

Mass Fractionation of the Lunar Surface by Solar Wind Sputtering

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The sputtering of the lunar surface by the solar wind is examined as a possible mechanism of mass fractionation. Simple arguments based on current theories of sputtering and the ballistics of the sputtered atoms suggest that most ejected atoms will have sufficiently high energy to escape lunar gravity. However, the fraction of atoms which falls back to the surface is enriched in the heavier atomic components in relation to the lighter ones. This material is incorporated into the heavily radiation-damaged outer surfaces of grains, where it is subject to resputtering. Calculations predict that an equilibrium surface layer, enriched in heavier atoms, will form with $\delta(^{18}\text{O}) \approx +20\text{‰} \approx \delta(^{30}\text{Si})$ and that oxygen will be depleted on the surface layers of grains relative to the bulk composition by about 12.5%. These results are in fair agreement with experiment. The dependence of the calculated results upon the energy spectrum of sputtered particles is investigated. We conclude that mass fractionation by solar wind sputtering is likely to be an important phenomenon on the lunar surface but that the complex isotopic variations observed in lunar soils cannot be completely explained by this mechanism.

INTRODUCTION

The bombardment of the moon by the solar wind has long been recognized as an important erosive mechanism of the surface layers of lunar material. *Wehner et al.* [1963a] irradiated metal, metal oxide, and mineral targets with low-energy hydrogen and helium ions and concluded that sputtering would eject matter from the moon into space with a distribution of velocities sufficiently high that most of this material would escape lunar gravity. Additional investigations [*Wehner et al.*, 1963b] of the behavior of metal oxides under simulated solar wind irradiation conditions suggested that sputtering would lead to mass fractionation of the lunar surface, with heavier mass elements being preferentially enriched in relation to lighter elements. This conclusion was based upon the experimental observation that for the case of certain metal oxides the surface of the target became enriched in the heavier metal following prolonged irradiation.

There is considerable experimental evidence demonstrating that the surfaces of lunar soil grains are enriched in the heavier isotopes of oxygen and silicon as well as indications that the surface Si/O ratio is enhanced in relation to the bulk composition [*Epstein and Taylor*, 1971, 1972; *Taylor and Epstein*, 1973]. A detailed explanation of these surface-correlated effects has not been forthcoming. Nevertheless, it seems clear that since the bulk isotopic abundances in lunar samples are rather constant and similar to terrestrial minerals, surface effects have arisen from dynamic processing by agents unique to the moon's environment. In this context, several authors have recognized that solar wind sputtering could give rise to effects qualitatively similar to those observed [*Epstein and Taylor*, 1971; *Housley et al.*, 1974; *Cassidy and Hapke*, 1975].

In this paper we present estimates of the mass fractionation of the lunar surface produced by solar wind sputtering. Most

of the material ejected by sputtering escapes the moon's gravity, but some returning matter settles back onto the surface. This material, which is somewhat richer in heavier atoms than the starting surface, is incorporated into the heavily radiation-damaged outer surfaces of grains, where it remains subject to resputtering. 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 $\sim 10^8$ -yr time scale.

Cassidy and Hapke [1975] have also discussed mass fractionation associated with gravitational escape of the sputtered atoms. They conclude that direct sputtering mass fractionation is not important, although the basis for this conclusion is not discussed. In this paper we come to the opposite conclusion. *Cassidy and Hapke* suggest that sputtered atoms have different sticking coefficients and conclude that mass fractionation, produced by multiple scattering of sputtered atoms from a rough lunar surface, must be considered to account for the experimental results for lunar soils. Only qualitative arguments are given for this conclusion, however. The most fundamental difference between our calculations and those of *Cassidy and Hapke* is that we do not just consider the mass fractionation from a single stage of sputtering; we also calculate the steady state surface composition, allowing for the effects of deposition and resputtering.

It should be emphasized that the purpose of this paper is not to build 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, in this evolution. Other mechanisms are undoubtedly also important [*Clayton et al.*, 1974].

DETAILS OF THE PROCESS OF DIFFERENTIATION

When a beam of ions strikes a solid, an interatomic cascade of particles is initiated [*Sigmund*, 1969]. Sputtering occurs when some of these moving atoms escape through a nearby surface. Sputtering is therefore expected to occur on the lunar

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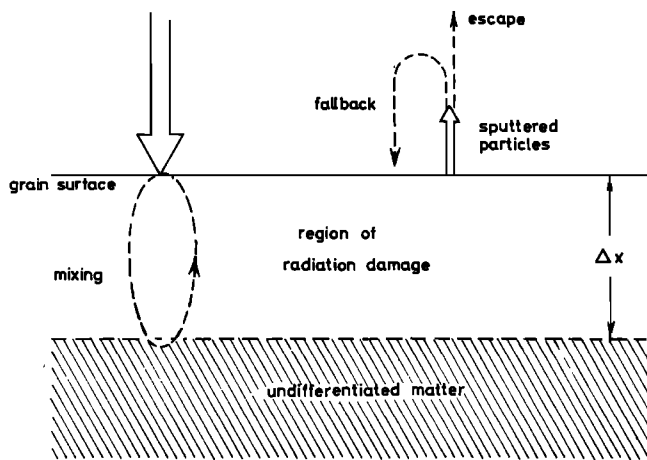


Fig. 1. Schematic diagram of processes initiated at the lunar surface by solar wind irradiation. Material sputtered by the solar wind largely escapes beyond lunar gravity. The small (in the case of lighter elements) returning component is enriched in heavier isotopes which are incorporated into a surface layer, Δx deep, by radiation-induced mixing. As the lunar surface is eroded, the active layer persists. Note that in practice, sputtered atoms returning on an area element of the lunar surface did not originate there. Therefore grain surfaces should reflect a homogenized sampling of a wide area of the moon.

surface as a result of bombardment by solar wind protons and alpha particles [see, e.g., *Maurette and Price, 1975*]. There is an important difference, however, between the conditions of a laboratory sputtering experiment and those encountered on the moon. In the former case, all the sputtered target material is typically collected on a catcher foil or otherwise permanently separated from the target. On the moon, gravitational forces are an important consideration: since the energies of ejected atoms are of the order of the energy required to escape lunar gravity, some atoms escape into space, while others fall back to the lunar surface. Since at the same energy the heavier of two particles has the lower velocity, there ought to be a natural winnowing mechanism operating on material tossed up from the moon by the solar wind. The fraction of sputtered material which returns to the lunar surface will be enriched in the heavier elements and isotopes in relation to their abundances in the undisturbed material. These returned atoms are, of course, subject to resputtering. Also, recoil implantation will drive atoms residing on a surface into the substrate following direct collisions with the primary ion [*Nelson, 1969; Perkins and Stroud, 1972; Stroud, 1972; Moline et al., 1974; Baranova et al., 1974*]. Such 'atomic mixing' of the surface region by the solar wind will blend some of this enriched matter into the undifferentiated substrate. Experimental support for the idea of radiation-induced mixing is found in the work of *Mertens [1975]*, who studied the sputtering of a 200-Å Cu film deposited on Al. During bombardment with a 250-keV Ar beam (whose range [*Lindhard et al., 1963*] in Cu is ~ 1400 Å) a zone quickly developed about the two-metal interface where the metals were well mixed over a region thicker than ~ 200 Å. The use of a thicker Cu coating or lower Ar beam energies might well have exposed a mixing depth that was much closer to the range of the incident beam. Ion-beam-induced intermixing at a palladium/silicon interface has also been reported [*van der Weg et al., 1974*]. *Cairns et al. [1971]*, *McHugh [1974]*, and *Zinner et al. [1976]* report distortions in implanted ion depth profiles produced by the analyzing ion

beam of an ion microprobe. This undoubtedly represents the first stage in the above mixing process. The mixing mechanism has been treated theoretically by *Ishitani et al. [1975]*, who used a Monte Carlo approach, and by *Haff and Switkowski [1977]*, who considered a diffusion model in which the mixing is assumed to have its basis, as does sputtering, in the collision cascades generated by the primary beam.

The exact thickness of this enriched layer is uncertain. Rather wide limits on the mixing depth Δx may be inferred from, on the one hand, the immediate depth of the sites from which the sputtered atoms are ejected (probably extending down to a few monolayers, ~ 10 Å [*Sigmund, 1969; Ishitani and Shimizu, 1975*]) to, on the other hand, the measured depth of the heavily radiation-damaged region of the surfaces of dust grains (~ 200 – 500 Å [*Borg et al., 1971*]). The penetration depth of solar wind protons, which is ~ 100 Å, provides a reasonable estimate for Δx . Such a value is consistent with computer simulation calculations of atomic mixing [*Ishitani and Shimizu, 1975*].

Consequently, on the lunar surface, after a sufficiently long time has elapsed, a thin enriched layer will exist in an equilibrium condition determined by the balance between atoms lost to outer space, atoms incorporated upon fallback, and atoms gained from the admixed subsurface material. Such a dynamic situation is depicted in Figure 1.

THEORY

Two component surface. Let us start with the simple picture of a moon consisting of only two elements, Si and O, present as their most abundant isotopes in the chemical form SiO_2 . (This assumption will be relaxed in the next section.) Within this scenario, expressions shall be derived for the evolution of the surface enrichment of Si relative to O and then extended to calculations of isotopic effects. It is useful to define the following quantities:

The quantity n_i is the normalized starting atomic abundance at the lunar surface of the element whose mass number is i . Thus $n_{16} = \frac{2}{3}$, $n_{28} = \frac{1}{3}$.

The quantity $N_i(t)$ is the fractional abundance of atoms of species i after a time t of bombardment by the solar wind; $N_i(0) = n_i$.

The quantity S is the sputtering rate constant, defined as the probability that an atom within Δx will be sputtered from the surface in 1 yr; i.e., sputtering erosion rate in angstroms per year is identical to $S\Delta x$. Although S may in reality depend (initially) upon the time t , 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 1 yr is then in lowest approximation $N_i S$.

The quantity f_i is the fraction of sputtered atoms i which falls back to the lunar surface. This quantity is expressed below in terms of the energy spectrum of sputtered particles and the lunar escape energy.

We can determine $N_{16}(t)$ and $N_{28}(t)$ in the following manner. Consider the surface layer Δx . With time, atoms are sputtered away. Some atoms escape, so new unfractionated material is introduced into the active region from the interior side of the layer. We require that the total number of atoms comprising this active region should be constant. An equation describing the amount by which the fraction of oxygen atoms in Δx at time $(t + \Delta t)$ differs from that present at t is given by

$$N_{16}(t + \Delta t) - N_{16}(t) = -N_{16}(t)S\Delta t + f_{16}N_{16}(t)S\Delta t + n_{16}(1 - f_{16})N_{16}(t)S\Delta t + n_{16}(1 - f_{28})N_{28}(t)S\Delta t \quad (1)$$

The first term on the right-hand side of (1) represents the total amount of O sputtered from Δx in time Δt , and the second term reflects the amount of O which returned to the surface having failed to escape lunar gravity. The difference in these two terms, $(1 - f_{16})N_{16}(t)S\Delta t$, is then the net loss from Δx of the O component through sputtering. In order to conserve the number of atoms in Δx , fresh material is mixed in from the reservoir of atoms within the grain in stoichiometric proportions. The filling of O 'vacancies' by O atoms is given by the third term, while the last term represents the filling of Si vacancies by underlying O atoms.

Relation (1) is equivalent to the differential equation

$$\frac{dN_{16}(t)}{dt} = -N_{16}(t)\gamma + C_{16} \quad (2)$$

where

$$\gamma = S[n_{28}(1 - f_{16}) + n_{16}(1 - f_{28})] \quad (3)$$

and

$$C_{16} = Sn_{16}(1 - f_{28}) \quad (4)$$

with the solution,

$$N_{16}(t) = (n_{16} - C_{16}/\gamma)e^{-\gamma t} + C_{16}/\gamma \quad (5)$$

An analogous equation pertains to $N_{28}(t)$. In arriving at (2)–(5) we have used the fact that $N_{16}(t) + N_{28}(t) = 1$.

The time constant for approach to equilibrium, T_{eq} , is γ^{-1} . For $t \gg T_{eq}$, the equilibrium condition obtained is

$$N_{16}(\infty) = C_{16}/\gamma = \frac{n_{16}(1 - f_{28})}{n_{28}(1 - f_{16}) + n_{16}(1 - f_{28})} \quad (6)$$

The ratio C_{16}/γ does not depend upon the value of S , and therefore the equilibrium concentrations do not depend upon the absolute rate at which particles are sputtered away. The equilibrium concentration is also independent of the thickness Δx of the active surface layer. The sputtering factor S does appear in the argument of the exponential in (5) which determines how fast the steady state condition is approached. Referring to the definition of S in terms of Δx , we see that the calculated equilibrium time will depend on the thickness of the layer Δx , with a larger thickness requiring a longer time to reach steady state.

In the above discussion we cited several experiments to justify the existence of a mixed layer. It is worth emphasizing that (6) is still valid even if the mixed layer does not exist. In this case, N_{16} and N_{28} give the average composition of the outer atomic layer, which is a mixture of redeposited and unsputtered atoms.

In order to proceed we need to know the energy spectrum of sputtered particles. In the absence of experimental data for silicate materials we must introduce a sputtering theory which will then allow calculation of f_i . A frequently used energy spectrum of sputtered particles, derived by *Thompson* [1968] and consistent with available experimental data, has the form

$$\varphi(E) = \frac{\varphi_0}{E^2(1 + U/E)^3} \quad (7)$$

where φ_0 is a constant and U is a surface binding energy for the material under bombardment. The behavior of $\varphi(E)$ at low energies goes as

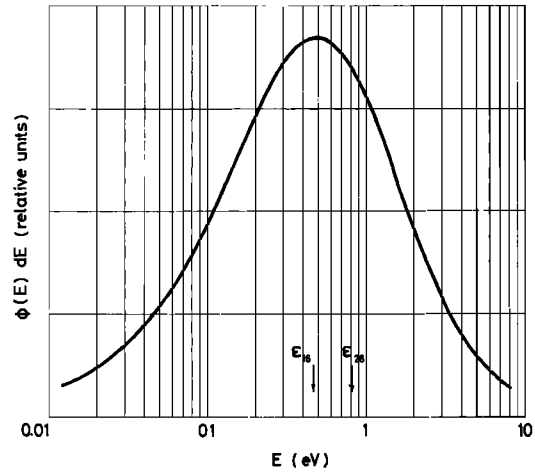


Fig. 2. Semilogarithmic plot of the energy distribution of sputtered particles; $\varphi(E) dE - [dE/E^2(1 + U/E)^3]$ for $U = 1$ eV. The lunar escape energies for atoms of mass 16 and 28 are indicated.

$$\varphi(E) \sim E \quad E \ll U \quad (8)$$

and at high energies,

$$\varphi(E) \sim 1/E^2 \quad E \gg U \quad (9)$$

The function $\varphi(E)$ peaks at an energy of $U/2$. Values of U are typically a few eV for oxides [*Kelly and Lam, 1973*], and we shall return later to a discussion of the value of U appropriate to heavily radiation-damaged mineral grain surfaces. For the purposes of illustration an energy spectrum calculated for $U = 1$ eV is shown in Figure 2.

We assume that the sputtered species are atomic Si and O. The fraction f_i of sputtered atoms i which does not escape from the moon is given by

$$f_i = \left[\int_0^{E_i} \varphi(E) dE \right] / \left[\int_0^\infty \varphi(E) dE \right] \quad (10)$$

$$f_i = \left(1 + \frac{U}{E_i} \right)^{-2} = \left(1 + \frac{U}{m_i g R} \right)^{-2} \quad (11)$$

where E_i is the lunar escape energy of element of mass m_i . R and g are the lunar radius and gravitational acceleration, and $(1 \text{ amu})gR = 0.0292$ eV. From (6) and (11) it is possible to calculate values for the equilibrium concentration of Si and O with the appropriate value of U .

Multicomponent surface. The formalism for differentiation of a two-component surface having been developed, it is now useful to generalize the theory to the case of a homogeneous multicomponent medium that would be a more realistic approximation to the composition of the lunar surface. It will then be possible to assess the effects of sputtering on isotopic enrichment as well as the effects on arbitrary pairs of elements.

Consider the case of a lunar surface composed of k different atomic species. If we label each constituent by a subscript ranging from 1 through k , then after the surface has reached equilibrium, the abundance N_1 of species 1 within Δx will satisfy the equation

$$N_1 = N_1 f_1 + n_1 N_1 (1 - f_1) + n_1 N_2 (1 - f_2) + \dots + n_1 N_k (1 - f_k) \quad (12)$$

The first term on the right-hand side is the number of sputtered atoms of species 1 which returns, and the subsequent terms

reflect the filling of species i ($i = 1$ through k) vacancies by species 1. Equation (12) may then be rewritten as

$$\frac{N_1}{n_1} (1 - f_1) = \sum_{i=1}^k N_i (1 - f_i) = \text{const} \quad (13)$$

since the summation covers all surface components. Since there is nothing special about the choice of species i above, we have in general

$$\frac{N_i/n_i}{N_j/n_j} = \frac{1 - f_j}{1 - f_i} \quad (14)$$

The conventional definition for δ in representing isotopic enrichments, relative to some arbitrary laboratory standard, $(n_i/n_j)_0$, is

$$\delta \equiv \frac{N_i/N_j}{(n_i/n_j)_0} - 1 \quad (15)$$

Combining (14) and (15) leads to

$$\frac{1 + \delta_{\text{surf}}}{1 + \delta_{\text{bulk}}} = \frac{N_i/N_j}{n_i/n_j} = \frac{(1 - f_j)}{(1 - f_i)} \quad (16)$$

A somewhat more natural quantity for expressing surface-correlated isotopic and elemental enrichments is defined by the equation

$$\epsilon(i/j) \equiv \frac{N_i/N_j}{(n_i/n_j)} - 1 = \frac{f_i - f_j}{1 - f_i} \quad (17)$$

for any two species i and j . Equation (17) makes a direct comparison between surface and bulk concentrations, without reference to an arbitrary standard. In practice, ϵ and δ differ by no more than about 5‰ (for oxygen), and it will be convenient to make use of both definitions. Note that the final expression in (17) is also the form that would have been derived for the simpler two-component case by using (3), (4), and (6). This then shows that the equilibrium fractionations are independent of the detailed composition of the medium if the energy spectrum of sputtered particles is not composition dependent.

EQUILIBRATION TIME

Before considering the equilibrium elemental and isotopic enrichments it is important to examine in more detail the time scale involved for achieving equilibrium. For the sake of illustration we consider the case of SiO_2 described by (5). In general, equilibration times will depend upon the detailed composition of the medium, but until generally accepted sputtering rates are available for relevant lunar materials, it is not possible to deal with this complexity.

It is now necessary to specify values for the surface binding energy U and sputtering constant S . There exists no measurement of U for heavily radiation-damaged minerals of the kind found on the lunar surface. Experiments [Kelly and Lam, 1973] have pointed to a value of 4 eV for SiO_2 , but this is likely to be significantly higher than the value appropriate to grain surfaces where extensive radiation damage has disrupted the atomic bonding. We expect that the effective binding energy may decrease with increasing solar wind irradiation. For the purposes of estimating the equilibration time we take silicon and oxygen both to be characterized by $U = 1$ eV, so that their energy spectra are the same. Noting that the lunar escape energies are $E_{16} = 0.467$ eV and $E_{28} = 0.818$ eV, (11) gives $f_{16} = 0.101$ and $f_{28} = 0.202$ (this factor of 2 being coincidental). Taking $\Delta x = 100 \text{ \AA}$ and the range of erosion rates by solar

wind sputtering in the current literature from 0.5 \AA/yr [Borg et al., 1974] to 0.03 \AA/yr [Zinner et al., 1976] then gives

$$S = 5 \times 10^{-8} \text{ to } 3 \times 10^{-4} \text{ yr}^{-1}$$

From (3) we obtain

$$T_{eq} \approx 240\text{--}4000 \text{ yr}$$

In the following sections we compare estimates of surface isotopic and elemental fractionations based on experimental data for lunar soil samples with the theoretical sputtering equilibrium surface fractionations as calculated from (14). This comparison is imperfect for many reasons. In the context of the above discussion it is important to consider whether it is reasonable that the surfaces of lunar soil grains will have achieved sputtering equilibrium. The question is then whether there are competing processes which bury or destroy sputtered surfaces in times less than $\sim 10^8$ yr. Two plausible processes are (1) impact mixing or volatilization and (2) deposition of 'fresh' surface layers of lunar materials vaporized by impacts at more distant points. Constant input (e.g., representing vapor deposition) and/or constant rate terms (i.e., proportional to the number of atoms in the sputtered layer representing, for example, impact burial) can easily be added to (2). In view of our limited objective of only defining the role of sputtering mass fractionation we feel that consideration of more complex equations is not profitable, principally because the appropriate rates and rate constants to be used are not well known. There appears to be no justification, however, for assuming that the rates of those competing processes are negligible. Gault et al. [1974] estimate impact vaporization rates that would correspond to deposition of impact-volatilized material at a rate of 0.1 \AA/yr . This is 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 destruction processes is to lengthen the equilibration time scale and, usually, decrease the mass fractionations from those calculated above. For example, rapid impact mixing on a sub-millimeter scale has the effect of just rotating 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 experimental measurements on bulk soil samples. If it is assumed that annealing rates for the sputtered layer are negligibly slow at cold lunar subsurface temperatures, the $\sim 10^8$ -yr equilibration time can be accumulated piecemeal; it need not be in a single exposure. It is reasonable to regard lunar soil grains with amorphous coatings [Borg et al., 1971] as being in sputtering equilibrium (see also Borg et al. [1974]). The estimated time scale for the formation of the amorphous layer (~ 2000 yr [Maurette and Price, 1975]) supports this assumption. Data presented by Maurette and Price [1975] on the fraction of grains having amorphous coatings indicate that except for some 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 appears to be some justification for the simplifying assumption, one that we shall make in the following discussion, that the surfaces of grains in a mature lunar soil sample are in sputtering equilibrium.

COMPARISON OF CALCULATIONS WITH EXPERIMENTAL DATA

On the basis of (14) and (16) we now calculate enrichment effects for the isotopes of O, Si, and S. Assuming $U = 1$ eV, we

obtain $f_{16} = 0.101$, $f_{18} = 0.119$, $f_{28} = 0.202$, $f_{30} = 0.218$, $f_{32} = 0.234$, and $f_{34} = 0.249$. These values lead to the following surface heavy isotope enrichments,

$$\delta(^{18}\text{O}) = 26.0\text{‰}$$

$$\delta(^{30}\text{Si}) = 20.2\text{‰}$$

$$\delta(^{34}\text{S}) = 19.1\text{‰}$$

using $\delta_{\text{bulk}}(^{18}\text{O}) = +5\text{‰}$, $\delta_{\text{bulk}}(^{30}\text{Si}) = -2\text{‰}$, and $\delta_{\text{bulk}}(^{34}\text{S}) = +0.5\text{‰}$. The approximate constancy of the surface δ values is a consequence of assuming that $U = 1$ eV (see discussion of Figure 4).

Epstein and Taylor [1971, 1972, 1975] and Taylor and Epstein [1973] chemically etched lunar soils with exposures to F_2 gas and monitored the isotopic enrichment as a function of the amount of oxygen removed from the grains. For Si and O they found strong enhancements of the heavier isotopes in the O and Si removed with very brief exposure; however, the isotope ratios approached the bulk values once approximately 1% of the mass of the grains had been removed. The early fractions presumably approximate the isotopic compositions of the surface layers. Noting that measurements of specific surface area in submillimeter lunar fines range from 0.2 to 0.6 m^2/g [Cadenhead et al., 1972; Holmes et al., 1973], we have assumed an effective grain diameter of 10 μ , so that the measurements of Epstein and Taylor define surface layers up to 170 \AA thick in which there are measurable isotopic fractionations. The values $\delta(^{18}\text{O})$ and $\delta(^{30}\text{Si})$ were found to vary quickly within this layer. Our model is unrealistic in that it does not consider the depth dependence of the isotopic distribution. The observed depth dependence of the isotopic variations probably reflects a complex gardening of the surface by atomic projectiles as well as some diffusion of the surface species. This process is quite likely a complicated one which does not lend itself to any plausible but straightforward description; and the assumption of a well-defined layer, Δx deep, is only a rough approximation. However, the first cuts of these fluorination 'stripping' experiments correspond to an effective sampling depth of ~ 40 \AA , and the enrichment effects were much diluted for depths greater than ~ 100 \AA (i.e., a depth of approximately Δx). For this outermost part of the sputtered layer it does appear reasonable to assume a well-mixed zone of material in sputtering equilibrium, as described by our equations. Thus we think that it is fair to 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 fluorination fractions. The results of our calculations are therefore in reasonable accord with the data of Epstein and Taylor, 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. We caution that there are several features which prohibit comparison beyond the order of magnitude level. The assumption of sputtering equilibrium has already been discussed. The interpretation of the fluorination experiments is also complex. As experiments are performed on a distribution of grain sizes, shapes, and compositions, 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 [Maurette and Price, 1975]) may have normal surface compositions. Another oversimplification in our calculations is the assumption that the sputtered species are Si and O atoms. There is some evidence for the sputtering of molecular species such as SiO

[Green et al., 1976]. If this is true, our $\delta(^{18}\text{O})$ values are overestimated, and our estimates of Si/O elemental fractionation will be low.

We have emphasized in the above discussion that our calculated mass fractionations are independent of the depth (Δx) chosen for our mixed layer and, in fact, independent of whether the mixed layer even exists. However, it should be equally strongly emphasized that the existence and thickness of the mixed layer are critical in comparing our calculations with the Epstein and Taylor experimental results. If the mixed layer is only the first atomic layer, then the mass fractionation in this layer must be enormous, because (1) even the first cut of the F_2 stripping contains much more material than the first atom layer and (2) it is very unreasonable to believe that alternative isotopic fractionation mechanisms (e.g., diffusion) would produce a 50- to 100- \AA -thick isotopically anomalous layer for Si and O. Thus if there is no mixed layer, our calculated isotopic fractionations for Si and O would be much less than what must actually be present, and some mechanism other than sputtering would be dominant. However, our interpretation is that there is sufficient evidence that the mixed layer really exists and that the sputtering should be regarded as a plausible mechanism for producing observed Si and O isotopic fractionations.

Bearing the above qualifications in mind, we return to a more detailed comparison with lunar data. Equation (11) shows that the fraction of sputtered atoms escaping is not linear in mass; however, because of the small fractionations involved in $\delta(^{18}\text{O})/\delta(^{17}\text{O})$, we calculate this ratio to be 2, in accord with the general expectation for a physical isotope separation process as well as with the measurements of Clayton et al. [1974].

Epstein and Taylor note also that total oxygen is depleted by $\sim 40\%$ relative to Si in the first cuts of the fluorine stripping. Qualitatively similar effects in the outermost atomic layers have been observed by Housley and Grant [1976] using electron spectroscopy for chemical analysis (ESCA). 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 \AA . In a manner analogous to the isotopic variations the amount of oxygen depletion caused by sputtering is calculated to be 12.5%. As is the case with $\delta(^{18}\text{O})$, the calculated fractionation is less than that measured. This is not what would be expected if the surfaces of the soil grains analyzed had not attained sputtering equilibrium. Possible ad hoc explanations for the lower calculated fractionations are that (1) volatilization and recondensation are important mechanisms for mass fractionation, (2) our adopted sputtering energy spectra are incorrect, (3) our calculated results reflect the average mass fractionation over a layer that is thicker than what is actually analyzed, or (4) the sputtering yield is mass dependent (see the section on mass dependence of the sputtering process).

Rees and Thode [1974] 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 [Barnes et al., 1973; Garner et al., 1975]. 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 has 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.

Equation (14) is also valid for the case of an element such as C, which is usually considered to be absent in lunar rocks except for solar wind implantation. In this case, n , in (14), refers to solar wind, not bulk, abundance. For our standard assumptions ($U = 1$ eV) we would predict $\epsilon(^{13}\text{C})$ to be only about 10‰. This is reasonably close to a bulk soil value, but surface carbon isotopic enrichments may be much larger ($\geq 50\%$) [Epstein and Taylor, 1975]. If the Epstein and Taylor results are accepted at face value, they would indicate that (1) our adopted sputtering energy spectrum is incorrect, (2) diffusion loss and reimplantation accompanied by large mass fractionation is the dominant effect controlling the surface C isotopic composition, or (3) the solar wind $\delta(^{13}\text{C})$ is $\geq 40\%$. The data of Epstein and Taylor [1975] indicate that the surface- and volume-correlated (bulk) C in lunar soil represents different sources and that the bulk C isotopic composition is irrelevant for our purposes. The bulk C may be meteoritic or lunar in origin. Significant lunar C inputs into the regolith are also required if suggestions are correct that CO in lunar rocks has produced metallic iron [Sato et al., 1973; Sato, 1976] or vesiculation [Goldberg et al., 1976].

Large $\delta(^{15}\text{N})$ values (up to 100‰) for lunar soils [Kerridge, 1975] do not appear to be related to lunar surface residence and thus probably cannot be explained by sputtering. Furthermore, it should be noted that to the extent that the form of our sputtering energy spectrum is correct (regardless of the value of U adopted) the $\delta(^{15}\text{N})$ produced by sputtering should not exceed 70‰.

For $U = 1$ eV we also expect $^{44}\text{Ca}/^{40}\text{Ca}$ variations corresponding to about $\delta(^{44}\text{Ca}) \sim 20\%$. Experiments to date [Russell et al., 1976, 1977] suggest that no variations greater than 3‰ are present. This is difficult to understand in view of the O, Si, and 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.

DISCUSSION

It is worthwhile here to reiterate the fundamental assumptions upon which the calculations depend and to note those aspects which require further experiments.

Energy distribution of sputtered particles. In order to produce significant mass fractionation the velocity distribution of the sputtered atoms must extend to sufficiently high velocities that there is significant mass loss from the moon. Although it is possible that heavy atoms tend to be emitted at lower energies than light atoms, as might be expected from arguments on the efficiency of collisional energy transfer, we have adopted the conservative assumption that the energy spectra are identical for all atomic species. An energy spectrum weighted more to lower energies for the heavier particles would, of course, magnify surface δ values still further.

The energy spectrum (7) was developed primarily to explain sputtering experiments with projectiles both heavier and more energetic than solar wind particles; however, it seems to hold also for lighter projectiles [Wehner et al., 1963a]. In any case, it is a useful parametrization, since by simply adjusting U , one can control the position of the peak of the energy distribution.

Figure 3 illustrates the variation in ϵ as a function of U for the three systems of interest. Decreasing U tends to increase all δ values and thereby to improve slightly the match to experiment. Thus if $U = 0.25$ eV, we find $\epsilon(\text{Si/O}) = 395\%$, $\epsilon(^{30}\text{Si}) = 48\%$, and $\epsilon(^{18}\text{O}) = 67\%$. Mass fractionation by the mechanism proposed here will of course apply to all elements across the periodic table. Figure 4 demonstrates how isotopic enrichments will vary as a function of mass number for isotopes differing in mass by two units.

An interesting feature of the form of the energy spectrum adopted here is the asymptotic behavior of ϵ when $U \rightarrow 0$. In this case, $\epsilon(i/j) = A_i/A_j - 1$ where $A_{i,j}$ are the mass numbers of the elements under consideration. Therefore if the energy spectrum of sputtered particles is peaked at very low energies, as might happen if the sputtered material which returns and adheres to the grain surfaces is only very weakly bound, then rather large heavy atom enrichments might result.

Such a discussion is speculative until experimental measurements are carried out of the energy distribution of each species of sputtered atoms under ~ 1 -keV/amu hydrogen and helium bombardment of targets whose composition, surface structure, and radiation history resembles that of the lunar surface. The absence of data in this area attests to the difficulty of such measurements.

Mass dependence in the sputtering process itself. This topic is receiving increasing theoretical [Andersen and Sigmund, 1974] and experimental attention [Shimizu et al., 1973; Poate et al., 1976]. While simple considerations of mass conservation require that after prolonged sputtering the composition of the ejected material should reflect the composition of the target, there may be important dynamic effects occurring during the irradiation which might produce anomalous surface compositions even in the absence of gravitational redeposition. Thus the sputtering rates of different atomic or isotopic species may differ from one another. Within certain approximations [Haff and Switkowski, 1976] the partial sputtering rate of species i is predicted to be $N_i S$, where S is the total rate. We have made this assumption above. In principle, however, it is possible for each species to be characterized by its own sputtering factor, so that $S_i \neq S_j$. In this case, (17) may be generalized to

$$\epsilon(i/j) = \frac{S_j(1 - f_j)}{S_i(1 - f_i)} - 1 \quad (18)$$

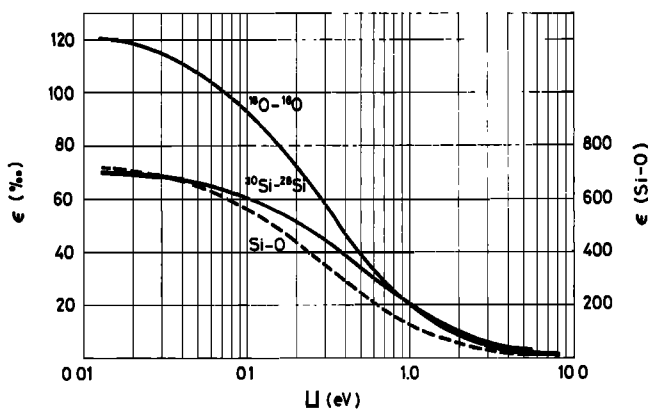


Fig. 3. Semilogarithmic plot of calculated values of ϵ versus U . Curves are shown for $^{18}\text{O}-^{16}\text{O}$, $^{30}\text{Si}-^{28}\text{Si}$, and Si-O (dashed curve). The scale for $\epsilon(\text{Si-O})$ is noted to the right of the figure. As $U \rightarrow 0$, $\epsilon(^{18}\text{O}) \rightarrow 125\%$, $\epsilon(^{30}\text{Si}) \rightarrow 71\%$, and $\epsilon(\text{Si/O}) \rightarrow 750\%$.

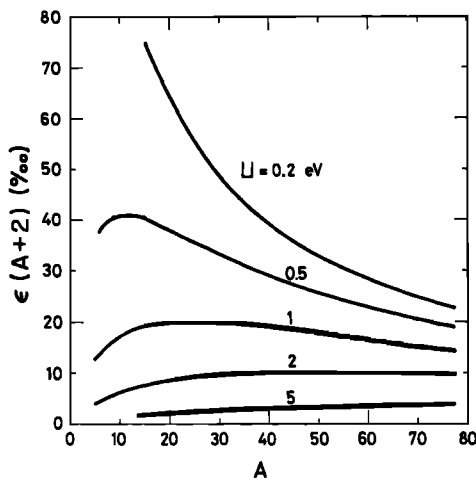


Fig. 4. Calculated mass enrichments per mil as a function of mass number for a range of values of U . The value ϵ is plotted for isotopes whose masses differ by 2 amu.

Contemporary theories of sputtering of complex targets [Andersen and Sigmund, 1974] suggest that the additional ratio S_j/S_i would be important only when the mass difference of the elements is very large.

Ionized components. In the above discussion we have assumed one-hop ballistic trajectories of ejected atoms. If a significant portion of the sputtered material consists of ions rather than neutral atoms, electric and magnetic fields present near the moon could strongly affect the ultimate fate of the sputtered particles. Laboratory evidence indicates that there is a significant ionic component only in the case of alkali metals [Krohn, 1962] and alkali halides [Richards and Kelly, 1973]. In most other cases reported so far, the overwhelming number of sputtered particles is neutral. Although ions may be produced by subsequent interaction of the sputtered atoms with solar photons, the probability of this occurring is negligible for those atoms whose velocity exceeds the lunar escape velocity (photo-ionization lifetimes near the moon are $\sim 10^5$ – 10^7 s). It is also reasonable to expect that returning Si and O will become bonded to the grain surfaces after, at most, a few hops and thereby will be trapped on the moon much more quickly than the unreactive noble gases. Atoms of these gases are probably released at thermal energies by diffusion loss and therefore bounce many more times, building up a measurable quantity until ionization processes begin to limit the atmospheric concentrations [Heymann and Yaniv, 1970; Manka and Michel, 1971]. In the unlikely event that sputtered Si and O similarly diffuse and bounce, the fractionations produced by this mechanism would enhance those produced by sputtering.

SUMMARY

Our calculations indicate that sputtering of the lunar surface by the solar wind will give rise to significant surface heavy atom enrichments if the grain surfaces are allowed to come into sputtering equilibrium. With the use of plausible parameters with the model, calculated δ values are seen to approach those measured for Si and O. A more detailed evaluation of the role of sputtering must await further experimental study of the fundamental sputtering processes involved. Nevertheless, it is very likely that this mechanism will account for at least some of the observed enrichments. Predictions are included for heavy isotope enrichments for elements extending beyond Si in

the periodic table. Enrichments can also be predicted for any pair of elements.

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