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RELEASE OF NOBLE GASES AND NITROGEN FROM GRAIN-SURFACE SITES IN LUNAR ILMENITE BY CLOSED-SYSTEM OXIDATION. Urs Frick, Richard H. Becker and R. O. Pepin, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455.

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Noble gases and nitrogen were extracted from a 100-150 $\mu$  ilmenite separate from lunar soil 71501 by closed-system stepped heating in  $\sim 10$  torr  $O_2$  at 300 $^\circ$ , 400 $^\circ$ , 500 $^\circ$ , 600 $^\circ$  and 630 $^\circ$ C, followed by stepped pyrolysis at ten temperatures between 680 $^\circ$  and  $\sim 1500^\circ$ C. The five oxidation steps together liberated  $\sim 65\%$  of the total  $^4He$ , 45% of the  $^{20}Ne$ , 23% of the  $^{14}N$  and  $^{36}Ar$ , 12% of the  $^{84}Kr$  and 8% of the  $^{132}Xe$  in the sample;  $^{20}Ne/^{36}Ar$  and  $^{20}Ne/^{22}Ne$  ratios agree with the Solar Wind Composition experiment(1), and  $^{84}Kr/^{36}Ar$  and  $^{132}Xe/^{36}Ar$  are within  $\sim 10\%$  of Cameron's(2) estimates for the sun and solar wind. The remaining gases, released above 630 $^\circ$ C by pyrolysis, are strongly fractionated with respect to the SWC-Cameron solar wind elemental composition. This imprints a fractionation pattern on the total gas composition in the sample which agrees with that measured in other lunar ilmenites.

These data point to the presence of an ilmenite grain-surface reservoir containing nearly unfractionated solar wind noble gases (with, however, some diffusive depletion of the lightest species:  $^4He/^{20}Ne$  in the summed 300-630 $^\circ$ C fractions is  $\sim 60\%$  of the SWC ratio, and  $^4He/^{3}He$  is somewhat higher than the SWC value). The gas release mechanism up to 630 $^\circ$ C presumably involves structural transformations induced by oxidation of  $FeTiO_3$  to  $Fe_2O_3 + TiO_2$ (3). We have no independent information on how deeply this oxidative alteration may have penetrated into grain surfaces. However, the more or less solar ratio of Xe to lighter gases suggests oxidation to at least the base of the implantation zone for solar wind Xe ions ( $\sim 500\text{\AA}$ ?).

The  $^{14}N/^{36}Ar$  ratio in gases released from the surface reservoir is more than an order of magnitude higher than Cameron's solar estimate. Neither N contamination nor an indigenous (non-solar-wind) N component can easily account for this excess. It could, however, be consistent with the presence of fractionated noble gases sited in grain interiors (below the surface reservoir). According to dynamic models developed by Maurette and co-workers at Orsay(4-6), lunar grains in this size range experience multiple exposures to the solar wind during an episode of residence near the top of the regolith. Each exposure populates the grain-surface reservoir with solar wind ions. But for most (>99%) of its residence lifetime in a surface stratum, between direct exposures to the wind at the surface, the average grain is shallowly buried in the thermally active upper regolith. During this time diffusive migration of noble gases both inward and outward from their implantation sites could generate the fractionated gases in grain interiors and depopulate the surface reservoir prior to the next exposure to the solar wind. The N excess in the surface reservoir is presumably then due to a much smaller diffusion coefficient (because of chemical bonding to the medium), leading to incomplete N depletion of the reservoir and superposition of multiple doses of solar wind N in grain surfaces.

Large concentrations of fractionated noble gases in grain interiors, their virtual absence in the relatively unfractionated surface gas reservoir, and the high N/noble gas ratio all imply that most of the solar wind noble gases initially implanted in grain surfaces are eventually lost by diffusion. Loss limits can be estimated by considering the following two scenarios. (in which we assume that Cameron's solar Xe/Ar and N/Xe estimates are approximately right for the solar wind):

(1) About 3/4 of the total N in 71501 ilmenite is released in the  $>630^\circ$ C pyrolysis steps, and thus appears to be sited in grain interiors ( $d \geq 500\text{\AA}$ ). If this N ( $\delta^{15}N = -10 \pm 10\%$ ,  $N = 4.3\text{ppm}$ ) is indigenous, then only the N in the surface reservoir is from solar wind. The ratio of this surface-sited

N to total Xe in the sample is within  $\sim 15\%$  of Cameron's solar N/Xe ratio. If this is not coincidental, it implies that neither N nor Xe has been lost to any significant extent (unless both species are implanted to the same depth and diffuse in the same way). Loss of a lighter noble gas such as Ar is then fixed by the depletion of the measured Ar/Xe ratio below solar. In the ilmenite, Ar/Xe is 29% of solar; therefore 71% of the Ar has been lost. This is a minimum loss factor for Ar in any scenario, since it depends only on total Xe and the solar Ar/Xe ratio.

The obvious difficulty with this model is its failure to account for the fact that only a small fraction of the total Xe (with  $\sim$  solar Xe/Ar ratio) is removed by the surface oxidation. If Xe has not been lost by outward diffusion, it should also not have diffused inward, and most of it would still be in grain-surface sites and susceptible to release by oxidation (with Xe/Ar  $> 4 \times$  solar). If oxidation did not penetrate to the base of the solar wind implantation zone, then of course much of the Xe in the zone would have been retained. But then one requires a double assumption: that Cameron's Xe/Ar estimate is too low, at least for the solar wind, by a factor of 4 or more; and that the Xe/Ar ratio in the gas that was released coincidentally mimics this incorrect value.

(2) If all the N in the ilmenite is of solar wind origin, the fact that  $3/4$  of it lies below the  $\geq 500\text{\AA}$  deep surface reservoir implies that it has been re-distributed by diffusion. Fick's Law calculations indicate that  $\sim 80\%$  of the initial inventory of N implanted in grain surfaces would have been lost during such a diffusive redistribution. N/Xe in the fractionated (grain interior) gases is  $3.9 \times$  solar. Therefore Xe must have been depleted by a factor  $\sim 3.9 \times 5 \approx 20$ . A similar result is obtained by applying Fick's Law directly to Xe diffusion. Since Xe/Ar in the surface reservoir is approximately solar, very little of the fractionated component can reside there as a "contaminant": only  $\sim 2\%$  of its Xe would have a  $\sim 30\%$  effect on the surface reservoir Xe/Ar ratio. Most of the fractionated Xe must thus lie below the depth of oxidation. The constraint that  $\geq 98\%$  of the Xe in the fractionated component must reside below the  $\geq 500\text{\AA}$  oxidation depth requires very extensive diffusive redistribution from its original implantation sites into this configuration. In the process,  $\geq 90\%$  of the initial Xe inventory, and  $\geq 97\%$  of the Ar, are lost.

We conclude therefore, that  $\sim 70 - 97\%$  or more of the Ar implanted in 71501 ilmenite grains by the solar wind has diffusively escaped, and that losses on the high end of this range are most probable.

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