Mass Fractionation of the Lunar Surface by Solar Wind Sputtering[*]

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ABSTRACT

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 relative to the lighter ones. This material is incorporated into the heavily radiation-damaged outer surfaces of grains where it is subject to resputtering. Over the course of several hundred years an equilibrium surface layer, enriched in heavier atoms, is found to form. Calculations predict that $\delta(^{18}O) \approx +20\ ^{o}/oo \approx \delta(^{30}Si)$ and that oxygen will be depleted in the outer regions of grains relative to the bulk composition. These results are in reasonable agreement with experiment. The dependence of the calculated results upon the sputtering rate and on the details of 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.

1. 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. The pioneering experiments of Wehner et al. [1963a], who irradiated metal, metal oxide and mineral targets with low energy hydrogen and helium ions, led to the conclusion that sputtering would eject from the moon a substantial amount of matter (approximately at the rate of 0.4 A^{o}/yr) into space with a distribution of velocities sufficiently high that most of this material would escape lunar gravity. Additional investigations by this group [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 relative to lighter elements. Such a conclusion was based upon the experimental observation that heavy atoms were ejected with lower velocities than lighter atoms and that, for the case of certain metal oxides, the surface of the target became enriched in the heavier metal following prolonged irradiation.

There is now considerable experimental evidence demonstrating that the surfaces of lunar soil grains are enriched in the heavier isotopes of oxygen and silicon [Epstein and Taylor, 1971, 1972, 1975; Taylor and Epstein, 1973] as well as indications that the surface Si/O ratio is enhanced relative 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].

In this paper we present a solar wind sputtering process which could produce mass fractionation of the lunar surface. 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. Within this model, calculations are presented which show that an equilibrium surface layer, with a level of isotopic fractionation rather close to that observed experimentally, is produced on grains on a time scale shorter than the typical surface residence time. In the following sections the details of the model are described in which the well known results of sputtering theory together with the ballistics of the ejected particles are combined to give rise naturally to a mass selecting process.

2. DETAILS OF THE PROCESS OF FRACTIONATION

When a beam of ions in the laboratory 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 surface as a result of bombardment by solar wind protons and alpha particles [Maurette and Price, 1975]. There is an important difference, however, between the conditions of a terrestrial 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, except for the usually small component of ionized atoms whose trajectories may be influenced by applied electric and magnetic fields. On the moon, gravitational forces are an important consideration: since the energies of ejected atoms are on 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, relative to their abundances in the undisturbed material. These returned atoms are, of course, subject to resputtering. However, the atomic mixing of the surface region by the solar wind will blend some of this enriched matter into the undifferentiated substrate. Consequently, 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 recovered from fall-back, and atoms gained from the admixed subsurface material. Such a dynamic situation is depicted in Figure 1.

The exact thickness of this enriched layer is uncertain. Rather wide limits on this 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, of ~ 10 A° [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 ($\sim$ 200-500 A° [Borg et al., 1971]). Probably the penetration depth of solar wind protons which is ~ 100 A° provides a reasonable estimate for Δx. Such a value is consistent with computer simulation calculations of atomic mixing [Ishitani and Shimizu, 1975]. There is also experimental support for the idea of radiation-induced mixing in the work of Mertens [1975] who studied the sputtering of a 200 A^o Cu-film deposited on Al. During bombardment with a 250-keV Ar beam (whose range [Lindhard et al., 1963] in Cu is ~ 1400 A^o) a zone quickly developed about the two metal interface where the metals were well mixed over a region thicker than ~ 200 A^o. 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. Similarly, 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.

In order to arrive at a quantitative analysis of mass fractionation we need to know, in addition to the depth, Δx, over which solar protons can effectively shuffle atoms, the sputtering rate applicable to the lunar environment and the energy distribution of the sputtered particles.

3. THEORY

A. 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 Section 3B.) 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:

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

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

S = sputtering rate constant, defined as the probability that an atom within Δx will be sputtered from the surface in one year, i.e., sputtering erosion rate in angstroms per year $\equiv S\Delta x$. Although S may in principle 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 one year is then in lowest approximation $N_i S$.

f_i = 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 fall back and 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. As the eventual enrichments are small on an absolute scale, there is no serious problem regarding the slightly varying mass of this volume. An equation describing the amount by which the fractionation of oxygen atoms in Δx at time $(t+\Delta t)$ differs from that present at t is given by

$$\begin{aligned} N_{16}(t+\Delta t) - N_{16}(t) &= - N_{16}(t)\, S\, \Delta t + f_{16}\, N_{16}(t)\, S\, \Delta t \\ &+ n_{16}\,(1-f_{16})\, N_{16}(t)\, S\, \Delta t + n_{16}\,(1-f_{28})\, N_{28}(t)\, S\, \Delta t. \end{aligned} \tag{1}$$

The first term on the RHS 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 represent the filling of Si 'vacancies' by underlying O atoms.

Relation (1) is equivalent to the differential equation

$$\frac{d\,N_{16}(t)}{dt} = -\,N_{16}(t)\,\gamma + C_{16} \qquad (2)$$

where

$$\gamma = S\left[n_{28}\,(1-f_{16}) + n_{16}\,(1-f_{28})\right] \qquad (3)$$

and

$$C_{16} = S\,n_{16}\,(1-f_{28}) \qquad (4)$$

with the solution,

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

An analogous equation pertains to $N_{28}(t)$. In arriving at Equations (3)-(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 obtains

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

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) and determines how fast the steady state condition is approached. Referring to the definition of S in terms of Δx, we see that the calculated equilibration time will depend on the thickness of the layer Δx, with a larger thickness requiring a longer time to reach steady state.

In order to proceed, we need to know the energy spectrum of sputtered particles. In the absence of experimental data pertinent to the case under consideration, 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], has the form

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

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

$$\varphi(E) \sim E \qquad \text{for } E \ll U \quad , \tag{8}$$

and at high energies

$$\varphi(E) \sim 1/E^2 \quad \text{for } E \gg U \quad . \tag{9}$$

$\varphi(E)$ 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.

Now, the fraction f_i of sputtered atoms i which does not escape from the moon is given by

$$f_i = \frac{\int_0^{\varepsilon_i} \varphi(E)\, dE}{\int_0^{\infty} \varphi(E)\, dE} \qquad (10)$$

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

where ε_i is the lunar escape energy of element of mass m_i. R and g are the lunar radius and gravitational acceleration. From (6) and (11) it is possible to calculate values for the equilibrium concentration of Si and O with the appropriate value of U.

B. Multi-component surface. Having developed the formalism for differentiation of a two component surface, it is now useful to generalize the theory to the case of a homogeneous multi-component 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 .... k, then after the surface has reached equilibrium, the abundance N_1 of species 1 within Δx will satisfy the equation

$$N_1 = N_1 f_1 + n_1 N_1 (1 - f_1) + n_1 N_2 (1 - f_2) + \text{---}\; n_1 N_k (1 - f_k) \;. \qquad (12)$$

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 the species i, i = 1 ... k, vacancies by species 1. Equation (12) may then be rewritten as

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

since the summation covers all surface components. Since there is nothing special about the choice of species 1 above, we have in general

$$\frac{N_i/n_i}{N_j/n_j} = \frac{1-f_j}{1-f_i}\,. \tag{14}$$

In terms of the conventional definition for δ in representing isotopic enrichments, relative to some arbitrary laboratory standard, $(n_i/n_j)_0$:

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

Combining (14) and (15) leads to

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

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

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

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 $^{0}/oo$ (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), (6). This then shows that the fractionation of the material proceeds in a manner which is independent of the detailed composition of the medium. If the increasing complexity of the medium is not accompanied by any modification to the energy spectrum of sputtered particles then the relative equilibrium enrichments of any two elements within a medium of arbitrary composition will remain the same.

4. EQUILIBRATION TIME

It is now possible to compute elemental and isotopic enrichments. Before considering the equilibrium results, it is interesting 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. However, this dependence is expected to be rather weak and uncertainties in the values of the parameters entering the theory are likely to be more significant than the differences between the results for a two component surface and that appropriate to a more complex surface.

It is now necessary to specify values for U and 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: $\varepsilon_{16} = 0.467$ eV and $\varepsilon_{28} = 0.818$ eV, (11) then gives that $f_{16} = 0.101$ and $f_{28} = 0.202$ (this factor of 2 being coincidental). Taking $\Delta x = 100$ A$^{\circ}$ and the currently accepted sputtering erosion rate by solar wind sputtering of 0.5 A$^{\circ}$/yr [Borg et al., 1974] then gives

$$S = 0.5/100 = 5 \times 10^{-3} \text{ yr}^{-1} .$$

From (3) we obtain

$$T_{eq} = 240 \text{ yrs.}$$

We note that arbitrarily increasing U will reduce T_{eq} down to only 1/S or 200 yrs, whereas for values of U as small as 0.2 eV, $T_{eq} = 490$ yrs.

These magnitudes are probably short compared to the total time most lunar dust grains are exposed to the solar wind [see, for example, Poupeau et al., 1975] so that it is likely that this process of fractionation usually reaches equilibrium.

5. COMPARISON OF RESULTS WITH EXPERIMENTAL DATA

We now calculate enrichment effects for the isotopes of O, Si, and S. Assuming U = 1 eV, we obtain $f_{16} = 0.101$, $f_{18} = 0.119$, $f_{28} = 0.202$, $f_{30} = 0.218$, $f_{32} = 0.233$, and $f_{34} = 0.248$. These values lead to the following surface heavy isotope enrichments,

$$\delta(^{18}O) = 25 \ ^{o}/oo ,$$

$$\delta(^{30}Si) = 18 \ ^{o}/oo ,$$

and

$$\delta(^{34}S) = 21 \ ^{o}/oo ,$$

where we have used (16) and the values $\delta_{bulk}(^{18}O) = +5 \ ^{o}/oo$, $\delta_{bulk}(^{30}Si) = -2 \ ^{o}/oo$, and $\delta_{bulk}(^{34}S) = +0.5 \ ^{o}/oo$. The approximate constancy of the surface δ-values is a consequence of assuming U = 1 eV (see discussion of Fig. 4).

In their analysis of isotopic concentrations in the surfaces of lunar grains, Epstein and Taylor [1971, 1972, 1973, 1975] chemically etched lunar soils with brief exposures to F_2 gas and monitored the isotopic enrichment as a function of the amount of oxygen removed from the grains. With respect to the Si and O isotopes they found strong surface enhancements of the heavier isotopes with isotope ratios approaching the bulk values once approximately 1% of the mass of the grains had been removed. Noting that measurements of specific surface area in submillimeter lunar fines range from 0.1 to 1 m^2/g [Cadenhead et al., 1972, Holmes et al., 1973] we have assumed an average grain diameter of 10 μ so that the measurements of Epstein and Taylor define a surface layer less than 170 A^o thick in which there was appreciable isotopic fractionation. $\delta(^{18}O)$ and $\delta(^{30}Si)$ were found to vary quickly within this layer. There is no provision within our model for the evaluation of the shape of the isotopic distribution. However, since the first cut of these fluorination 'stripping' experiments probably sampled an average depth of ~ 40 A^o and the enrichment effects were much diluted for depths greater than ~ 100 A^o (i.e., a depth $\approx \Delta x$), it is reasonable to compare the model predictions to the enrichments measured right at the grain surfaces. Experimentally, $\delta(^{18}O)$ was found to range up to ≈ 50 $^o/oo$ and $\delta(^{30}Si)$ up to ≈ 25 $^o/oo$ in the fluorination fractions. The results of our calculations are therefore in rather good accord with their data.

While 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 it is already a significant achievement of the model to account rather quantitatively for the experimental observations with the use of plausible but conservative estimates for parameters which are not well determined by independent experiments. In fact, there are several features noted briefly above which prohibit comparison beyond the order of magnitude level. As experiments are performed on a distribution of grain sizes, uncertainties exist in the conversion of gas fraction of oxygen removed to an equivalent depth of surface layer. Furthermore, within any given sample, individual grains will not reflect identical composition or history. Additionally, the depth dependence of the enrichment factors 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 active layer, Δx deep, is only a rough approximation. However, as noted earlier, the equilibrium concentration within Δx does not depend upon the choice of this depth.

Equation (11) shows that the fraction of sputtered atoms returning is not linear in mass; however, because of the small fractionations involved in $\delta(^{18}O)/\delta(^{17}O)$, 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 fluorination stripping. Qualitatively similar effects in the outermost atomic layers have been observed by Housley et al. [1976] using ESCA techniques. In an analogous manner as the isotopic variations, it is interesting to compare with the amount of oxygen depletion caused by sputtering, which is calculated to be 12.5%. Because the experimental measurement may apply to a thinner layer than the calculated depletion, it seems that the Si/O data might provide further support for the fractionation mechanism proposed here.

Rees and Thode [1974] have used S isotopic analyses of grain-sized fractions to estimate a surface $\delta(^{34}S)$ enrichment of about 20 $^o/oo$, in agreement with our calculations.

Relatively large $^{39}K/^{41}K$ depletions have been reported for bulk soil samples (5-10 $^o/oo$) but these do not appear to be surface correlated [Barnes et al., 1973, Garner et al., 1975]. The large bulk isotopic enrichments for K (and S) may reflect cycling of sputtered surface material into the bulk of the soil as a result of impact melting (e.g., by agglutinate formation), but we have not yet attempted to evaluate this process quantitatively.

Equation (14) is also valid for the case of an element such as C, which can be considered to be absent in lunar rocks except for solar wind implantation. In this case n, in Eq. (14), refers to solar wind, not bulk, abundance. For our standard assumptions (U = 1 eV) we would predict $\epsilon(^{13}C)$ to be only about 10 $^o/oo$. This is reasonably close to a bulk soil value, but surface carbon isotopic enrichments appear much larger ($\gtrsim$ 50 $^o/oo$) [Epstein and Taylor, 1975]. This may 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 $\delta(^{13}C)$ is about 40 $^o/oo$. The data of Epstein and Taylor [1975] indicate that the surface and volume (bulk) correlated C in lunar soil represent different sources and that the bulk C isotopic composition is irrelevant for our purposes. The bulk C is probably meteoritic or lunar in origin. Significant lunar C inputs into the regolith are required if suggestions are correct that CO in lunar rocks has produced metallic iron [Sato et al., 1973, 1976] or vesiculation [Goldberg et al., 1976].

Large $\delta(^{15}N)$ values (up to 100 $^o/oo$) for lunar soils [Kerridge et al., 1975] do not appear to be surface correlated [Becker and Clayton, 1975] and thus 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 $\delta(^{15}N)$ produced by sputtering should not exceed 70 $^o/oo$.

For U = 1 eV, we also expect $^{44}Ca/^{40}Ca$ variations corresponding to about $\delta(^{44}Ca) \sim 20$ $^o/oo$. Experiments to date [Russell et al., 1976] suggest that no variations greater than 2 $^o/oo$ are present. This is difficult to understand in view of the O, Si, S, data, regardless of the fractionation mechanism.

In summary, it seems inescapable that sputtering/gravitational mass fractionation is a major process in 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.

6. DISCUSSION

It is worthwhile summarizing the main features of the model presented here, drawing attention to the fundamental assumptions upon which the calculations depend and noting those aspects which require further experiments in order to check the validity of this approach.

A. Energy distribution of sputtered particles. In order for an effect to occur that is consistent with the experimental observations, the velocity distribution of the sputtered atoms must extend to sufficiently high velocities that there is significant mass loss from the moon. Although there appears to be some evidence [Andersen and Bay, 1972] 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 at 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. Still it is a useful parametrization in our case, since by simply adjusting U one can control the position of the peak of the energy distribution. It is interesting to investigate the dependence of the results on the value of U. Figure 3 illustrates the variation in ϵ as a function of U for the three systems of interest. Decreasing the binding energy tends to increase all ϵ-values and thereby to improve slightly the match to experiment. Thus if $U = 0.25$ eV, we find $\epsilon(Si/O) = 395\ ^{o}/oo$, $\epsilon(^{30}Si) = 48\ ^{o}/oo$ and $\epsilon(^{18}O) = 67\ ^{o}/oo$. 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 $U \to 0$. In this case, it is easy to show that $\epsilon(i/j) = A_i/A_j - 1$ 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 largely speculative until experimental measurements are carried out of the energy distribution of each species of sputtered atoms under $\sim$ 1 keV/amu hydrogen and helium bombardment of targets whose composition, surface structure and irradiation history resembles that of the lunar surface. The absence of data in this area attests to the difficulty of such measurements.

B. Rate of Erosion by Sputtering. The surface equilibrium mass abundances are, of course, independent of the sputtering rate itself. However, values for the sputtering rate have ranged from 0.05 to 0.5 A^o/year implying e-folding times between 2400 and 240 years. These wide variations in S need not necessarily be discrepant as the rate of erosion is a sensitive function of the surface history of the samples [Andersen and Bay, 1972]. Furthermore, there exist examples of minerals such as ilmenite which are especially radiation damage resistant — implying very low sputtering yields [Maurette and Price, 1975]. In the context of lunar surface fractionation, once the time to approach mass fractionation equilibrium becomes comparable to, or shorter than, the integrated time that grains spend exposed to the solar wind, the enrichment factors will be correspondingly less pronounced. Consequently, systematic measurements of total erosion rates under simulated solar wind conditions are required. Once a complete set of sputtering rates is compiled it may become possible to infer surface residence times from isotopic effects. On the other hand, the detailed nature of the model presented here might be probed by measuring, for example, O-isotope enhancements in ilmenite grains which have not reached equilibrium.

The topic of mass dependence in the sputtering process itself is receiving increasing theoretical [Andersen and Sigmund, 1974] and experimental attention [Shimizu et al., 1973; Poate et al., 1975]. While simple considerations of mass conservation require that after prolonged sputtering the composition of the ejected material reflect the composition of the target, there may be important dynamic effects occurring during the irradiation which might disturb the balance. Then the sputtering rates of different atomic or isotopic species may differ from one another. In such a case, temperature sensitive diffusion processes may, for example, maintain a surface which is fractionated from the bulk even neglecting return of sputtered material. The thermal cycling of the outer few centimeters of the moon might provide the necessary stimulus for such a process.

Within certain approximations [Haff and Switkowski, to be published], 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 Eq. (17) may be generalized to

$$\delta(i/j) = \frac{S_j \, (1 - f_j)}{S_i \, (1 - f_i)} - 1 \quad . \tag{18}$$

Contemporary theories of sputtering of complex targets [Andersen and Sigmund, 1974] suggest that the additional ratio S_j/S_i might introduce a factor significantly less than the mass ratio of species i and j and would be important only when the mass difference of the elements is very large. However, until more experimental and theoretical work has been done on the sputtering rates and energy spectra associated with complex targets, we feel it is premature and perhaps misleading to go beyond the simplest possible sputtering model.

C. Ionized components. In the treatment presented herein, we have neglected processes which may affect the one-hop ballistic trajectories of ejected atoms which we have assumed to occur. Thus, 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 and thereby our conclusions. 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. Still, ions may be produced by subsequent interaction of the sputtered atoms with solar photons. The probability of this occurring is certainly negligible for those atoms whose velocity exceeds the lunar escape velocity, since photoionization lifetimes near the moon tend to be $\sim 10^5$-10^7 sec. 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 trapped on the moon much more quickly than the unreactive noble gases. Atoms of these gases are probably released at thermal energies by diffusion and therefore enter the atmosphere 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, then the fractionations produced by this mechanism would enhance those produced by sputtering.

7. CONCLUSIONS

It seems that sputtering of the lunar surface by the solar wind will give rise to significant surface heavy atom enrichments. With the use of plausible parameters within the model, calculated δ-values are seen to approach those measured for Si and O. A more detailed evaluation 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. Important tests of the model lie in the observation of enrichments in other elements, e.g., S. K and Ca. Data for more than two isotopes are especially valuable for comparison with the calculations. Enrichments are also predicted for any pair of elements and experimental measurements of cases where complicating effects due to chemical fractionation, etc. may be explicitly accounted for would be interesting.

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FIGURE CAPTIONS

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.

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

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

Fig. 4. Calculated mass enrichments in $^o/oo$ as a function of mass number for a range of values of U. ϵ is plotted for isotopes whose masses differ by 2 a.m.u.

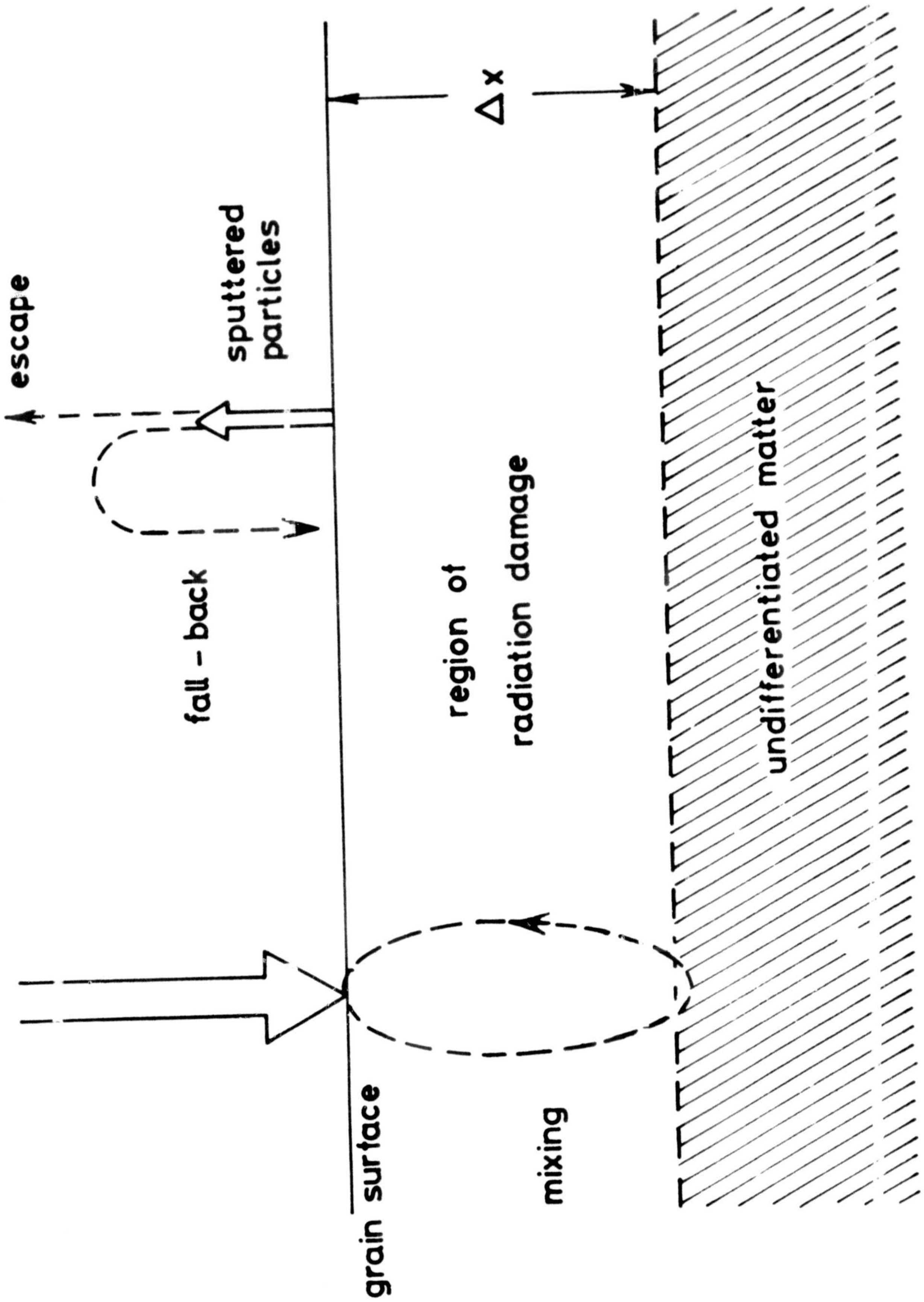
grain surface
mixing
region of
radiation damage
undifferentiated matter
Δ x
fall - back
sputtered
particles
escape

Fig. 1

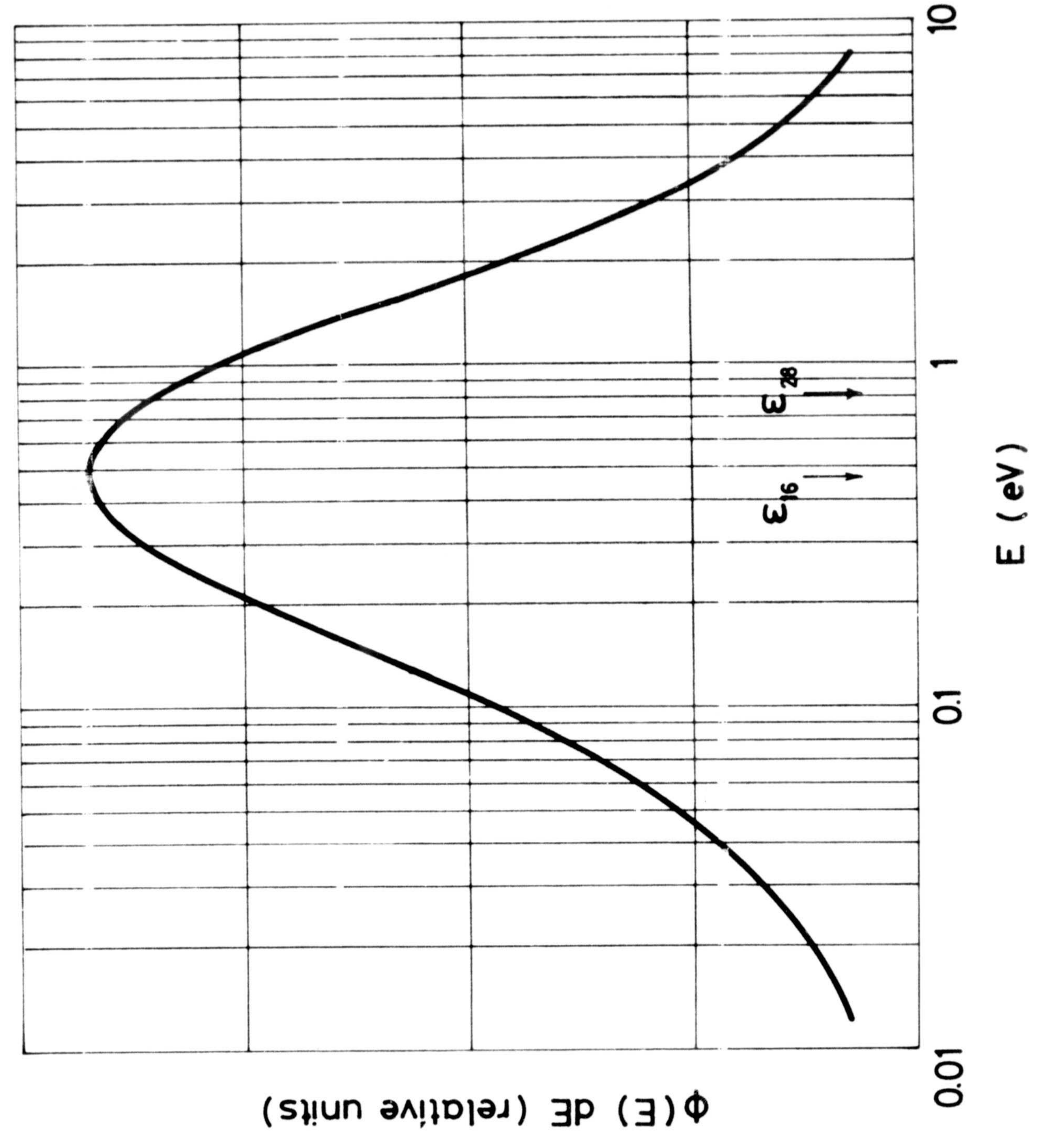
Φ(E) dE (relative units)
E (eV)
0.01
0.1
1
10
ε_{16}
ε_{28}

Fig. 2

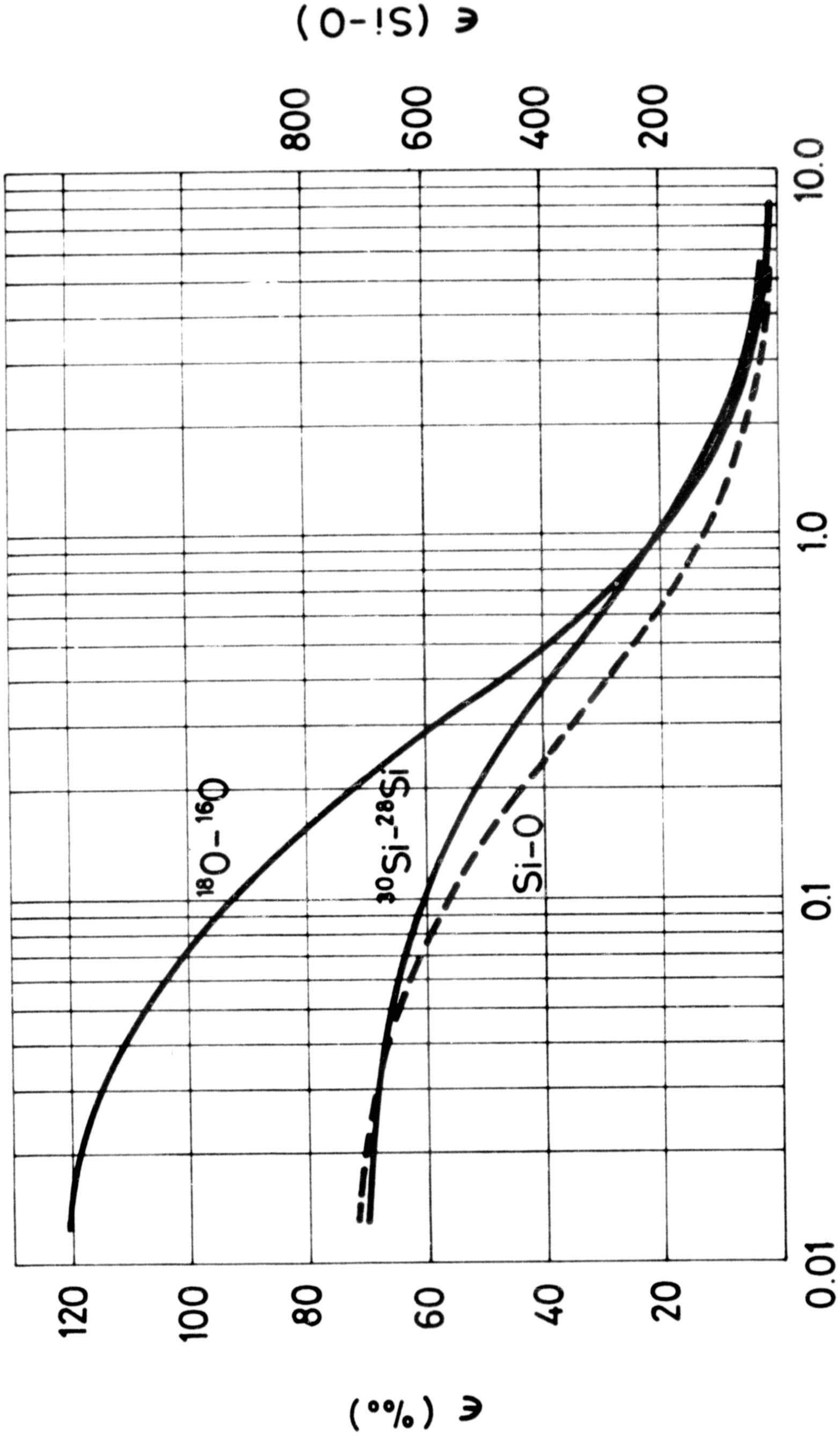
ε (‰)
120
100
80
60
40
20
0.01
0.1
1.0
10.0
E (eV)
ε (Si-O)
800
600
400
200
$^{18}O-^{16}O$
$^{30}Si-^{28}Si$
Si-O

Fig. 3

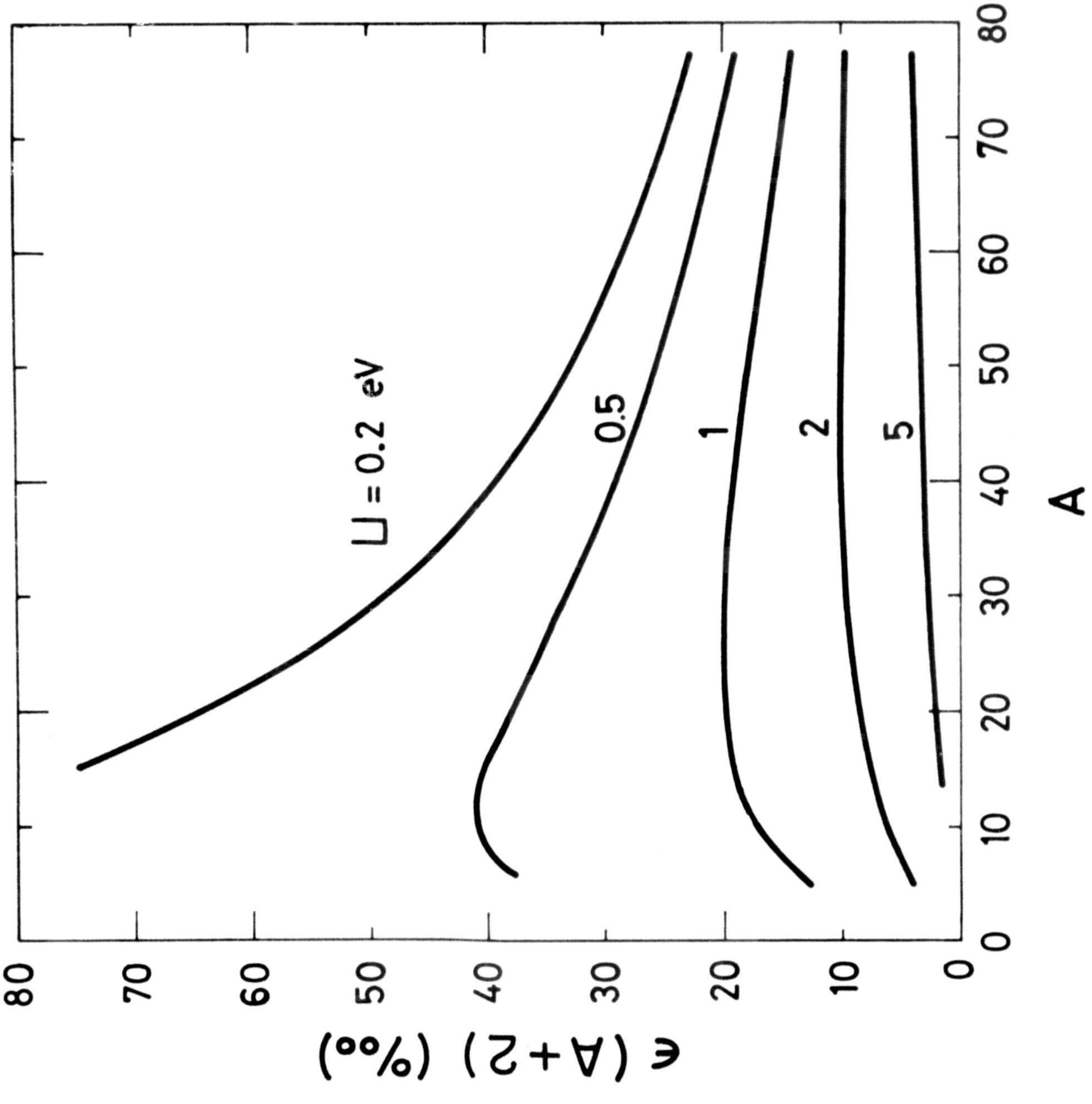

Fig. 4