

MASS FRACTIONATION BY SOLAR WIND SPUTTERING

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There is no generally accepted explanation for measured enrichments in the heavier isotopes of oxygen and silicon and in Si/O on the surfaces of lunar soils [1]. However, several authors have recognized that solar wind sputtering could give rise to effects qualitatively similar to those observed [1-4]. We present estimates of the mass fractionation produced by solar wind sputtering. Our calculations show that, if lunar grain surfaces are in equilibrium with respect to sputtering erosion and redeposition, a level of isotopic fractionation close to that observed experimentally is produced on grains on a $\sim 10^3$ yr time scale. However, we are not presenting a complete model for the evolution and composition of the surface layers of lunar materials. Our objectives are more limited, viz to define, as quantitatively as possible, the role of a single mechanism, solar wind sputtering.

At the same energy, the heavier of two particles has the lower velocity, thus there is a winnowing mechanism operating on sputtered material by the lunar gravity field. The fraction of sputtered material which returns will be enriched in the heavier atoms. These returned atoms are, of course, subject to resputtering. Recent laboratory sputtering studies suggest that atomic mixing of the surface region by the incoming ions [5] will blend some of this enriched matter into the undifferentiated substrate. Consequently, after a sufficiently long time has elapsed, a thin enriched layer of thickness $\Delta x \sim 100 \text{ \AA}$ will exist in an equilibrium condition determined by the balance between atoms lost, atoms redeposited, and atoms gained from the admixed subsurface material. Let S = sputtering rate constant, i.e., the probability that an atom within Δx will be sputtered from the surface in one year. The sputtering erosion rate in angstroms per year = $S\Delta x$. Although S may in reality depend (initially) upon the time, we take its value to be constant. Any time variation of S would lead to changes in the estimates of equilibration times, but would not affect general considerations of the equilibrium state with which we are mainly concerned. The probability that an atom of species i is sputtered from Δx in one year is then in lowest approximation $N_i S$. We adopt an energy spectrum of sputtered particles, consistent with available experimental data, which has the form $E^{-2}(1+U/E)^{-3}$ where U is a surface binding energy for the material under bombardment, estimated as ~ 1 eV. We assume all sputtered atoms, regardless of mass, have the same energy distribution. The fraction of material which does not escape is then $f_i = (1+U/M_i g R)^{-2}$ where M_i is the atomic mass and R and g are the lunar radius and gravitational acceleration. The equilibrium fractional enrichment between two species, i and j , is:

$$\epsilon(i/j) \equiv \frac{N_i/N_j}{(n_i/n_j)} - 1 = \frac{f_i - f_j}{1 - f_i}$$

where N refers to the sputtered layer and n to the bulk material. The equilibrium concentrations do not depend either upon the absolute rate at which particles are sputtered away, upon the thickness Δx of the mixed surface layer or upon the detailed composition of the sputtered surface. The equilibration time, t , given by $1/t = S[1/3(1-f_{16}) + 2/3(1-f_{28})]$, does however depend on the sputter erosion rate, thickness of the mixed layer and composition. For sim-

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plicity the above equation is given for SiO_2 . Taking $\Delta x \sim 100 \text{ \AA}$ and the range of erosion rates by solar wind sputtering from 0.5 \AA/yr [6] to 0.03 \AA/yr [7] gives $t=240-4000$ yrs.

Our equations predict the following surface isotopic enrichments, $\delta(^{18}\text{O}) = 26.0 \text{ ‰}$, $\delta(^{30}\text{Si}) = 20.2 \text{ ‰}$, and $\delta(^{34}\text{S}) = 19.1 \text{ ‰}$. The approximate constancy of the surface δ -values is a consequence of assuming $U = 1 \text{ eV}$. Epstein and Taylor [1] found strong enhancements of the heavier isotopes in O and Si removed with very brief exposure to F_2 gas; however the isotope ratios approached the bulk values once $\sim 1\%$ of the mass had been removed ($\approx 170 \text{ \AA}$). $\delta(^{18}\text{O})$ and $\delta(^{30}\text{Si})$ appear to vary quickly within the 170 \AA layer. Our model is unrealistic in that it does not consider the depth dependence of the isotopic distribution. However, the first cuts of the fluorination experiments correspond to an effective sampling depth of $\sim 40 \text{ \AA}$, for which it does appear reasonable to assume a well-mixed zone of material in sputtering equilibrium, as described by our equations. Thus we compare the model predictions to the maximum measured enrichments, i.e. those which apply to the thinnest surface layers. Experimentally, $\delta(^{18}\text{O})$ was found to range up to $\approx 50 \text{ ‰}$ and $\delta(^{30}\text{Si})$ up to $\approx 25 \text{ ‰}$ in the initial fractions. The results of our calculations are therefore in reasonable accord with the data, although the measured isotopic enrichment for O is more pronounced by a factor of 2 than for the Si isotopes in contrast to our calculations. The comparison with experimental data is imperfect for many reasons. First it is important to consider whether it is reasonable that the surfaces of soil grains will be in sputtering equilibrium. The question is then whether there are competing processes which bury or destroy sputtered surfaces in times less than $\sim 10^3$ yrs. Two plausible processes are a) impact mixing or volatilization and b) deposition of fresh surface layers of lunar materials vaporized by impacts at more distant points. We have not included these effects in our equations, principally because the appropriate rates and rate constants are not well-known, but the rates of these competing processes may not be negligible. Gault et al., [8] estimate impact vaporization rates that would correspond to deposition of impact volatilized material at a rate of 0.1 \AA/yr , within the range of sputtering erosion rates considered above. Consideration of more complex models shows, in accord with intuition, that the effect of burial and destructive processes is to lengthen the equilibration time scale. For example, rapid impact mixing on a submillimeter scale just rotates soil grains in the solar wind flux. This obviously increases the time to achieve equilibrium but also produces more uniformly sputtered surfaces, which makes a more realistic comparison between our calculations and measurements on bulk soils. The $\sim 10^3$ yr. equilibration time can be cumulatively accumulated; it need not be in a single exposure. It is reasonable to regard lunar soil grains with amorphous coatings as being in sputtering equilibrium. The estimated time scale for the formation of the amorphous layer (~ 2000 yr., [9]) supports this assumption. The fraction of grains having amorphous coatings [9] indicates that, except for a few immature soils, greater than 50% of the micron-sized grains have amorphous coatings. Since most of the surface area in a lunar soil sample resides in the smaller grains, there is some justification for the assumption that the surfaces in a mature soil are in sputtering equilibrium. The interpretation of the fluorination experiments is also complex because they are performed on a distribution of grain

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sizes, shapes and compositions. Thus uncertainties exist in the conversion of the fraction of oxygen removed to an equivalent depth of surface layer. Furthermore, grains without amorphous layers (10-50% in mature soils [9]) may have normal surface compositions.

Epstein and Taylor note that O/Si is depleted by ~40% in the first cuts of the fluorine stripping. Qualitatively similar effects in the outermost atomic layers have been observed by Housley et al., [10] using ESCA techniques. The fact that larger variations were not observed in the ESCA measurements is an argument for a well mixed layer in at least the outer 40 Å. We calculate the amount of oxygen depletion caused by sputtering to be 12.5%. As with $\delta(^{18}\text{O})$ the calculated fractionation is less than that measured. Rees and Thode [11] have used S isotopic analyses of grain-size fractions to estimate a surface $\delta(^{34}\text{S})$ enrichment of about 20 ‰, in excellent agreement with our calculations. Relatively large $^{39}\text{K}/^{41}\text{K}$ depletions have been reported for bulk soil samples (5-10 ‰) but these do not appear to be surface correlated [12]. A speculative possibility is that the large bulk isotopic enrichments for K (and S), compared to the absence of equivalent effects for Si and O, may indicate that a large fraction of the K and S in lunar soils have been on surfaces. For example most K and S may have originally been emplaced as vapor deposits on surfaces and later incorporated into larger grains by impact melting or agglutinate formation. For C we would predict only about 10 ‰ surface enrichment in ^{13}C . This is reasonably close to a bulk soil value, but surface carbon isotopic enrichments may be much larger (~ 50 ‰) [13]. Accepting the results of [13] at face value, they would indicate that (a) our adopted sputtering energy spectrum is incorrect, (b) diffusion loss and reimplantation accompanied by large mass fractionation is the dominant effect controlling the surface C isotopic composition, or (c) the solar wind $\delta(^{13}\text{C})$ is about 40 ‰. Large $\delta(^{15}\text{N})$ values (up to 100 ‰) for lunar soils [14] do not appear to be related to lunar surface residence time and thus probably cannot be explained by sputtering. We expect $^{44}\text{Ca}/^{40}\text{Ca}$ variations corresponding to about $\delta(^{44}\text{Ca}) \sim 20$ ‰. Experiments (Russell et al., this volume) suggest that no variations greater than 2 ‰ are present. This is difficult to understand in view of the O, Si, S data, regardless of the fractionation mechanism.

In summary, it seems likely that sputtering/gravitational mass fractionation is one of the important processes determining the chemical and isotopic composition of lunar surface layers, but this mechanism cannot account for all isotopic data. We are still far from a comprehensive picture of the sources and mechanisms for the concentrations and isotopic compositions of light elements in lunar soils. A manuscript on this work has been submitted to J. Geophys. Res. Work supported in part by NSF Grant PHY76-02724.

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