

# Sputtering in Planetary Science

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## Synopsis

The interaction of energetic atoms and molecules with solid materials occurs in a variety of astrophysical environments: molecular clouds; stellar atmospheres; forming planetary systems; and satellite surfaces and atmospheres. It should, therefore, be no surprise that sputtering phenomena take place and often play important roles in the evolution of the materials involved. In this review I shall endeavor not only to show the ubiquity of sputtering in such situations but also to indicate how laboratory experiments, molecular dynamics simulation, and theory can be used together to understand better the astrophysical and planetary processes themselves. It is also important to consider that it now may be possible that the atoms/ions sputtered from planetary surfaces by the solar wind may allow remote mapping measurements of planetary surface compositions.

## 1 Introduction

The existence of stellar winds, magnetospheric trapping, and energetic shock fronts provides many environments in the universe where energetic ions, atoms, and molecules can be accelerated sufficiently to cause sputtering. A decade ago I was asked to review how sputtering was involved in solar system processes (Tombrello, 1982); this paper is intended to update and extend that report. In several ways, however, this paper will have a somewhat different emphasis. Generally, I shall concentrate on collisional sputtering; there has been a recent review of electronic excitation induced desorption/sputtering that should give the reader adequate references to the role played by such processes for the Jovian and Saturnian satellites (Johnson & Sundqvist, 1992).

A large part of my previous review was devoted to the description of how solar wind erosion of a planetary atmosphere unshielded by a magnetic field or ionosphere could gradually change the atmospheric composition (Haff et al., 1978). Examples were given for the  $^4\text{He}$  budget of Venus (Watson et al., 1980) and the erosion and

Table I. Sputtering in shock fronts. A shock velocity of 100 km/sec implies a proton energy of 50 eV and an alpha particle energy of 200 eV; at 200 km/sec these energies quadruple, i.e., 200 and 800 eV, respectively. The sputtering yield data were taken from Roth et al., (1979).

Substance	$S_p(50 \text{ eV})$	$S_p(200 \text{ eV})$	$S_\alpha(200 \text{ eV})$	$S_\alpha(800 \text{ eV})$
C	$4 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	0.07	0.09
Fe	-	$3 \cdot 10^{-3}$	0.05	0.15
Al <sub>2</sub> O <sub>3</sub>	-	$4 \cdot 10^{-3}$	0.01	0.17
SiC	$4 \cdot 10^{-4}$	$6 \cdot 10^{-3}$	0.08	0.13
SiO <sub>2</sub>	$10^{-3}$	$1 \cdot 10^{-2}$	0.03	0.13
ZrC	-	$3 \cdot 10^{-5}$	0.01	0.05
Mo	-	$10^{-5}$	0.02	0.05

differentiation of the Martian atmosphere (Haff et al., 1978; Watson et al., 1980; Haff & Watson, 1980). Although this phenomenon seems to be very far afield from our usual picture of sputtering, it represents a straightforward application of the original ideas of Thompson (1968) and Sigmund (1969), in which the surface binding energy is replaced by the gravitational potential energy (Haff et al., 1978). Since there have been few significant advances in this area, this topic will not be discussed in greater detail herein.

The moon's surface is virtually unshielded from solar wind bombardment; thus, solar wind implantation and sputtering is a significant factor in lunar surface modification (Wehner et al., 1963). One should, however, note that here (as well as on all planetary satellites) the effect of micrometeorites is usually greater (Schneider et al., 1973). Thus, it is important to understand that only when sputtering, electronic desorption, uv ionization, volcanic outfall (e.g, on Io), and meteoritic impact are put together into a comprehensive model are we likely to provide a realistic picture of planetary surface modification. Since this has not been attempted I shall deal in sect. 3 with solar wind sputtering in a more limited sense - the opportunity it may provide for surface elemental analysis from orbit.

The greatest advance that has occurred during the decade has been the unambiguous identification of grains from meteorites that show clearly their formation in stellar atmospheres (section 2.2.2). Their exposure there and subsequently in the interstellar medium to ion/atom bombardment is an important factor in determining their survival probability. For that reason, the next section will be devoted to presenting that material in detail.

## 2 Irradiation Effects on Extraterrestrial Grains

### 2.1 Formation and Destruction of Grains

It seems well established that grains are formed in the mass loss processes of red giant stars (Knapp & Morris, 1985) and novae (Gehrz et al., 1980). In the case of the former the total mass of grain production is about equally divided between oxygen-rich red giants (where silicate grains are thought to be formed (Lafont et al., 1982)) and their less common carbon-rich relatives (where carbon or SiC grains are created (Thaddeus et al., 1984)). Supernovae are also conjectured as producing grains, but this is not yet confirmed to be competitive with the red giant and nova sources (Dwek & Werner, 1981). All the known circumstellar grain creation processes (which is not expected to be a complete list) can reproduce the amount of observed interstellar dust in  $3 \times 10^9$  y (Dwek & Scalo, 1980). This material is likely to be a mix of carbon and carbide grains and refractory silicates,  $\text{Al}_2\text{O}_3$ , and  $\text{MgAl}_2\text{O}_4$  particles. These may have acquired mantles of deposited/accreted material, which in some cases are adsorbed or implanted C, N, H species and in others are composed of more refractory material that was condensed sequentially during the later stages of grain formation (Draine, 1984; Greenberg, 1984).

The subsequent history of such grains involves their exposure to supernova-generated shock fronts of the neutral gas in the interstellar medium that may destroy them before they have an opportunity either to be added to newly forming stars or perhaps to become larger solid bodies in a planetary system (Draine & Salpeter, 1979).

Sputtering from gas-grain interactions in shocks is thought to be the main destruction mechanism; the effect of grain-grain collisions has not been studied in as much detail (Seab & Shull, 1983; Seab & Shull, 1985<sup>1</sup>; Seab, 1987). Typical shock fronts that are violent enough to destroy grains have velocities between 30 and 400 km/sec (Seab & Shull, 1983; Seab & Shull, 1985; Seab, 1987); at velocities much above 100 km/sec Fe and Si in the shocked volume are observed to have cosmic abundances, i.e. virtually all the grains must be destroyed (Cowie, 1978). A relative velocity of 100 km/sec corresponds to sputtering at 50 eV/atomic mass unit. Thus, it is clear that the hydrogen plays only a small role in the sputtering ( $\lesssim 10\%$ ) and the  $^4\text{He}$  dominates (Seab & Shull, 1983; Seab & Shull, 1985; Seab, 1987) (see table I). It is estimated that shocks of this magnitude (originating in supernovae) are encountered by a grain on the average every  $10^8$  years (McKee & Ostriker, 1977). This result creates for us a dilemma – why are there any grains around that preserve details of their formation if they are created an order of magnitude more slowly [ $\sim 3 \times 10^9$  y, (Dwek & Scalo, 1980)] than they are destroyed? Below I list the evidence

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<sup>1</sup>this ref. will appear often, abbreviated hereafter as IACIID

that leads one to suspect that some grains do indeed survive and carry with them the clear mark of their creation sites.

## 2.2 Preservation of a Prior History of Stellar Grain Creation that is Indicated by the Observation of Isotopic Fractionation and Anomalies in Meteorites

The presence of significant deviations from terrestrial isotopic abundance patterns in meteoritic materials shows that they preserve information about a previous period of processing. There are clear radioactive parent-daughter associations, especially  $^{26}\text{Al}$ - $^{26}\text{Mg}$ , that point at an episode of nucleosynthesis just before the solar system formed as well as to the preservation of the signatures of stellar element formation earlier (Kerridge, 1985; Lee, 1979; Niederer & Papanastassiou, 1984).

These heterogeneities give us both insights about and constraints upon the sites where nuclear synthesis occurs. They also may preserve evidence of other types of solar system processes involving, for example, sputtering (Russell et al., 1980; Esat & Taylor, 1986) or molecular reactions (Thiemens & Heidenreich, 1983; Heidenreich & Thiemens, 1985; Bhattacharya & Thiemens, 1989) that affect isotopic distributions. In either case, these anomalies give us many clues about the formation of the solar system that we have begun to untangle, although it is certainly no exaggeration to note that so far no unique scenario has been suggested by these data (Wood, 1985).

Below I list several examples of meteoritic components that, as shown by such isotopic heterogeneities, preserve traces of their history as stellar-produced grains.

### 2.2.1 Calcium-Aluminum-Rich Inclusions (CAIs)

In meteorites one finds inclusions that have the Ca-Al-rich compositions that one would expect from the first materials to condense out of an initially-hot solar nebula (Grossman & Larimer, 1974). However, detailed study has shown that these inclusions cannot be simply accounted for by a single gas-solid fractionation process, but involved a number of stages of reprocessing (Kerridge & Bunch, 1979; Ireland, 1988; Armstrong, 1989; Keller & Buseck, 1989); some have been melted - many have been exposed to secondary lower-temperature alterations. For example, the fact that the rare earth elements have abundance patterns associated with their relative volatilities (rather than their ionic sizes as in terrestrial materials) attests to such complex processing (Kornacki & Fegley, 1986; Ireland et al., 1988). The inclusions show that at least some parts of the solar nebula were hot, but despite the evidence of a 'classical' cooling, well-mixed solar nebula, variations in the pattern of isotopes show that heterogeneities from earlier periods are preserved, although the

original interstellar materials may not have survived intact. These minerals include hibonite, perovskite, melilite, spinel, Ti-rich pyroxene, and anorthite. They contain an extremely rich (albeit confusing) assortment of isotopic heterogeneities that show unusual isotopic fractionation as well as unmistakable evidence for nucleosynthetic processes (Kerridge, 1985; Lee, 1979; Niederer & Papanastassiou, 1984).

One of the first and perhaps the most widely visible heterogeneity is in the isotopic fractionation of the oxygen isotopes. On a three isotope plot there is a unit slope for  $[^{17}\text{O}/^{16}\text{O}]$  versus  $[^{18}\text{O}/^{16}\text{O}]$  as opposed to the  $\sim 0.5$  slope exhibited by the typically fractionated terrestrial samples (Clayton, 1978; Clayton & Mayeda, 1989). Most isotopic fractionation processes observed in nature are linear in the mass difference; thus,  $^{17}\text{O}$  is usually fractionated half as much as  $^{18}\text{O}$  when both are compared to the most abundant isotope,  $^{16}\text{O}$ . This deviation from what is typical for terrestrial materials has commonly been interpreted as reflecting a reservoir (whose material form is still unspecified) of virtually pure  $^{16}\text{O}$  as well as at least two other distinct (though also unspecified) solar system oxygen reservoirs (Clayton et al., 1985). The 'pure'  $^{16}\text{O}$  could be a relic of an oxygen-rich red giant star or perhaps a supernova source based on the evolution of one (Clayton, 1975; Cameron & Truran, 1977).

Two Allende inclusions show Nd and Sm isotope distributions that reflect stellar r- and p-process material (sample, EK-1-4-4) and p-process material alone (sample, C-1) that seem to indicate a super nova origin (Lugmair et al., 1978; Wasserburg et al., 1979). (The r-process involves rapid neutron capture relative to beta decay; the p-process involves proton-induced nuclear reactions.)

Also seen in Ca-Al-rich inclusions are strong mass-dependent fractionations of the Si, Mg, and Ca isotopes (Niederer & Papanastassiou, 1984) as well as excesses of  $^{50}\text{Ti}$  (Niemeyer & Lugmair, 1984),  $^{54}\text{Cr}$  excesses that are correlated with the  $^{50}\text{Ti}$  (Birck & Allegre, 1984), and deficits of  $^{47}\text{Ti}$  (Niemeyer & Lugmair, 1984). It is curious that the presence of these anomalies occurs in the presence of a normal Mg isotopic distribution.

Another dramatic clue in these inclusions has been the discovery of  $^{26}\text{Mg}$  excesses that are associated with the  $^{27}\text{Al}$  concentration. In many cases the excess  $^{26}\text{Mg}$  is in a single mineral phase; thus, it can conceivably be attributed to relic  $^{26}\text{Mg}$  from previous  $^{26}\text{Al}$  decay (Gray & Comston, 1974). However,  $^{26}\text{Mg}$  excesses have also been found that correlate with  $^{27}\text{Al}$  in a number of coexisting phases within the inclusion. This is best explained by the in situ decay of  $^{26}\text{Al}$  that must have been produced less than  $3 \times 10^6$  years before its incorporation into the inclusion (Lee et al., 1977). That the effect was locally heterogeneous is shown by the fact that  $^{26}\text{Mg}$  deficits also occur (Kerridge, 1985; Lee, 1979; Niederer & Papanastassiou, 1984). One should note that gamma rays that follow the decay of  $^{26}\text{Al}$  have been observed in the direction of the galactic center; thus, this apparent

novae-produced  $^{26}\text{Al}$  could have been responsible for the incorporation of either 'live'  $^{26}\text{Al}$  or its relic  $^{26}\text{Mg}$  into the solar system early in its history (Mahoney et al., 1984; Share et al., 1985).

### 2.2.2 Bulk and Acid-Resistant Residues from Carbonaceous Chondrites

Neon data from carbonaceous chondrites was one of the earliest indications that there were heterogeneities in the isotopic patterns of some elements. In this case a neon component (Ne-E) that was virtually pure  $^{22}\text{Ne}$  was identified (Black, 1972). This material may be due to the very short lived parent  $^{22}\text{Na}$  ( $T_{1/2} \sim 2.5$  years) perhaps produced by proton irradiation; however, there has been no association of the Ne-E component with a Na mineral, so the path by which this isotope arrived in its meteoritic home is so far totally unspecified (Eberhardt et al., 1981).

Probably the clearest and most dramatic association of a meteoritic mineral fraction with a specific stellar origin is provided by Xe. By subjecting a carbonaceous chondrite to a sequence of acid dissolution steps, one is left with an acid-insoluble residue. Two of its components bear the unmistakable signatures of their origin. One is carbon in the form of diamond which has a Xe isotope pattern (Xe-HL) that is enriched in both the lightest and the heaviest isotopes, i.e. p- and r-process Xe that would have come from a supernova (Tang et al., 1988; Anders et al., 1989).

Although its designated source is more ubiquitous, the other component, SiC, is no less significant. The Xe in the SiC has an s-process Xe isotopic pattern, a big Ne-E component ( $^{22}\text{Ne}$ ), enrichments in  $^{29}\text{Si}$  and  $^{30}\text{Si}$ , as well as depletions of  $^{12}\text{C}$  and  $^{14}\text{N}$ . (The s-process involves neutron capture reactions that are slow compared with beta decay.) Thus, the origin of the SiC in a carbon-rich red giant (with perhaps proton irradiation and even supernova components as well) seems unavoidable. There is apparently a  $^{21}\text{Ne}$  excess, which if it is cosmic ray produced, indicates that the material was incorporated into the meteorite within 40My (Anders et al., 1989; Lewis et al., 1990). It is indeed a puzzle how so many noble gas atoms could be implanted into a grain without causing its destruction. Thus, one can only surmise that these atoms were incorporated simultaneously with the accretion of the grain.

Unlike isotopic heterogeneities associated with the calcium-aluminum rich inclusions, both the diamond and SiC thus seem to have been delivered to us in a pristine condition - despite the fact that we expect such grains to have been destroyed (or at least appreciably modified - thereby losing the Xe and Ne). Some SiC grains have been large enough to be analyzed individually and show uniform C, N, Si compositions with depth. These grains could be products from a single star,

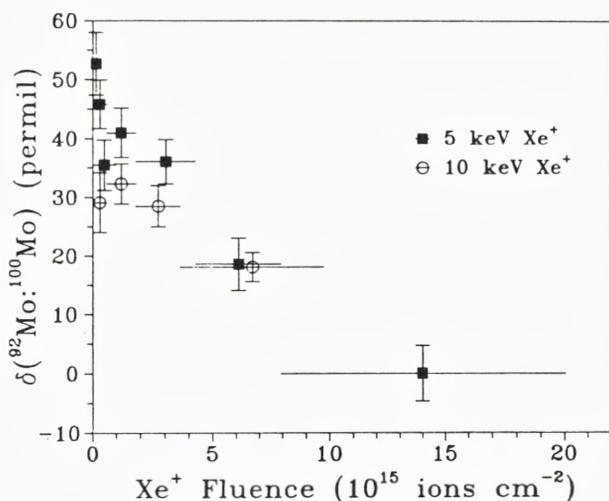


Figure 1. Isotopic fractionation of the Mo flux sputtered into near-normal directions ( $\theta \simeq 17^\circ$ ) vs. the bombarding fluence for  $\text{Xe}^+$  projectile. Each symbol is plotted at the midpoint of the fluence range used for the corresponding collection; the horizontal bar through each symbol indicates this range. Uncertainties indicated by the vertical error bars are  $\pm 2\sigma$ . Taken from Weathers et al. (1992).

but to be confident of this interpretation, knowledge of grain destruction lifetimes is required.

### 2.2.3 Interplanetary Dust Particles (IDPs)

Our information about grains in the neighborhood of the sun comes not only from their observation in the scattering of electromagnetic radiation (as for their interstellar cousins) (Mathis, 1985) but also from their detailed study as micrometeorites that are collected in sediments and the stratosphere (interplanetary dust particles/IDPs/Brownlee particles), in space, and perhaps as constituents of meteorites (Walker, 1985). We, of course, are close to the point where we shall have an even greater supply of these small objects from the space station and perhaps a cometary-sample-return mission. The IDPs have a variety of forms; some are compact with densities near  $2 \text{ g/cm}^3$ ; others are porous/fluffy. Their compositions/structure can be associated with 'olivine', 'pyroxene', and 'layer lattice silicates' (Walker, 1985). It is not unreasonable to assume that they are at least in part the building blocks from which some of the larger meteorites formed, and their optical properties have already been shown to be similar to those of comets (Sandford & Walker, 1985). So far none of these objects has a strong resemblance

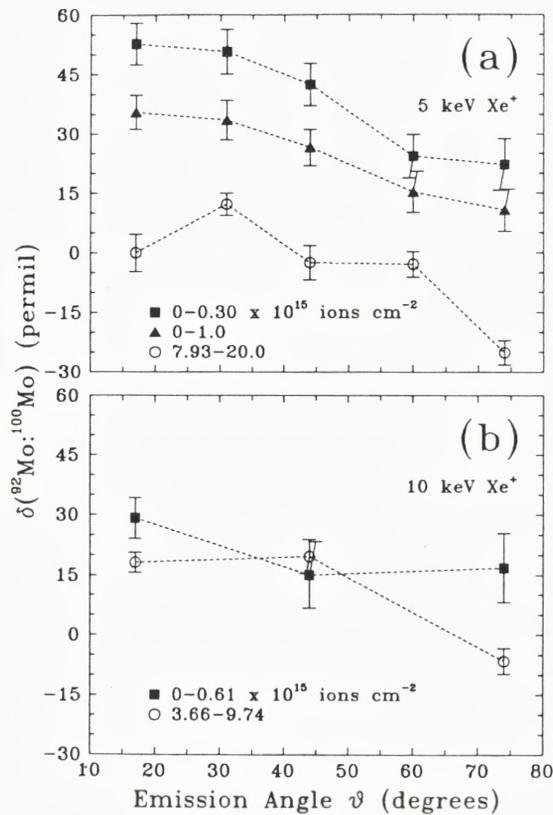


Figure 2. Isotopic fractionation of sputtered Mo vs. emission angle measured from the target normal for different indicated fluence ranges of (a) 5 keV  $\text{Xe}^+$  and (b) 10 keV  $\text{Xe}^+$  projectiles. Indicated uncertainties are  $\pm 2\sigma$ . Taken from Weathers et al. (1992).

to the interstellar grains that we briefly surveyed above, e.g. no refractory cores (Tomecka & Buseck, 1984); however, many contain carbon (mostly amorphous) compounds (Christofferson & Buseck, 1983; Rietmeijer & Mackinnon, 1985). Most of the objects at hand seem to have been formed by vapor phase condensation (Bradley et al., 1983). They have been exposed to intense ion bombardment in the early stages of the formation of the solar system as well as more recently to the solar wind. Because of their small size this irradiation may have been especially significant in altering their elemental and isotopic compositions.

Generally, the small size of these objects has precluded the use of the full arsenal of isotopic measurements that have been done on meteorites. Deuterium has large

enrichments ( $\sim 25\%$ ) which are variable on a few-micron scale. This excess seems to be associated with carbon but not with OH. The carbon isotopic ratios are constant over a given grain but vary from grain to grain. Mg and Si isotopes show terrestrial ratios (Walker, 1985).  $^{16}\text{O}$ -rich oxygen has been found in a few IDPs but with enrichments within the range of other meteoritic materials. The grains probably have too few noble gas atoms for isotopic analyses to be performed on individual grains.

## 2.3 Basic Questions about Grain Sputtering that Need to be Answered

We see from the examples in the previous section that although grains coming from stellar sources are exposed to sputter erosion, some individual grains apparently survive having preserved a clear signature of stellar nucleosynthetic processes. Better knowledge of sputtering is, therefore, important in two respects. First, we need reliable estimates of what types of grain materials are likely to survive and the statistical lifetimes involved. Second, we need to know to what extent sputtering, which is known to produce elemental and isotopic fractionation itself, has distorted the image that is retained by the surviving grains.

### 2.3.1 Sputtering Yields and Fractionation

Although there is much data on the sputtering yields from ion bombardment (sputtered atoms/ion) for elemental metallic targets, there is much less for compounds and virtually none for refractory minerals of the types discussed in section 2.2.1 (Kaminsky, 1965; Behrisch, 1981,1983). Generally, yields can vary substantially and the role of adsorbed layers or overlying mantles can modify the yields. One must also note that preferential sputtering is important in the context discussed herein because it can lead to altered surface layers on the grains that have very different properties than those of the bulk material. Such selective effects obviously lead to the preferential destruction or preservation of particular grain types. (See table I for examples of sputtering yields in order to get a feeling for the range of values for different materials (Roth et al., 1979).) In addition to obtaining more complete laboratory data there is also a clear need to improve the molecular dynamics simulations that can both give us better intuition about preferential sputtering processes and also allow extrapolations to situations not possible in the laboratory, e.g. sputtering of small objects, rough surface effects, coating layers, etc. Such simulations have already had a major impact on our knowledge of isotopic fractionation by sputtering (Shapiro et al., 1985; Shapiro et al., 1988; Lo et al., 1989).

Early measurements by our group for Ca minerals showed enrichment of 1-2% in the total yield of  $^{40}\text{Ca}/^{44}\text{Ca}$  at moderate fluences and a 1.5-2% fractionation between ejection normal and oblique to the surface even at large fluences where the material removed overall was in isotopic equilibrium, i.e. equivalent to the bulk value (Russell et al., 1980). Simulations to understand these data at a more fundamental level showed that the observed fractionations should have been much larger ( $\sim 10\%$ ) (Shapiro et al., 1985; Shapiro et al., 1988; Lo et al., 1989); the Ca effects had been diluted by too large a bombarding fluence. Subsequent data for secondary ions of Mo, Li, etc. (Gnaser & Hutcheon, 1988) and of boron (Baumel et al., 1988) showed large effects that agreed with the simulations. These prompted our examination of the sputtering of neutral atoms from Mo, which was chosen because it represented a low sputtering yield typical of interstellar grain materials (see table I) and because we could conveniently make a pure metallic target of 50%  $^{92}\text{Mo}$ -50%  $^{100}\text{Mo}$  to give an easily visible effect for comparison with the molecular dynamics simulations. Examples from these data are shown versus ion fluence in Figure 1 and versus angle from the surface normal in Figure 2; one observes that the effects are enormous both at low fluences ( $\sim 6\%$ ) and across the range of ejection angles ( $\sim 2\%$ ) independent of fluence (Weathers et al., 1989; Weathers et al., 1993). Other recent isotopic fractionation data are given in table II (Gnaser & Hutcheon, 1988; Baumel et al., 1988; Weathers et al., 1989; Weathers et al., 1992; Gnaser & Oechsner, 1989; Gnaser & Oechsner, 1990).

In our Ca experiment we showed that  $^{43}\text{Ca}/^{44}\text{Ca}$  was fractionated linearly relative to  $^{40}\text{Ca}/^{44}\text{Ca}$ , although the precision ( $\sim 0.1\%$ ) was not as good as one would like due to the low abundance of  $^{43}\text{Ca}$  (Russell et al., 1980). It is especially important to determine if sputtering produces effects that are linear in the mass difference; if it does not (as suggested by Esat and Taylor (1986)) then it is possible that some anomalies attributed to nucleosynthetic processes may arise from a more prosaic source.

Since sputtering is expected to play a significant role in the processing of every interstellar grain, we should have quantitative data about how this processing modified the elemental and isotopic composition of what survives. To do this properly suggests that data be obtained for relevant materials (e.g., C, SiC, and CAI minerals) that give overall erosion yields as well as establishing the degree of fractionation that can arise. One might also consider the co-deposition of noble gas atoms with Si and C to determine whether the SiC grains observed by Lewis et al. (1990) could have been formed in this way. These data should be tied together by molecular dynamics (MD) simulations, and careful modeling of sputtering in shocks should be repeated using these data. Examples of the relevant shock and grain history models are Seab & Shull, (1983) and Liffman & Clayton, (1988); Seab et al., (1985); Liffman, (1990), respectively.

Table II. Low-fluence isotopic fractionation data from other experimental studies. In the upper group of measurements, intensities of positive secondary ions were observed; in the lower group, intensities of sputtered neutrals were observed. In all cases, the lowest bombarding fluences were  $\sim 1 \cdot 10^{15}$  ions/cm<sup>2</sup>. Taken from Weathers et al. (1993).

Ref.	Projectile	$\theta(\text{deg})^{\text{a}}$	Fluence to Steady State (ions/cm <sup>2</sup> )	Target	Isotope Pair	Mass Ratio $M_{\text{H}}/M_{\text{L}}$	$\theta(\text{deg})^{\text{b}}$	$\delta(^{\circ}/\infty)^{\text{c}}$
f)	14.5 keV O <sup>-</sup>	$\sim 10$	$\sim 5 \cdot 10^{16}$	TiO <sub>2</sub>	<sup>46</sup> Ti <sup>+</sup> ; <sup>50</sup> Ti <sup>+</sup>	1.0869	$\lesssim 15$	$63 \pm 13$
"	"	"	NA <sup>d</sup>	Natural Mo	<sup>92</sup> Mo <sup>+</sup> ; <sup>100</sup> Mo <sup>+</sup>	1.0870	$\lesssim 15$	$49 \pm 4.3$
g)	100 keV Ar <sup>+</sup>	30	$\sim 3 \cdot 10^{17}$	Natural B	<sup>10</sup> B <sup>+</sup> ; <sup>11</sup> B <sup>+</sup>	1.0995	0	$51.8 \pm 1.8$
g)	100 keV Ne <sup>+</sup>	"	$\sim 2 \cdot 10^{18}$	"	"	"	0	$46.1 \pm 2.4$
h)	5 keV Ar <sup>+</sup>	30	$\sim 6 \cdot 10^{16}$	Natural Mo	<sup>92</sup> Mo; <sup>100</sup> Mo	1.0870	0	$51 \pm 4$
h)	"	0	"	"	"	"	30	$65 \pm 14$
h)	"	30 <sup>e</sup>	"	"	"	"	60	$57 \pm 12$
i)	5 keV Ar <sup>+</sup>	30	$\sim 2 \cdot 10^{16}$	Ge (100) Crystal	<sup>70</sup> Ge; <sup>76</sup> Ge	1.0858	0	$52 \pm 5$

a) Projectile angle of incidence, measured from the target normal.

b) Angle of ejection of the sputtered material, measured from the target normal.

c) Isotopic fractionation measured at the lowest bombarding fluences, normalized to the steady-state isotope ratio at the same ejection angle, indicated uncertainties are  $\pm 2\sigma$ .  $\delta$  given in parts per thousand ( $^{\circ}/\infty$ )

d) Not available.

e) The direction of incidence was such that the angle between the projectile path and the emission direction of the analyzed material was also 30°.

f) Gnaser and Huchon (1988).

g) Baumel et al. (1988).

h) Gnaser and Oechsner (1989).

i) Gnaser and Oechsner (1990).

### 2.3.2 Grain-Grain Collisions

Although one might not automatically make the connection, the collisions of small grains in the interstellar medium are not really very different from the impacts of large molecular ions (cluster ions) on surfaces. This topic has become an exciting area in ion-solid interactions both because it represents an extreme case of non-linear energy deposition and because of its technological applications.

It has not only been possible to do experiments with such ions, it has also been possible to simulate the gross features of such impacts by molecular dynamics models. These simulations show that at the bombarding energies corresponding to an interstellar shock front ( $\sim$  keV/atom), the grains are expected to be completely destroyed in such collisions (Shapiro & Tombrello, 1990, 1991). However, at low energies ( $\sim$ eV/atom), where the simulations were performed to guide thin film deposition attempts, there was a high probability for their sticking together (Hsieh & Averbach, 1990). Obviously, at intermediate velocities one expects to find to an increasing degree crater formation, fragmentation, etc. (Hsieh & Averbach, 1990; Pelletier et al., 1992).

This area of simulation appears to have the potential for improving our intuition about such grain collision phenomena. For example, to what degree are the volatile mantle materials evaporated, ablated, etc. in soft collisions (eV/atom)? This is important because the grain surfaces may serve as sites for the formation of some types of organic molecules that are observed in the interstellar medium (Watson, 1976). It is also suggested from the simulations that the heating induced even in the softer collisions may also cause substantial alteration of the grain-core composition itself.

## 3 Using Solar Wind Sputtering for Remote Planetary Surface Analysis

Because the moon's surface is virtually always exposed to bombardment by the solar wind, surface atoms are always being sputtered. There have been several proposals to detect the neutral atoms (Tombrello & Neugebauer, 1990) or the ions (Elphic et al., 1991; Johnson & Baragiola, 1991) from lunar orbit.

At the earth's orbit the solar wind consists mainly of hydrogen and helium ions. The flux is about  $3 \times 10^8$  protons/cm<sup>2</sup>sec having energies of  $\sim$  1 keV and  $10^7$  alpha particles/cm<sup>2</sup>sec with energies of  $\sim$  4 keV (Feldman et al., 1977). The sputtering yields (ejected atoms per incident ion) on typical lunar surface materials will be like those of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, which are of the order of 0.02 for the protons and 0.1 for the alphas (Roth et al., 1979). Thus, the exposed lunar surface yields  $\sim 7 \times 10^6$

atoms/cm<sup>2</sup>sec from these solar wind components. Although the heavier ions in the solar wind have higher sputtering yields, their lower abundances cause their contributions to the overall ejected atom yield to be  $\sim 10\%$  of that from hydrogen and helium. The energy spectrum (Thompson, 1968) of atoms sputtered by keV projectiles has the approximate form

$$\frac{E}{(E + B)^3}, \quad (1)$$

where B is the surface binding energy of an atom in the target material. Typically,  $B \sim 5$  eV, so that the peak of this spectrum, which occurs at  $B/2$ , is at  $\sim 2.5$  eV. The escape velocity for the moon is  $2.37 \times 10^5$  cm/sec; for oxygen atoms this corresponds to 0.5 eV, while for Si, 0.8 eV. The ability to escape depends also on the direction of motion of the sputtered atom, but most are expected to escape or at least reach spacecraft altitude (100 km for the proposed Lunar Observer Mission (Nash, 1990)). The angular distribution of sputtered atoms from a smooth surface is  $\cos^n \theta$ , where  $\theta$  is measured from the normal to the surface and  $n$  is 1-2, although surface roughness tends to make  $n \lesssim 1$ . In addition, the angular distribution seen from a spacecraft will be affected by the large-scale topography of the planet. As a result of the long-term solar wind irradiation, lunar soil surfaces are expected to have reached steady state with respect to sputtering; thus, the relative fluxes of sputtered atoms give the composition directly.

The intent of these proposals is to explore the feasibility for a flight instrument on the orbiter which will measure the atom/ion composition sputtered from the lunar surface. Such an instrument would give a SIMS-like analysis of the lunar surface that would complement the planned  $\gamma$ -ray and x-ray fluorescence measurements since the sputtered atoms would come mainly from the major surface constituents, whereas the x-rays only provide information on the light elements Mg, Al, and Si and the  $\gamma$ -rays come mainly from radioactive elements (natural and produced by energetic cosmic ray and solar flare particles) that lie within  $\sim 1$  m of the surface and only provide information on a subset of heavier elements. Generally, the sputtered atom distributions should allow the determination of the basic lithology of the surface (e.g., rock and mineral types) for the major elemental constituents down to  $\sim 1\%$  levels - instrumental and spacecraft background permitting. It should also be possible to obtain information on minor components as well, but those would be averaged over much larger areas of the surface. Thus, one would get information on all major elements present (such as Ca, which is not determined from the x- and  $\gamma$ -rays), and we would be consistently analyzing the surface material.

Much photo-geologic evidence suggests that certain fairly extensive dark mantling deposits on the moon are products of volcanic fire fountains (Hawke, 1990).

Laboratory study of homogeneous lunar glass spherules thought to be representative of such fire fountain material show surface enrichments of a number of elements including K, halogens, S, and Zn (Meyer, 1990). This suggests the interesting possibility that a mass spectroscopic instrument such as those being considered could identify and map pyroclastic deposits. This takes advantage of the fact that since sputtered atoms come primarily from the surface atomic layer of the material, these thin surface deposits might be detected.

## 4 Conclusions

It was not my intention in this review to cover all possible ways in which sputtering can affect the properties of planetary materials. In the case of the interstellar grains that may have been an ingredient in the formation of our solar system, I have tried to provide a systematic introduction for the reader who may be interested in learning more about this subject. This story is certainly one of the most exciting that has arisen recently, i.e., that we can see the clear signs of the stellar origins of some of this material, preserved in what seems to be nearly pristine form. How this observation can be reconciled with the high probability for the sputter-destruction or modification of such grains should provide us with many research topics.

In the case of solar wind sputtering of planetary surfaces I have attempted to show the yet untested potential for such observations to provide remote analyses of planetary surfaces. Overcoming the obvious technical difficulties of these proposals will not be easy; however, the technique offers a unique opportunity that is well matched to low-cost space missions that should not be ignored. Here we need first to explore carefully the limitations of the technique in the laboratory as a prelude to designing flight instruments.

In my desire to hold this review to within reasonable limits, I have managed to slight the role played by sputtering in many other planetary contexts. In addition to those other topics listed in the introduction (e.g., atmospheric sputtering and electronic excitation mediated desorption) one obviously could add many more - the endless variety of environments in the universe provides so many opportunities for energetic particle bombardment. I can only assume that if I am asked to do this again in a decade hence, that paper will look as different from this one as this does from its predecessor.

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## References

- Anders E, Lewis RS, Tang M and Zinner E, 1989: IAU Symposium 135, NASA-Ames Research Center, California, July 1988
- Armstrong JT, 1989: Lunar Planet. Sci. **XX**, 23
- Baumel LM, Weller MR, Weller RA and Tombrello TA, 1988: Nucl. Instrum. Methods B **34**, 427
- Behrisch R (ed.), 1981: *Sputtering by Particle Bombardment I*, Top. Appl. Phys. **47**, (Springer Verlag, NY)
- Behrisch R (ed.), 1983: *Sputtering by Particle Bombardment II*, Top. Appl. Phys. **52**, (Springer Verlag, NY)
- Bhattacharya SK and Thiemens MH, 1989: Lunar and Planet. Sci. **XX**, 71
- Birck JL and Allegre CJ, 1984: Geophys. Res. Lett. **11**, 943
- Black DC, 1972: Geochim. Cosmochim. Acta **36**, 377
- Bradley JP, Brownlee DE and Veblen DR, 1983: Nature **301**, 473
- Cameron AGW and Truran JM, 1977: Icarus **30**, 447
- Christofferson R and Buseck PR, 1983: Lunar Planet. Sci. **XIV**, 411
- Clayton DD, 1975: Astrophys. J. **199**, 765
- Clayton RN, 1978: Ann. Rev. Nucl. Part. Sci. **28**, 501
- Clayton RN and Mayeda TK, 1989: Lunar Planet. Sci. **XX**, 169
- Clayton RN, Mayeda TK and Molini-Velsko CA, 1985: *Protostars and Planets II* (Univ. of Arizona, Tucson), p. 755
- Cowie LL, 1978: Astrophys. J. **225**, 887
- Draine BT, 1984: *Protostars and Planets II*, ed. T. Gehrels (Univ. Ariz. Press, Tucson)
- Draine BT and Salpeter EE, 1979: Astrophys. J. **231**, 438
- Dwek E and Scalo JM, 1980: Astrophys. J. **239**, 193
- Dwek E and Werner MW, 1981: Astrophys. J. **248**, 138
- Eberhardt P, Jungck MHA, Meyer FO and Niederer FR, 1981: Geochim. Cosmochim. Acta **45**, 1515
- Elphic RC, Funsten HO III, Barraclough BL, McComas DJ, Paffett MT, Vaniman DT and Heiken G, 1991: Geophys. Res. Lett. **18**, 2165
- Esat TM and Taylor SR, 1986: Lunar Planet. Sci. **XVII**, 208
- Feldman WC, Asbridge JR, Bame SJ and Gosling JT, 1977: *The Solar Output and its Variation*, O. R. White, ed. (Colorado Associated University Press, Boulder) pp. 351-382
- Gehrz RD, Grasdalen GL, Hackwell JA and Ney EP, 1980a: Astrophys. J. **237**, 855
- Gehrz RD, Hackwell JA, Grasdalen GL, Ney EP, Neugebauer G, Sellgren K, 1980b: Astrophys. J. **239**, 570
- Gnaser H and Hutcheon ID, 1988: Surface Sci. **195**, 499
- Gray CM and Comston W, 1974: Nature **251**, 495
- Greenberg JM, 1984: *Laboratory and Observational Infrared Spectroscopy of Interstellar Dust* (Royal Obs., Edinburgh) p. IV
- Grossman L and Larimer JW, 1974: Rev. Geophys. Space Phys. **12**, 71
- Haff PK and Watson CC, 1980: J. Geophys. Res. **82**, 8436
- Haff PK, Zwitkowski ZE and Tombrello TA, 1978: Nature **272**, 803

- Hawke BR, 1990: *Lunar Volcanic Glasses: Scientific and Resource Potential*, J. W. Delano and G. H. Heiken, eds. (Lunar and Planetary Inst., Technical Report 90-02) pp. 34-40
- Heidenreich JE and Thiemens MH, 1985: *Lunar Planet. Sci.* **XVI**, 335
- Hsieh H and Averbach RS, 1990: *Phys. Rev.* **B42**, 5365
- Ireland TR, 1988: *Geochim. Cosmochim. Acta* **52**, 2827
- Ireland TR, Fahey AJ and Zinner EK, 1988: *Geochim. Cosmochim. Acta* **52**, 2841
- Johnson RE and Baragiola R, 1991: *Geophys. Res. Lett.* **18**, 2169
- Johnson RE and Sundqvist BUR, 1992: *Phys. Today* **45**, 28
- Kaminsky M, 1965: *Atomic and Ion Impact Phenomenon Metal Surfaces* (Springer, Berlin)
- Keller LP and Buseck PR, 1989: *Lunar Planet. Sci.* **XX**, 512
- Kerridge JF, 1985: IACIID, p. 71 (refer to Seab & Shull, 1985 for complete description of this reference source)
- Kerridge JF and Bunch TE, 1979: *Asteroid* (Univ. of Arizona, Tucson), p. 745
- Knapp GR and Morris M, 1985: *Astrophys. J.* **292**, 640 [also see erratum (1986) *Astrophys. J.* **303**, 521]
- Kornacki AS and Fegley B, Jr., 1986: *Earth Planet. Sci. Lett.* **79**, 217
- Lafont S, Lucas R and Omont A, 1982: *Astr. & Astrophys. J.* **106**, 201
- Lee T, 1979: *Rev. Geophys. Space Phys.* **17**, 1591
- Lee T, Papanastassiou DA and Wasserburg GJ, 1977: *Astrophys. J. Lett.* **201**, L107
- Lewis RS, Amari S and Anders E, 1990: *Nature* **348**, 293
- Liffman K, 1990: *Astrophys. J.* **355**, 518
- Liffman K and Clayton DD, 1988: *Proc. Eighteenth Lunar and Planetary Sci. Conf.*, p. 637
- Lo DY, Tombrello TA and Shapiro MH, 1989: *Nucl. Instr. Meth.* **B40/41**, 270
- Lugmair GW, Marti K and Scheinin NB, 1978: *Lunar Planet. Sci.* **IX**, 677
- Mahoney WA, Ling JC, Wheaton WA and Jacobson S, 1984: *Astrophys. J.* **286**, 578
- Mathis JS, 1985: IACIID p. 29 (refer to Seab & Shull, 1985 for the complete description of this reference source)
- McKee CF and Ostriker JP, 1977: *Astrophys. J.* **218**, 148
- Meyer C, 1990: *Lunar Volcanic Glasses: Scientific and Resource Potential*, J. W. Delano and G. H. Heiken, eds. (Lunar and Planetary Inst., Technical Report 90-02) pp. 50-51
- Nash DB, ed., 1990: *Lunar Observer: An Essential Robotic Mission to Prepare for Human Exploration of the Moon*, (JPL), draft
- Niederer FR and Papanastassiou DA, 1984: *Geochim. Cosmochim. Acta* **48**, 1279
- Niemeyer S and Lugmair GW, 1984: *ibid*, 1401
- Pelletier JD, Shapiro MH and Tombrello TA, 1992: *Nucl. Instr. Meth.* **B67**, 296
- Rietmeijer FJM and Mackinnon IDR, 1985: *Nature* **315**, 733
- Roth J, Bohdansky J and Ottenberger W, 1979: *Data on Low Energy Light Ion Sputtering*, IPP 9/26 (Max-Planck-Inst. für Plasmaphysik, Garching bei München)
- Russell WD, Papanastassiou DA and Tombrello TA, 1980: *Radiat. Eff.* **52**, 41
- Sandford S and Walker RM, 1985: *Astrophys. J.* **291**, 838
- Schneider E, Sturzer D, Hartung JB, Fechtig H and Gentner W, 1973: *Geochim. Cosmochim. Acta Suppl.* **4** 3277
- Seab CG, 1987: *Interstellar Processes*, eds. D. J. Hollenbach and H. A. Thronson, Jr. (Reidel Publ. Co., Boston) p. 491
- Seab CG and Shull JM, 1983: *Astrophys. J.* **275**, 652
- Seab CG and Shull JM, 1985: *Interrelationships Among Circumstellar, Interstellar and Interplanetary Dust*, eds. J. A. Nuth and R. E. Stencel (NASA Conf. publications 2403) p. 37
- Seab CG, Hollenbach DJ, McKee CF and Tielens AGGM, 1985: IACIID, p. A-28
- Shapiro MH and Tombrello TA, 1990: *Phys. Rev. Lett.* **65**, 92

- Shapiro MH, Haff PK, Tombrello TA and Harrison DE, Jr., 1985: Nucl. Instr. Meth. **B12**, 137
- Shapiro MH, Tombrello TA and Harrison DE, Jr., 1988: Nucl. Instr. Meth. **B30**, 152
- Share GH, Kinzer RL, Kurfess JD, Forrest DJ, Chupp EL, and Rieger E, 1985: Astrophys. J. **292**, L61
- Sigmund P, 1969: Phys. Rev. **184** 383
- Tang M, Lewis RS, Anders E, Grady MM, Wright IP and Pillinger CT, 1988: Geochim. Cosmochim. Acta **52**, 1235
- Thaddeus P, Cummins SE and Linke RA, 1984: Astrophys. J. Lett. **283**, L45
- Thiemens MH and Heidenreich JE, 1983: Science **219**, 1073
- Thompson MW, 1968: Phil. Mag. **18**, 377
- Tombrello TA, 1982: Rad. Eff. **65**, 149
- Tombrello TA and Neugebauer MM, 1990: Proposal to the Caltech President's Fund, unpublished
- Tomeoka K and Buseck PR, 1984: Lunar Planet. Sci. **IV**, 858
- Walker RM, 1985: Ibid, p. 55
- Wasserburg GJ, Papanastassiou DA and Lee T, 1979: *Les Elements et Leurs Isotopes dan l'Univers*, (Liege) p. 203
- Watson CC, Haff PK and Tombrello TA, 1980: Geochim. Cosmochim Acta (Proc. Lunar Sci. Conf. 11th, Houston, TX) p. 2479
- Watson WD, 1976: Rev. Mod. Phys. **48**, 513
- Weathers DL, Hutcheon ID, Gnaser H, Tombrello TA and Wasserburg GJ, 1989: Lunar Planet. Sci. **XX**, 1185
- Weathers DL, Spicklemire SJ, Tombrello TA, Hutcheon ID and Gnaser H, 1993: Nucl. Instr. Meth. B **73**, 135
- Wehner GK, Kennight C and Rosenberg DL, 1963: Planet. Space Sci. **11**, 885
- Wood JA, 1985: (working group chm.) IACIID, p. W6-33

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