

THERMAL REDUCTION OF SURFACE ROCKS ON AIRLESS PLANETS. J.K. Meen^{1,2}, D.C. Barker³, M.R. Martinez^{1,4}, C. Obasi^{1,4}, and K. Müller¹. Texas 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, (douald.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), (chinasa.obasi@gmail.com), (kmueller@uh.edu)

Introduction: We previously [1] approached beneficiation of metal from rocks on airless planets from the point of view of thermal reduction. The reduction of oxide species in minerals depends on not only the intrinsic redox potential of the oxide species and on the kinetics of the reduction potential but also on the thermodynamic stabilization yielded by the chemical environment of the oxide species. While the thermodynamics of the individual oxide species and of relatively simple environments (e.g. pure minerals) can be calculated, the effects of kinetics and of complex chemical environments require experimental determination.

Herein we contrast the calculated behaviors and the experimentally determined behaviors of simple chemical systems in an attempt to predict the conditions under which thermal reduction of different oxides occur in an airless (e.g. lunar surface) environment.

Reduction of Simple Oxides: Meen *et al.* [1] used Ellingham diagrams to predict the order of reduction of the common rock-forming oxide species at low pressure in markedly reducing environments. The order, which contrasts in some respects with that expected from melting environments under pressure, is (at 10^{-13} bars O_2) NiO, K_2O , FeO, Na_2O , Cr_2O_3 , MnO, SiO_2 , TiO_2 , MgO, CaO, Al_2O_3 .

Role of Kinetics: The importance of kinetics in retarding redox reactions at low temperature is clear. The equilibrium $P(O_2)$ for the hematite-magnetite buffer (Fe_2O_3 - Fe_3O_4) at 300 °C is near 10^{-30} bars so one could argue that the equilibrium iron oxide on the surface of the Moon is hematite. The existence and distribution of lunar surface hematite has been demonstrated by remote sensing but the exact reasons for its formation remains unknown [2]. Heating minerals on the lunar surface must destabilize some oxide components relative to metal + oxygen but the process of losing oxygen from a crystalline material is slow, especially at low temperatures. As we shall show, even loss from a melt can be a protracted process.

Mineral Stabilization: The classic Ellingham diagrams [3] used by Meen *et al.* [1] are based on reduction of metal oxides. But very few simple metal oxides exist in nature: most elements are incorporated in complex silicates or multi-element oxides. In most (but not all) cases, this stabilizes the oxide with respect to re-

duction. The degree of stabilization differs markedly from mineral to mineral and from oxide to oxide. The alkali metal oxides are greatly protected from reduction if incorporated into a feldspar structure. Figure 1 shows the reduction curves for Na_2O in both the simple oxide and in $NaAlSi_3O_8$ and for K_2O also in the oxide and $KAlSi_3O_8$.

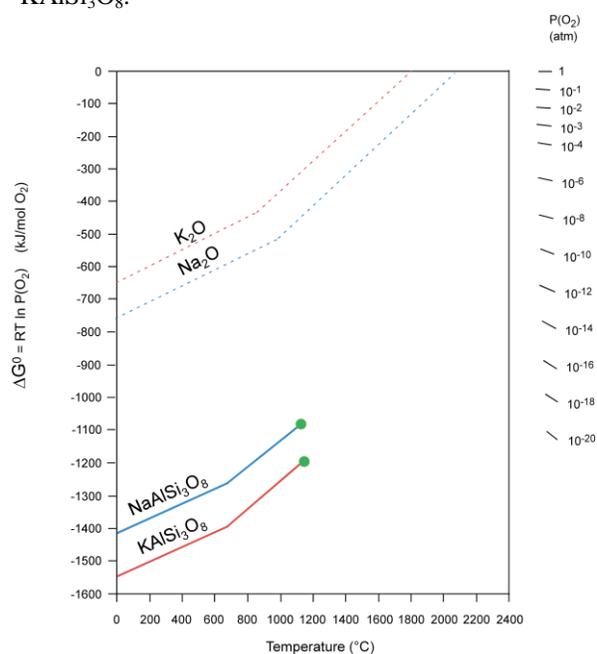


Figure 1. Ellingham diagram in which ordinate is ΔG^0 of reaction producing one mole O_2 . Each line has slope equal to ΔS of reaction. $P(O_2)$ is to the right of diagram; an isobar joins each label and origin at 0 J/mol, 0 K. Reactions are $2M_2O=4M+O_2$; $4MAISi_3O_8=4M+(2/3)Al_6Si_2O_{13}+(32/3)SiO_2+O_2$ where M is Na or K. The kinks in the oxide curves reflect boiling of the metal. Green dots are melting points of the feldspars. Data from [4]

The alkali metal oxides are each stabilized with respect to reduction by the feldspar structure. The data for albite and orthoclase glasses are slightly less exothermic, which suggests that the incorporation of the alkali metal ion in the holes in the tectosilicate framework is largely responsible for this stabilization. Heating of the feldspar liquid presumably results in depolymerization and the alkali metal oxide reduction curves approach

those of the binary oxides at sufficiently high temperatures.

FeO is barely stabilized with respect to iron and oxygen by incorporation in mineral species. Iron oxide in ilmenite requires about 30 kJ/mole O₂ more for reduction than it does in wüstite. Reduction of FeO in olivine has essentially the same energy requirement as does wüstite.

Prediction of the relative reduction of oxides in silicate liquids is tenuous as little thermodynamic data exist, and therefore experiments are required to determine the temperatures at which each oxide is reduced.

Haplogranodiorite Melting: A haplogranodiorite was chosen for initial melting experiments, not because of its lithologic applicability to the Moon, but because it contains, in addition to large amounts of albite and orthoclase, significant anorthite, and CaO is amongst the most resistant oxides to reduction. The minimum liquid was synthesized from CaCO₃, Na₂CO₃, K₂CO₃, Al₂O₃, and SiO₂ as a mixture of glass and fine crystals at 1100 °C that was ground and sintered three times. Some of this was mounted on Pt loops and equilibrated for 96 hours with P(O₂) = 10⁻⁶ bars (Ar-O₂ mixture) at 1100 °C, 1200 °C, or 1400 °C before quenching into mineral oil and measured by microprobe. These run products contain glasses that are near the minimum melting composition of haplogranodiorite and have essentially the same composition at each temperature. The experiments were then repeated with P(O₂) held at 10⁻³⁰ bars. The charge at 1100 °C was very similar at this oxygen pressure but the higher temperature charges contained crystals of silica (presumably tridymite) and its composition was peraluminous and had lower alkali metal contents. The margins and centers of the charges were compositionally the same for each charge. A further large volume sample was fired in an alumina crucible at 1400 °C, and 10⁻³⁰ bars O₂ for 168 hours and then mounted and sectioned for study. The charge included crystals of silica and a glass that was analyzed from the alumina crucible wall to the interface with the atmosphere, and was found to be without systematic compositional variations. The glass was reduced in Na and K by about 16% of the starting content and about 15% of the glass recrystallized as silica. The area of charge studied was ≈1800 μm (horizontal) by ≈700 μm (vertical). Within this were located three oval regions, each about 4 μm across, and highly depleted in Na and K. They were aligned near vertically. One was about 70 μm below the top of the glass, the next 12 μm below it, and the third another 27 μm down. No more were located in this section. The centers of these fluctuations contained <0.3% Na₂O and 0.3-0.7% K₂O and gradients at the edges suggest that

the alkali metals are diffusing back into these fluctuations.

The mechanism of degassing is not known but these alkali-reduced glasses may be remnants from outgassing at the top of the liquid and reincorporated into the liquid. Plausibly they form by heterogeneous nucleation, perhaps on tridymite surfaces with the alkali metals being volatilized to the atmosphere. Given that the fluctuations comprise 0.006% of the charge, even complete loss of alkalis from each, followed by reincorporation into the liquid is a relatively slow process.

Potential loss of alkali metals from lunar rocks has been reported by [5] Gibson and Hubbard (1972), who heated lunar materials at 10⁻⁹ bars total pressure, showing that Rb was lost at ≤950 °C (subsolidus), K at 950 °C, and Na at ≥1050 °C. They modeled the loss on relative volatility of the oxides. Loss of alkali metals from doped haplobasalt at 1400 °C were measured for various times in static air, in flowing Ar₉₀:H₂10, and in continuous pumped vacuum <10⁻⁶ bars. In each case, the loss of alkali metals was Cs>Rb>K>Na [6].

Experimental Thermal Reduction of Minerals and Melts: Thermodynamic calculations show that the alkali metals leave as atomic gases not as oxide gases. The experiments just described could be consistent with loss of oxide gases or of gases composed of metals and oxygen gas. Experiments on alkali metal containing minerals and metals are in work. Atmospheres are controlled using a precursor furnace containing a metal-oxide buffer (e.g. Si-SiO₂) at controlled temperature in order to maintain P(O₂) of the gas flowing over the sample held in a crucible in a DTA/TGA set-up, thus experiencing a controlled heating trajectory. The evolved gas is analyzed by gas chromatography-mass spectrometry (GC-MS) and using an oxygen sensor. The GC-MS scans over all masses of interest so that any material volatilized from the source material is documented.

These experiments are conducted at controlled P(O₂) but at total pressure of 1 bar. Results of another series of experiments conducted under vacuum but with a reduced gas introduced and drawn off multiple times before heating will also be conducted. The oxygen pressure of the evolved gas in these cases cannot be measured but the GC-MS indicates the gaseous species generated during heating.

References: [1] Meen *et al.* (2019) 50th Lunar and Planet. Sci. Conf. (No. 2132) 1652; [2] Li *et al.* (2020), *Sci. Adv.*, 6; [3] Ellingham, (1944) *Trans. & Comms, J. Soc. Chem. Ind.*, 63; [4] Robie *et al.* (1979) *USGS Bull*, 1452, Washington DC, 456; [5] Gibson and Hubbard (1972) *Geochim. Cosmo. Acta*, 2; [6] Kreuzberger *et al.* (1986) *Geochim. Cosmo. Acta*, 50.