conducted in this manner between the temperatures of 800  $^{\circ}$ C and 1200  $^{\circ}$ C.

For final reporting, the flux was converted to  $g/h/m^2$  by multiplying the evaporation flux by  $3600 \times M_i$ . This conversion was performed to provide a more meaningful value for future process estimations and modelling.

## 3. Results

## 3.1. Surface Area Change Due to Sintering

The surface area versus temperature plot of sintered LMS-1 simulant pellets is shown in Figure 1. Figure 1 shows surface areas calculated using BET analysis for sinter temperatures down to 400 °C as well as an unsintered feed material shown at 25 °C. A surface area reduction from 1.04 m<sup>2</sup>/g at 800 °C to 0.09 m<sup>2</sup>/g at 1150 °C was seen in samples. Minimal further surface area reduction was seen between 1150 and 1200 °C (<0.002 m<sup>2</sup>/g).



Figure 1. Calculated surface area changes due to sintering of LMS-1 simulant.

Figure 2 shows micrographs of cross-sections of the sintered samples at 1100, 1150, and 1200 °C. This figure clearly shows the increased sintering of particles in the samples at higher temperatures resulting in the consequent reduction in surface area shown in Figure 1. Note that while the calculated surface area did not change significantly between the 1150 and 1200 °C samples, the sample morphology is noticeably different. The 1200 °C sample shows more spherical-shaped pores. The presence of these minimal surface structures suggests that the effect of surface tension compared to the viscosity of the surrounding material is higher than that observed in the lower temperature samples, this indicates the presence of liquid phases in the samples at 1200 °C.

## 3.2. Saturated Vapor Pressure Modelling and Sublimation Flux Calculation

A comparison between the predicted and measured saturated vapor pressure of species Fe, Na, and K above a sample of Apollo #12022 regolith is shown in Figure 3. Significant discrepancy can be seen between the predicted values and the measured values for this material. For Fe and Na, this discrepancy is in the order of one magnitude, for K this difference increases to over 2.5 orders of magnitude at the lower temperatures. Given the significant underestimation of saturated vapor pressure by the FactSage software for the Apollo #12022 feedstock, it was determined that these predictions were not accurate enough to be included in the kinetics modelling and that an alternate dataset must be found. The measured KEMS results did not contain data at enough temperature points to be usable for the modelling.



**Figure 2.** Micrographs of: (**a**) unsintered feed material, and sample cross-sections sintered for 2 h at: (**b**) 1100 °C, (**c**) 1150 °C, and (**d**) 1200 °C.



**Figure 3.** Comparison between measured saturated vapor pressure of species Fe, Na, and K from De Maria et al. [15] shown in blue, and the prediction by FactSage 8.2 software shown in orange, given the Apollo sample #12022 feed shown in Table 1.

As per the methods described above, predicted saturated vapor pressures from a set of pure oxide, binary, and ternary oxide systems were also generated using FactSage. The oxide systems determined to provide the most accurate prediction were FeO for Fe,  $Al_2O_3$ -CaO-Na<sub>2</sub>O for Na, and  $Al_2O_3$ -K<sub>2</sub>O for K. Figure 4 shows the comparison of the measured KEMS results with the FactSage predictions for a pure oxide system (green) and in the case of Na and K the closest ternary and binary system, respectively. Binary and ternary oxide systems for Fe were not considered as the prediction from a pure oxide (FeO) feed proved to be accurate.



**Figure 4.** Comparison between measured saturated vapor pressure of species Fe, Na, and K from De Maria et al. [15] shown in blue, FactSage prediction assuming a pure oxide feed in green, and the closest oxide solution (FactSage) in yellow. The oxide systems represented by the yellow trend are Al<sub>2</sub>O<sub>3</sub>-CaO-Na<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O for Na and K, respectively.

The predicted saturated vapor pressure of the species Fe, Na, and K between the temperatures of 800 °C and 1200 °C are shown in Table 2. Table 2 also shows the calculated evaporation flux in mol/s/m<sup>2</sup> determined using the HKL equation given the predicted saturated pressures for each species. As described above, the saturated vapor pressure for Fe was predicted from an FeO system, Na from an Al<sub>2</sub>O<sub>3</sub>-CaO-Na<sub>2</sub>O system, and K from an Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O system.

**Table 2.** Predicted vapor pressures (FactSage), and calculated evaporation flux (HKL equation) of the elements Fe, Na, and K from an Apollo sample #12022 feedstock.

|                     | F                            | <sup>7</sup> e                        | N                            | la                                    | К                           |                                       |
|---------------------|------------------------------|---------------------------------------|------------------------------|---------------------------------------|-----------------------------|---------------------------------------|
| Temperature<br>(°C) | p <sub>Fe,sat</sub><br>(atm) | Evap. Flux<br>(mol/s/m <sup>2</sup> ) | p <sub>Na,sat</sub><br>(atm) | Evap. Flux<br>(mol/s/m <sup>2</sup> ) | p <sub>K,sat</sub><br>(atm) | Evap. Flux<br>(mol/s/m <sup>2</sup> ) |
| 800                 | $5.6 	imes 10^{-13}$         | $3.2 	imes 10^{-11}$                  | $3.8 	imes 10^{-11}$         | $3.4	imes10^{-9}$                     | $3.1 	imes 10^{-11}$        | $2.1 	imes 10^{-9}$                   |
| 900                 | $2.5	imes10^{-11}$           | $1.4	imes10^{-9}$                     | $9.6	imes10^{-10}$           | $8.2	imes10^{-8}$                     | $9.1	imes10^{-10}$          | $6.0	imes10^{-8}$                     |
| 1000                | $6.0	imes10^{-10}$           | $3.1	imes10^{-8}$                     | $1.9	imes10^{-8}$            | $1.6	imes10^{-6}$                     | $1.5	imes10^{-8}$           | $9.7	imes10^{-7}$                     |
| 1050                | $2.5 	imes 10^{-9}$          | $1.3	imes10^{-7}$                     | $7.3	imes10^{-8}$            | $5.9	imes10^{-6}$                     | $5.4	imes10^{-8}$           | $3.3	imes10^{-6}$                     |
| 1100                | $9.1	imes10^{-9}$            | $4.6	imes10^{-7}$                     | $2.6	imes10^{-7}$            | $2.0	imes10^{-5}$                     | $1.7	imes10^{-7}$           | $1.0	imes10^{-5}$                     |
| 1150                | $3.0	imes10^{-8}$            | $1.5	imes10^{-6}$                     | $8.1	imes10^{-7}$            | $6.3	imes10^{-5}$                     | $5.0	imes10^{-7}$           | $3.0	imes10^{-5}$                     |
| 1200                | $9.4	imes10^{-8}$            | $4.6	imes10^{-6}$                     | $2.4 	imes 10^{-6}$          | $1.8	imes10^{-4}$                     | $1.4 	imes 10^{-6}$         | $8.0	imes10^{-5}$                     |

The evaporation flux data shown in Table 2 were combined with the surface area analysis presented in Figure 1 to calculate the predicted sublimation rate of regolith material in grams per hour per gram of regolith. Figure 5 shows the calculated surface area in orange, the predicted evaporation flux in grey, and the predicted evaporation rate in blue, for Fe, Na, and K from lunar regolith.



**Figure 5.** Predicted sublimation rate of elements Fe, Na, and K from lunar regolith, evaporation rate calculated using the HKL equation, surface area calculated from the sintering of LMS-1 simulant.

## 4. Discussion

In general, the evaporation rate of a substance is expected to increase with an increase in temperature. However, it was hypothesized that in some select cases the surface area reduction in the sublimating substance caused by solid state sintering, and thus the reduction in the area available for sublimation at high sub-liquidus temperatures, could result in a local peak in the evaporation rate lower than the melting point of the system. As such the modelling conducted in the current work included the surface area reduction in lunar regolith as a factor, as calculated by the BET analysis of sintered regolith simulant pellets.

The FactSage predictions of saturated vapor pressure are clearly not consistent with the experimental results obtained by De Maria et al. [15] from KEMS analysis of the Apollo sample #12022. This discrepancy suggests some issues with either the data being used in the package or the solution models applied to these systems. While the easiest solution in this case would be to use the measured KEMS results to calculate evaporation flux, the data available were limited to small temperature ranges. As such in the current work the predicted saturated vapor pressure of Fe, Na, and K above single, binary, and ternary oxide systems were compared to the measured results to find a best fit.

In the case of iron, De Maria et al. [15] noted that the activity in the KEMS analysis was close to unity. Indeed, this observation was corroborated in the current work which shows that the calculation of Fe-saturated vapor pressure over pure FeO is accurate for the prediction of Fe over the regolith material. Given the prevalence of nano-phase iron, and ilmenite grains in the lunar regolith [27] this is perhaps not surprising. While McGee et al. [28] reported Fe-containing pyroxene phenocrysts in the #12022 sample which would be expected to affect the activity of the Fe contained within, significant further analysis would be required to determine the effect of specific regolith compositions on the activity of Fe in lunar regolith samples.

Unfortunately, in the case of Na and K, the activity of these elements in the system was not unified, and no accurate solution could be found. The most complex and closest system composition study included in the FactSage databases is that by Kim [29] who optimized the K<sub>2</sub>O-Na<sub>2</sub>O-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. Other complex (non-single of binary system) data included in the FactSage databases are: the Na<sub>2</sub>O-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system [30], the Na<sub>2</sub>O-FetO-SiO<sub>2</sub> system [31], the Al<sub>2</sub>O<sub>3</sub>+Na<sub>2</sub>O+SiO<sub>2</sub> system [32], the K<sub>2</sub>O-MgO-SiO<sub>2</sub> system [33], and the K<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub> system [34]. While the combination of these databases is intended to provide a reasonable prediction of the behavior of complex silicate systems, in the case of the current work they are clearly insufficient. It is noted that in future, when the prediction of complex systems for resource processing operations in space becomes more commonplace, the generation of a detailed thermochemical database from the analysis of extra-terrestrial ores will be extremely valuable.

Given that accurate data for the Na and K were not available, a closest fit needed to be found for the required temperature range. The binary and ternary oxide combinations that were found to result in saturated vapor predictions closest to that of the measured Apollo sample data were the  $Al_2O_3$ -CaO-Na<sub>2</sub>O system for Na, and the  $Al_2O_3$ -K<sub>2</sub>O system for K. These were used for the calculation of evaporation flux from regolith. Since Na and K in the regolith are often associated with aluminosilicate minerals [27,35], the inclusion of Al, and in the case of Na, Ca, in the closest oxide system estimate is not surprising. However, this reasoning would suggest that the modelling would further improve in accuracy with the inclusion of Si. The fact that the further inclusion of SiO<sub>2</sub> in the system throws the predictions off is curious and suggests more complex interactions affecting the activity of these elements within lunar regolith systems.

The use of the HKL equation to calculate evaporation flux represents a best-case scenario for the current work. The equation assumes consistent Langmuir evaporation from all free surfaces and does not account for rate limitation due to diffusion of the target elements to the evaporation surface. The combination of the calculated flux with the surface area change due to sintering reveals an interesting trend. While the initial hypothesis of a local peak in evaporation rate due to the surface area reduction was concluded to be false, a distinct plateau in the evaporation rate was observable in this temperature region. This suggests there may be a feed material type and composition in which this hypothesis is correct. The current work concludes that the ideal temperature for Fe, Na, and K sublimation from a kinetic perspective is in fact the highest temperature reachable before partial melting begins (~1200 °C) and thus sublimation is, by definition, not possible. However, it is noted that in the development of future sublimation-based processes there may be the potential for energy savings where the rate of change of the evaporation flux is less or the reduction in surface area due to sintering is greater causing this local peak in evaporation rate at a temperature below the melting point.

When considering the inclusion of the change in surface area of the reacting solid, it is important to note the limitations inherent in the current work. The calculations presented here are based on a snapshot at the 2-h mark of sintering under consistent temperature. For more comprehensive modelling, the temporal factors need also be considered. For example, even at temperatures nearing or exceeding the liquidus, there will be a select period of time where the high surface area of the material is maintained while the increased evaporation flux from high temperatures is also occurring. With time, this surface area will reduce, and the rate of this surface area reduction will vary depending on the temperature. As such, the practical evaporation rate would be higher than the rate calculated in this work initially and would drop off over time as the sintering continues to reduce the surface area. Similarly, the surface area reduction due to sintering calculated in the current work is applicable to a system that is composed of unprocessed, compressed regolith that has

undergone an even heating profile. The surface area reduction seen in a process that, for example, involved only surficial heating of an uncompressed regolith bed, would differ significantly. In this sense, the current work has provided a baseline method for analyzing the maximum expected kinetics of metal sublimation rather than a definitive analysis of the expected kinetics from a specific reactor geometry or process.

### 5. Conclusions

The modelling of the rate of evolution of Fe, Na, and K from lunar regolith has been presented. The Apollo #12022 sample composition was used for the modelling in this work as it allowed for comparison to the measured KEMS data.

The surface area change of a compressed pellet of lunar regolith simulant LMS-1 due to sintering at varying temperatures was measured via BET analysis using nitrogen gas. The analysis of pressed LMS-1 pellets sintered for 2 h under low vacuum conditions ( $\sim 10^{-3}$  atm), showed a reduction in surface area from 3.29 m<sup>2</sup>/g in the unreacted sample, to 1.04 m<sup>2</sup>/g in the samples sintered at 800 °C and down to 0.09 m<sup>2</sup>/g in the sample sintered at 1150 °C.

The saturated vapor pressure of the species Fe, Na, and K above a sample with the major oxide concentration of Apollo #12022 was calculated using the FactSage thermochemical modelling software package. Comparison of the predicted saturated vapor pressures with the measured KEMS results showed that the modelling package was underestimating the pressures by over an order of magnitude. The modelling of more simple systems resulted in predicted vapor pressures more closely matching the measured values to be determined. In this case, it was determined that for the prediction of Fe vapor pressure, the use of a pure FeO system was accurate. In the case of Na and K, no system was found that accurately predicted the published results. The closest systems found, and used in the current work, were the Al<sub>2</sub>O<sub>3</sub>-CaO-Na<sub>2</sub>O system for Na, and the Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O system for K.

The predicted maximum evaporation flux was calculated using the saturated vapor pressures and the HKL equation. Langmuir evaporation was assumed for these calculations, and the coefficient of evaporation was assumed to be unity. The combination of the flux calculations with the surface area change due to sintering allowed for the maximum evaporation rate to be predicted. No local maxima below the melting point was found for the current system, as such the highest rate of sublimation was determined to be 1200 °C for all species. The predicted maximum rate of sublimation for the species Fe, Na, and K at 1200 °C was 0.08, 1.38, and 1.02 g/h/g of regolith, respectively.

It is concluded that Na and K extraction via vacuum thermal dissociation from lunar regolith is predicted to be kinetically viable at sub-liquidus temperatures. The sublimation of Fe and other less volatile elements from a similar feedstock, while thermodynamically viable, is kinetically limited. Future work that would increase the accuracy of similar kinetic modelling would be the generation of detailed databases of thermodynamic data for complex systems similar in composition to lunar regolith.

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## References

- 1. Stern, S.A. The lunar atmosphere: History, status, current problems, and context. Rev. Geophys. 1999, 37, 453–491. [CrossRef]
- Senior, C. Lunar oxygen production by pyrolysis. In Proceedings of the Space Programs and Technologies Conference, Huntsville, AL, USA, 24–27 March 1992; p. 1663.
- Nakamura, T.; Senior, C.L. Solar thermal power system for lunar ISRU processes. In Proceedings of the AIP Conference Proceedings 746, Albuquerque, NM, USA, 13–17 February 2005; pp. 1206–1215.
- 4. Sauerborn, M. Pyrolyse Von Metalloxiden Und Silikaten Unter Vakuum Mit Konzentrierter Solarstrahlung; Universitäts-und Landesbibliothek Bonn: Bonn, Germany, 2005.
- Sauerborn, M.; Neumann, A.; Seboldt, W.; Diekmann, B. Solar heated vacuum pyrolysis of lunar soil. In Proceedings of the 35th COSPAR Scientific Assembly, Paris, France, 18–25 July 2004; p. 2975.
- Cardiff, E.H.; Pomeroy, B.R.; Banks, I.S.; Benz, A. Vacuum pyrolysis and related ISRU Techniques. In Proceedings of the AIP Conference Proceedings, Albuquerque, NM, USA, 13–17 February 2005; pp. 846–853.
- Cardiff, E.; Pomeroy, B. Development of vacuum pyrolysis techniques. In Proceedings of the Space Resources Roundtable VIII: Program and Abstracts (LPI Contribution No. 1332), Golden, CO, USA, 31 October–2 November 2006; p. 14.
- 8. Matchett, J. Production of Lunar Oxygen through Vacuum Pyrolysis; George Washington University: Washington, DC, USA, 2006.
- 9. Steurer, W. Vapor phase pyrolysis. *Space Resour.* **1992**, *3*, 210.
- 10. Isachenkov, M.; Chugunov, S.; Landsman, Z.; Akhatov, I.; Metke, A.; Tikhonov, A.; Shishkovsky, I. Characterization of novel lunar highland and mare simulants for ISRU research applications. *Icarus* 2022, *376*, 114873. [CrossRef]
- 11. Shaw, M.G.; Brooks, G.A.; Rhamdhani, M.A.; Duffy, A.R.; Pownceby, M.I. Thermodynamic modelling of ultra-high vacuum thermal decomposition for lunar resource processing. *Planet. Space Sci.* **2021**, 204, 105272. [CrossRef]
- 12. Dollimore, D.; Spooner, P.; Turner, A. The bet method of analysis of gas adsorption data and its relevance to the calculation of surface areas. *Surf. Technol.* **1976**, *4*, 121–160. [CrossRef]
- 13. *ASTM C1274-12(2020);* Standard Test Method for Advanced Ceramic Specific Surface Area by Physical Adsorption. ASTM International: West Conshohocken, PA, USA, 2000. [CrossRef]
- 14. Hackley, V.A.; Stefaniak, A.B. "Real-world" precision, bias, and between-laboratory variation for surface area measurement of a titanium dioxide nanomaterial in powder form. *J. Nanoparticle Res.* **2013**, *15*, 1–8. [CrossRef]
- 15. De Maria, G.; Balducci, G.; Guido, M.; Piacente, V. Mass spectrometric investigation of the vaporization process of Apollo 12 lunar samples. *Proc. Lunar Sci. Conf.* **1971**, *2*, 1367.
- 16. Hertz, H. Ueber die verdunstung der flüssigkeiten, insbesondere des quecksilbers, im luftleeren raume. *Ann. Der Phys.* **1882**, 253, 177–193. [CrossRef]
- 17. Knudsen, M. Die gesetze der molekularströmung und der inneren reibungsströmung der gase durch röhren. *Ann. Der Phys.* **1909**, 333, 75–130. [CrossRef]
- 18. Langmuir, I. The evaporation, condensation and reflection of molecules and the mechanism of adsorption. *Phys. Rev.* **1916**, *8*, 149. [CrossRef]
- 19. Bale, C.; Bélisle, E.; Chartrand, P.; Decterov, S.; Eriksson, G.; Hack, K.; Jung, I.-H.; Kang, Y.-B.; Melançon, J.; Pelton, A. FactSage thermochemical software and databases—Recent developments. *Calphad* **2009**, *33*, 295–311. [CrossRef]
- Bale, C.W.; Bélisle, E.; Chartrand, P.; Decterov, S.; Eriksson, G.; Gheribi, A.; Hack, K.; Jung, I.-H.; Kang, Y.-B.; Melançon, J. Reprint of: FactSage thermochemical software and databases, 2010–2016. *Calphad* 2016, 55, 1–19. [CrossRef]
- 21. Bale, C.W.; Chartrand, P.; Degterov, S.; Eriksson, G.; Hack, K.; Mahfoud, R.B.; Melançon, J.; Pelton, A.; Petersen, S. FactSage thermochemical software and databases. *Calphad* 2002, *26*, 189–228. [CrossRef]
- 22. CRCT-PC. FactSage Database Documentation. Available online: http://www.crct.polymtl.ca/fact/documentation/ (accessed on 15 September 2019).
- 23. Snyder, G.A.; Neal, C.R.; Taylor, L.A.; Halliday, A.N. Anatexis of lunar cumulate mantle in time and space: Clues from traceelement, strontium, and neodymium isotopic chemistry of parental Apollo 12 basalts. *Geochim. Et Cosmochim. Acta* **1997**, *61*, 2731–2747. [CrossRef]
- 24. Bond, M.; Struchtrup, H. Mean evaporation and condensation coefficients based on energy dependent condensation probability. *Phys. Rev. E* 2004, *70*, 061605. [CrossRef]
- Sossi, P.A.; Fegley, B., Jr. Thermodynamics of element volatility and its application to planetary processes. *Rev. Mineral. Geochem.* 2018, 84, 393–459. [CrossRef]
- 26. Littlewood, R.; Rideal, E. On the evaporation coefficient. Trans. Faraday Soc. 1956, 52, 1598–1608. [CrossRef]
- 27. Papike, J.; Simon, S.B.; Laul, J. The lunar regolith: Chemistry, mineralogy, and petrology. *Rev. Geophys.* **1982**, 20, 761–826. [CrossRef]
- McGee, P.E.; Warner, J.L.; Simonds, C.H. Introduction to the Apollo Collections: Part 1. Lunar Igneous Rocks; Lyndon, B., Ed.; Johnson Space Center: Houston, TX, USA, 1977.
- 29. Kim, D.-G. Coupled Experimental Study and Thermodynamic Optimization of the K<sub>2</sub>O-Na<sub>2</sub>O-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> System. Ph.D. Thesis, McGill University, Montreal, QC, Canada, 2017.
- 30. Moosavi-Khoonsari, E.; Jung, I.-H. Critical evaluation and thermodynamic optimization of the Na<sub>2</sub>O–FeO–Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. *J. Eur. Ceram. Soc.* **2017**, *37*, 787–800. [CrossRef]

- 31. Moosavi-Khoonsari, E.; Jung, I.-H. Thermodynamic modeling of sulfide capacity in Na<sub>2</sub>O-FetO-SiO<sub>2</sub> system. In Proceedings of the 5th International Congress on the Science and Technology of Steelmaking 2012, Dresden, Germany, 1–3 October 2012.
- 32. Lambotte, G.; Chartrand, P. Thermodynamic modeling of the (Al<sub>2</sub>O<sub>3</sub>+ Na<sub>2</sub>O),(Al<sub>2</sub>O<sub>3</sub>+ Na<sub>2</sub>O+ SiO<sub>2</sub>), and (Al<sub>2</sub>O<sub>3</sub>+ Na<sub>2</sub>O+ AlF<sub>3</sub>+ NaF) systems. *J. Chem. Thermodyn.* **2013**, *57*, 306–334. [CrossRef]
- Kim, D.-G.; Konar, B.; Jung, I.-H. Coupled experimental study and thermodynamic optimization of the K<sub>2</sub>O-MgO and K<sub>2</sub>O-MgO-SiO<sub>2</sub> systems. *Metall. Mater. Trans. B* 2017, *48*, 2788–2803. [CrossRef]
- 34. Kim, D.-G.; Moosavi-Khoonsari, E.; Jung, I.-H. Thermodynamic modeling of the K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub> systems with emphasis on β-and β<sup>''</sup>-aluminas. *J. Eur. Ceram. Soc.* **2018**, *38*, 3188–3200. [CrossRef]
- 35. Papike, J.J.; Ryder, G.; Shearer, C.K. Lunar samples. Rev. Mineral. Geochem. 1998, 36, 5-1-5-234.

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