

IN SITU RESOURCE UTILIZATION OF LUNAR REGOLITH BY THERMAL REDUCTION—A NEW LOOK. J.K. Meen^{1,2}, D.C. Barker³, M.R. Martinez^{1,4}, D. Luna¹, and K. Müller¹, ¹Texas Center for Superconductivity, University of Houston, Houston Science Center, 3201 Cullen Blvd, Rm. 202, Houston, Texas 77204 USA (jmeen@uh.edu), ²Department of Chemistry, University of Houston, Lamar Fleming Jr. Building, 3507 Cullen Blvd, Houston, Texas 77204 USA, ³Department of Earth and Atmospheric Sciences, University of Houston, Science & Research Building 1, 3507 Cullen Blvd, Rm. 312, Houston, Texas 77204 USA, (donald.c.barker@att.net), ⁴Department of Mechanical Engineering, University of Houston, Cullen College of Engineering, 4722 Calhoun Rd., Houston TX 77204 USA (martinezhenriquez@hotmail.com), (dluna5@uh.edu), (kmueller@uh.edu)

Introduction: Beneficiation of metal from terrestrial rock relies on geologic concentration of that metal in an economically viable deposit [1]; target metal(s) are purified by industrial processes. Is this the same approach that should be employed on the Moon or other airless bodies that have ubiquitous comminuted materials covering their surfaces? We examine the thermodynamics of thermal reduction in an anoxic system and argue that several abundant metals (and oxygen) can be sequentially recovered from abundant unconcentrated materials by heating the materials in an environment of very low oxygen pressure.

The Source: The lunar surface is enveloped by a 5-10 m thick layer of impact-gardened regolith originally derived from anorthosites and basalts that dominate the lunar crust. In addition to extreme heating and shock which this material experienced during excavation by asteroid bombardment, it has been overturned, heated, and melted by lesser impacts and modified by solar wind and cosmic rays [2]. In the end, though, it is still dominated by O, Si, Al, Fe, Mg, and Ca, with lesser Na, Ti, Cr, K, Ni, P, S, and Mn. Extracting elements such as Fe and Ti from such a rock on the Earth would be cost prohibitive; generating K or Ca would be exorbitantly expensive. But lunar conditions are different. We consider thermodynamics of simple oxides first.

Ellingham Diagrams: Reduction of oxides at low pressure and high temperature are modeled on an Ellingham diagram [3] that plots temperature against ΔG^0 of the reduction reaction (producing one mole O_2). The slope of the line for each reaction is ΔS of $(2MO=2M+O_2)$ which is close to S of one mole of O_2 for solid metal and oxide. A change of state of metal or oxide causes a change in the reaction curve.

$2K_2O=4K+O_2$ has a marked change in slope at 759 °C as K boils. In comparison, $2FeO=2Fe+O_2$ has a uniform slope as Fe boils at 2862 °C. Above 1000 °C, K_2O is more easily reduced than FeO (Fig. 1) and K is generated as vapor.

In the regolith, K is dominantly in glasses and feldspars, not as oxide. K in $KAlSi_3O_8$ is only reduced at much lower $p(O_2)$ than for the oxide (Fig. 2).

On the moon, the entire regolith contributes all its elements to the liquid. Heating this liquid under oxygen

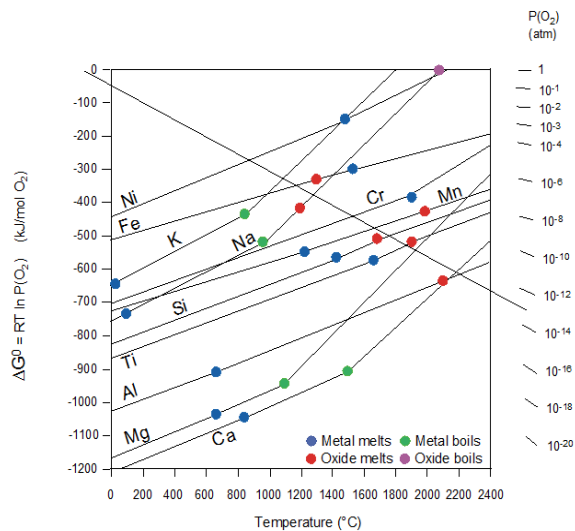


Fig. 1, Ellingham diagram for oxides of several abundant elements. Ordinate is ΔG^0 of reaction producing one mole O_2 . Each line has slope equal to ΔS of reaction. Melting metal or oxide causes a small change in ΔS ; boiling causes a major change. $P(O_2)$ is to the right of diagram; an isobar joins the labeled value and origin at 0 J/mol, 0 K. The $p(O_2)=10^{-13}$ bars isobar is shown.

deficient conditions results in each oxide being reduced in a discrete temperature range (Fig. 1), which ranges are dependent on the $p(O_2)$ maintained. At 10^{-13} bars, the order is Ni(s), K(g), Fe(s), Na(g), Cr(s), Mn(l), Si(l), Ti(l), Mg(g), Ca(g), Al(l) (Fig. 1).

Oxygen: The lunar exosphere is dominated by He, Ne, and Ar [e.g. 5]. The upper limit of the density of O species in the exosphere is $\approx 700 \text{ cm}^{-3}$ [6]. In comparison, lunar basalts have intrinsic $f(O_2)$ near 10^{-13} bars at 1000 °C [7]; the initial regolith had a similar redox state. As solar wind replaces H in the lunar regolith, the latter may have been reduced from that initial state.

A liquid on the lunar surface will attempt to come into equilibrium with its surroundings but can only achieve this temporarily. Simple calculations provide insight into what can happen. Regolith density is $\approx 1.5 \text{ g/cm}^3$. On complete melting, the porous rock is replaced by a liquid ($\rho \approx 2.8 \text{ g/cm}^3$) and a void. For the void to be filled at $p(O_2)=10^{-6}$ bars, <1 ppb of K_2O

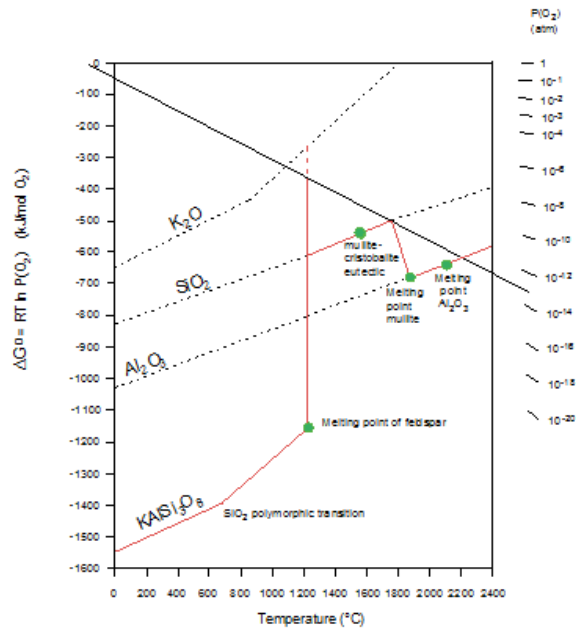


Fig. 2. Ellingham diagram for $KAlSi_3O_8$ (axes as in Fig. 1). The crystal energy of feldspar [4] means that K_2O in feldspar is reduced at much lower $p(O_2)$ than in free oxide. On melting (vertical red line), this stabilizing energy is reduced. If K is liberated, the liquid will recrystallize to mullite and cristobalite that could follow the red pathway, with silica reduced and melted at much higher temperatures to leave corundum.

(or other oxide) in the liquid is reduced to provide oxygen. Such a concentration of gas rapidly disperses. Isothermal reduction will replenish the oxygen.

Protracted heating in a static environment produces a steady state in which oxygen from the liquid replenishes O_2 dispersing into its surrounds. If reduction kinetics are sufficiently fast, the $p(O_2)$ is that defined by the appropriate reduction curve at the relevant temperature. In the (likelier) case of slower kinetics, $p(O_2)$ is less. Under equilibrium conditions, $p(O_2)$ cannot exceed the buffer value until the oxide is totally consumed by reduction.

Impact heating is both transient and highly dynamic so steady state is not achieved. Small impacts cause reduction and volatilization of K and Na. Alkaline earth oxides are reduced at very high temperatures so that, despite relatively low boiling points (1091 °C; Mg; 1484 °C; Ca), they will not volatilize unless extreme conditions are imposed. NiO and FeO are relatively easy to reduce (Fig. 1) but the metals have boiling points of 2862 °C and 2730 °C, respectively. Small meteorite impacts, therefore, cause enhanced emission of only Na and K in the exosphere.

Resource Production: Controlled heating of collected and contained regolith will initially volatilize elements like S and Cl. On melting regolith (≈ 1050 °C)

thermal reduction attempts to establish an equilibrium $p(O_2)$. At low temperatures, this will be a slow process with Ni solid and K and Na vapor produced. Mechanical (ISRU) removal of O_2 would cause continued reduction.

Production of considerably more oxygen would occur when conditions are appropriate for reduction of FeO. At low $p(O_2)$, reduced Fe will separate as solid masses. When temperatures exceed 1538 °C Fe melts, dissolves the small amount of Ni that may have been retained, and can be separated from the less dense silicate liquid. Loss of relatively non-refractory K, Fe, and Na changes the composition of the liquid; aluminous phases may precipitate. At temperatures near 1700 °C, Si liquid forms and the reduction of SiO_2 releases a large amount of O_2 . If Fe were still present, a single Fe-S liquid should form but, in resource utilization, the Fe liquid has already been removed. Ti liquid forms at a little higher temperature and there is the potential for precipitation of titanium silicide.

The remaining liquid is a Ca-Mg aluminate. Further heating of this material can generate Mg and Ca vapors and Al liquid, although the last-named has such a high vapor pressure that it readily boils off. Alternatively, the liquid aluminate can be cast into blocks for construction as the liquid will crystallize to spinel ($\rho=3.6$ g/cm³; hardness=7.5; see [8]) and calcium aluminate (ceramic cement; [9]).

Summary: High-temperature experimentation is required to determine the T- $p(O_2)$ values for thermal reduction curves for oxides in a multi-element silicate liquid. Thermodynamics of the process show that stepwise heating of a mafic liquid under highly reducing conditions results in sequential release of metals and their bonded oxygen. As each reduction reaction buffers $p(O_2)$ of the transient atmosphere, each oxide must be consumed before progressing to the next reduction reaction (unless the curves cross in Fig. 1). Thermal reduction of the mafic liquid allows almost total separation of each element in the source.

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