SOLAR WIND OXYGEN, DIFFUSION, AND OXIDATION IN THE LUNAR REGOLITH. T. R. Ireland, M. Honda, and H. St. C. O'Neill, Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia.

Introduction: The natural Genesis experiment involves searching for oxygen implanted by the solar wind in low oxygen lunar substrates such as metal and sulfide grains [1,2]. However, this has revealed a similar diversity of components in the lunar soil to those present in meteorites. Of prime importance is the issue concerning which of these components could be representing the solar wind, but it is doubtful that this will be resolved until the analysis of Genesis collectors. The question will then arise as to what the other components in the lunar soil represent.

Oxygen Isotopic Components: Metal grains from the lunar regolith show an extensive range in compositions. Hasizume and Chaussidon [1] found that most grains in a lunar regolith breccia (79035) have Δ^{17}O values close to the intrinsic lunar values. Some of these are substantially mass fractionated generally with heavy isotope enrichment. Several grains show increasing enrichments in ^{16}O (towards low Δ^{17}O) with depth with the maximum deviation being approximately -20 ‰. However, this component neither lies on the ^{16}O mixing line, nor attains an equilibrium composition. Ireland et al. [2] have found a component in recently exposed lunar soil 10084 that is enriched in ^{17}O and ^{18}O with the majority of analyses lying close to the 1:1 ^{16}O fractionation line. This component reflects a constant composition with depth (in terms of Δ^{17}O). Hashizume and Chaussidon [1] suggest that the ^{16}O-rich component is solar, whereas Ireland et al. [2] make the case that the ^{17}O,^{18}O-rich component is solar; most analyses of lunar materials are close to terrestrial and this remains a viable possibility too.

Rims: The metal grains typically have oxygen-rich rims although the thicknesses of these rims are distinctly different. In the 10084 lunar soil metal grains, the surface oxygen concentration can be as low as ~4 wt% and only tens of nanometers thick, whereas in the 79035 regolith breccia grains, the concentration can be as high as 30 wt% and with thicknesses of several micrometers. Mineralogically there is only a small range in oxygen concentration between wüstite (~23 wt% O), magnetite (~28 wt% O) and hematite (~30 wt% O). Thus it appears that the rims with the highest oxygen concentrations could be hematite, while the rims with the lowest concentrations must either be mixtures of wüstite and Fe, or have oxygen distributed through the metal at the atomic level. The latter would be the case only for recent solar wind implanted oxygen. At equilibrium, the concentration of oxygen in Fe metal would be very low [3] and oxygen would likely react with Fe to form an oxide phase. Even at low oxygen partial pressures, oxides (including wüstite, magnetite, and hematite) quickly form on Fe metal substrates [4].

In an experiment that is closely analogous to solar implantation of oxygen, Anandan and Rajan [5] used plasma immersion ion implantation with 20 keV oxygen ions to examine the effects on stainless steel. Implantation was carried out at 400 °C for 30 minutes followed by rapid cooling to room temperature. They found that iron on the surface was present as Fe^{2+} and Fe^{3+} with 2-3 μm oxide islands of several tens of nanometers height on an underlying oxide layer. Enhanced oxide growth along grain boundaries is attributed to diffusion. These data also support rapid diffusion of O in Fe.

Once oxides are produced, they appear to be stable even in reducing atmospheres such as hydrogen and carbon monoxide [6]. In these experiments [6], direct reaction of oxides with H to form metal appears to be an unfavourable reaction path. Disproportionation of wüstite to form magnetite plus iron metal is more likely to occur particularly at low temperature [6].

Implantation and Sputtering: At median solar wind velocities (ca. 400 km/s) particles have energies of around 1 keV/nucleon. This results in oxygen being implanted to a depth of around 50 nm into an iron metal target. However, the target is also being implanted with, and sputtered by hydrogen and other heavy ions, and surface topography (cracks, pits etc) will also affect the distribution of solar wind implanted material into the surface. As such, after long duration exposure on the lunar surface, a mineral surface will not retain a theoretical solar implantation curve, but should be expected to show variability due to a number of effects, but particularly diffusion (as in the experiment of Anandan and Rajan [5]).

Diffusion: Thermodynamic equilibrium partitioning indicates that oxygen concentrations in natural Fe metals coexisting with silicates are very low [3]. Hence, following solar wind exposure, implanted oxygen is in a substrate in which it would not normally be contained. As indicated above, oxygen generally reacts quickly with Fe metal to form oxides and will migrate by diffusion. However, at low oxygen levels, it is not clear whether oxide formation would occur, or whether thermal diffusion would enhance oxide grain production or allow diffusion of oxygen to the surface. The 10084 data suggest that diffusion might have occurred because the high concentration of oxygen at the surface still has an anomalous composition (high $\Delta^{17}O$).

The thermal diffusion rate for oxygen in iron metal is difficult to determine experimentally. In part this is due to the low concentration of oxygen in iron, but is also a result of the propensity for metals to form impermeable armouring oxide layers that restrict further oxidation. Takada et al. [7,8] use the rate of internal oxidation since they argue that the oxidation front is determined by the diffusion of oxygen through the metal. Using these data, Ireland et al. [2] calculated that under solar radiation and lunar surface temperature of approximately 100 °C, the oxygen diffusion rate would suggest migration of oxygen over micrometer distances in a period of weeks to months.

However, it is unlikely that thermal diffusion alone is operating. Interestingly, it has been shown that under proton bombardment the diffusion rate can rise by three orders of magnitude [9]. Effectively this allows access to the samples by residual oxygen in the irradiation chamber. It should be noted that these experiments are carried out at MeV energies rather than keV energies appropriate for solar wind. Nevertheless, it appears that particle disruption will affect diffusion rates making them faster than the rate effected by thermal diffusion alone.

Solar Wind Exposure: Lunar soil 10084 is highly enriched in solar wind isotopes (He, Ne, Ar etc), has a high proportion of grains with particle tracks. We have examined individual olivine grains as small as 3 µg and found the He and Ne isotopic signature of solar wind. In other noble gas studies of lunar soils, mineral separations with oxides have lower noble gas concentrations, and metals are lower still [10]. The determination of abundant solar wind He and Ne in the smallest of grains suggests that these effects are likely due to diffusive loss of noble gas rather than lack of exposure.

Solar Wind Oxygen: Ireland et al. [2] made the case for solar oxygen being enriched on the basis of the depth distribution of the anomalous component. It was envisaged that some grains would have oxidized rims and that these grains would not be suitable samples to look for solar wind. Nevertheless, it does not appear that solar wind oxygen is present in all grains even with minimal rims and low overall oxygen concentration. In this case, diffusion of oxygen out of the grains may have occurred, or these grains were situated at depth in the soil and never saw surface exposure. Given the near ubiquity of solar wind exposure effects in silicates, this would require special circumstances such as density settling preventing the metal grains from always getting to the top layer. A key issue then is to find a clear signal of solar wind exposure in the individual metal grains that record different oxygen isotopic compositions.

References: [1] Hashizume K. and Chaussidon M. (2005) *Nature* **434**, 619-622. [2] Ireland T. R. et al. (2006) *Nature* **440**, 776-779. [3] Wriedt H. A. (1993) in Monograph Series on Alloy Phase Diagrams Vol. 9, 280-306. [4] Goursat A. G. and Smeltzer W. M. (1973) *Oxidation of Metals* **6**, 101-116. [5] Anandan C. and Rajan K. S. (2007) *Applied Surface Science* **253**, 6854-6859. [6] Jozwiak W. K. et al. (2007) *Applied Catalysis A: General* **326**, 17-27. [7] Takada J. et al. (1986) *Oxidation of Metals* **25**, 93-105. [8] Takada J. et al. (1986) *Z. Metallk.* **77**, 6-11. [9] Roller T. and Bolse W. (2007) *Phys. Rev. B* **75**, 054107. [10] Becker R. H. and Pepin R. O. (1994) *Meteoritics* **29**, 724-738.