

of the lactose operon. In our view, the model is fundamentally correct and consistent with experimental results.

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# The Loss of Atmosphere from Mars

Luhmann *et al.* (1) and Jakosky *et al.* (2) showed that the Martian atmosphere was eroded (sputtered) by energetic  $O^+$  ions that are formed from escaping O and accelerated back into the atmosphere by the solar wind fields. This collisional ejection process appears to explain measured isotope ratios for Ar and N in the martian atmosphere (2, 3) and it may affect the early evolution of this atmosphere (1–3). More recently, D. M. Kass and Y. L. Yung (4) presented a more detailed calculation of the loss of Martian atmosphere. They found that 3 bars of  $CO_2$  are driven off by sputtering, an amount three times greater than the size of Earth's atmosphere. This is a huge increase in atmospheric loss over the earlier estimate of about 0.1 bars (1, 2). This increase came about because Kass and

Young assumed that full dissociation of  $CO_2$  ( $\rightarrow C + 2O$ ) occurs readily in collisions of an incident O with  $CO_2$ . Therefore, C atoms, which have much lower gravitational escape energies than  $CO_2$  or CO, are efficiently formed and energized, which increases the loss of C dramatically.

Because the collisional dissociation cross sections in the energy range of interest ( $\sim 20$  eV to 1 keV) have not been measured, the dissociation cross section used by Kass and Yung essentially maximized the atmospheric loss process. The cross section they used for dissociation in  $O + CO_2$  collisions can be compared to a molecular dynamics calculation (Fig. 1). In that calculation, the energetic O interacts with each of the atoms in the molecule that are bound together by pair potentials chosen to reproduce the binding energies and interatomic separations of  $CO_2$  and the dissociation product CO. Although the use of pair potentials in this manner typically leads to an overestimate of the dissociation cross section, the threshold for full dissociation (solid curves) described by Kass and Yung is shifted by about a factor of 5 from that calculated, and the size of their cross section is more than an order of magnitude larger than that calculated. Because the size of their cross section is roughly that of the elastic collision cross section, the net contribution of dissociation to the atmospheric loss process is more than an order of magnitude too large. In addition, the primary collisional dissociation channel is seen to be  $CO_2 \rightarrow O + CO$ , so that only a small fraction of the struck  $CO_2$  produces C atoms. Therefore, although it is correct that including  $CO_2$  dissociation in all stages of the cascade of collisions initiated by an incident  $O^+$  increases the C loss rate over that described earlier (1, 2), Kass and

Yung's estimate of the effect is an order of magnitude too large.

Although over the history of Mars it is certainly possible that more atmosphere may be driven off by sputtering than the amount given by Luhmann *et al.* (1) and by Jakosky *et al.* (2), it cannot occur in the manner suggested by Kass and Yung (4), even if their cross sections were correct. That is, as the atmospheric escape rate increases, the region in which the solar wind ionizes and accelerates the escaping atoms occurs at larger distances from the planet (5), reducing the fraction of these ions that impact the atmosphere. In the earliest martian epoch this feedback process is already problematic for the much lower escape rates calculated by Luhmann *et al.* (1) and by Jakosky *et al.* (2).

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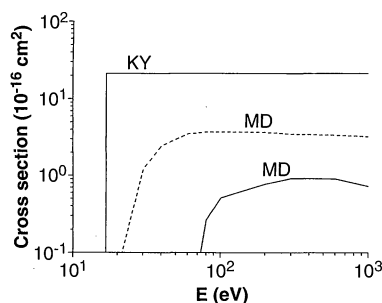
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**Response:** The results presented in our report (1) indicated that it was necessary to consider dissociation during all collisions in calculating the atmospheric loss from Mars that results from sputtering. With the use of the newly calculated cross sections presented by Johnson and Liu in our model, we find that Mars has lost about 1 bar of  $CO_2$ . The revised cross sections reduce our sputtering yields (Table 1), but do not bring our results into agreement with Luhmann *et al.* (2) and Jakosky *et al.* (3).

The effective decrease in the collisional cross section pointed out by Johnson and Liu of  $CO_2 \rightarrow CO + O$  (channel I) by a factor of about 5 and of  $CO_2 \rightarrow C + 2O$  (channel II) by a factor of about 50 will not result in decreases of 5 and 50, respectively, in the collision frequency with  $CO_2$ . At the important energies for sputtering, collisions with  $CO_2$  result in some form of dissociation (Table 1).

The changes in the cross section (a factor of 5 for channel I and a factor of 10 for channel II) do not have a linear effect on the collision probability, but the ratio of



**Fig. 1.** Dissociation cross sections for  $O + CO_2$  collision plotted as a function of the energy of the O atom. Solid lines:  $O + CO_2 \rightarrow O + C + 2O$ ; dashed line:  $O + CO_2 \rightarrow O + CO + O$ . Line labelled KY, cross section assumed by Kass and Yung (1); curves labelled MD, calculated values using molecular dynamics with the universal interaction potential (6) for the interaction of the energetic O with individual atoms in  $CO_2$ . Three pair potentials are used for  $CO_2$ , which gives the correct dissociation energy for  $CO_2$  and for the resulting CO.

the total cross section for the species to the total cross section of the entire atmosphere does. "Total cross section" refers to the product of the number density and the actual cross section (consider the trivial case of a mono-species atmosphere where changing the cross section of the species has no effect because only that species can be sputtered). At the altitudes of interest,  $\text{CO}_2$  is the dominant (75%) constituent. Decreasing its cross section will also decrease significantly that of the entire atmosphere, and the net effect of the decrease will be much smaller. For channel I, the effective decrease is only about a factor of 2; for channel II, it is about a factor of 4.

The effect of changing the cutoff energy for dissociation does not linearly affect the collision frequency. With regard to the results of our model, 85% of the O in collisions that are above the dissociation threshold stated in our report (1) are above that of channel I, and 40% are above that of channel II. In the affected collisions, most of the energy goes into breaking the molecule, so almost none of the particles from such collisions have sufficient energy to escape, further reducing the effects of changing the cutoff energies. Our revised model indicates that the higher cutoff energies have no effect in channel I and results in a factor of two decrease in yield for channel II.

While channel I does not produce C directly, it is still relevant to the process. First, the mass of CO is less than a third

that of  $\text{CO}_2$ . It thus has a significantly lower escape energy, and even partially dissociating the  $\text{CO}_2$  increases the sputtering yield. Second, the mean number of collisions that an escaping  $\text{CO}_2$  fragment undergoes is about four (and over 75% undergo at least two collisions). Thus, while the  $\text{CO}_2$  will not be completely dissociated in its first collision, subsequent ones will finish it. The C will end up escaping in elemental form as our original model assumed, giving it the significant mass advantage that accounted for so much of the difference between our results and those made earlier (2, 3). This advantage allows channel I (which does not directly produce C) to contribute significantly to the final sputtering yield. These two effects allow channel I to be less efficient than complete dissociation by only a factor of 2.

As in our report, we used the impacting ion flux used by Luhmann (2) and Jakosky (3). There is a feedback between the escaping flux and the impacting flux, but this does not affect the actual sputtering yields. Calculated total  $\text{CO}_2$  loss is affected, but there are other, larger uncertainties in the impacting flux. There are two typographical errors in table 2 of our report (1). The Exospheric O value at 1 EUV should read  $8 \times 10^{25}$  and the Escaped  $\text{H}_2\text{O}$  at 6 EUV should read  $1.9 \times 10^{28}$ . Neither error affects the calculations or figure 1 of our report (which were done with the correct values).

With both channels contributing to the sputtering of C (either as C or as CO), our revised model implies a loss of about 1 bar of  $\text{CO}_2$  (not  $\sim 3$  bar, as we originally stated). This decrease can be attributed to the decrease in effective yield of channel I by a factor of four and that of channel II by a factor of eight relative to the cross section stated in our report (1). This is only a small part of the total difference between our results and those of Luhmann (2) and Jakosky (3). One bar of  $\text{CO}_2$  is the canonical amount needed by greenhouse models to create the warmer, wetter early Martian atmosphere (4). Our revised results imply that, because of dissociation during collisions, sputtering is an important loss mechanism.

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**Table 1.** Effects of the revised cross sections. First column is the actual change between the cross section presented in our report (1) and in the comment by Johnson and Liu; second is the effect that Johnson and Liu state that this change will have on the number of collisions (and thus the sputtering yield); third is the effect that we attribute based on statistics from our model. Plateau is the value over the "flat" portion of the cross section. Cutoff is the minimum energy required for the collision to occur. Inefficiency is the reduction in effect in channel I because it does not directly produce C. Values are all expressed as multiplicative factors. In all cases, the final values are smaller than those calculated earlier. Not calculated, -.

|              | Cross<br>section<br>change | Stated<br>effect<br>(J&L) | Modeled<br>effect<br>(K&Y) |
|--------------|----------------------------|---------------------------|----------------------------|
| Plateau      |                            |                           |                            |
| Channel I    | 5                          | 5                         | 2                          |
| Channel II   | 10                         | 10                        | 4                          |
| Cutoff       |                            |                           |                            |
| Channel I    | 1.2                        | -                         | 1                          |
| Channel II   | 5                          | 5                         | 2                          |
| Inefficiency |                            |                           |                            |
| Channel I    |                            | $\infty$                  | 2                          |
| Total        |                            |                           |                            |
| Channel I    | 6                          | -                         | 4                          |
| Channel II   | 50                         | 50                        | 8                          |
| Combined     | 5                          | 50                        | 3                          |

## Alzheimer's Precursor Protein and the Use of Bathocuproine for Determining Reduction of Copper(II)

Gerd Multhaup *et al.* (1) report the ability of amyloid precursor protein (APP) to reduce Cu(II) to Cu(I) as determined through use of a specific colorimetric ligand for Cu(I), bathocuproine disulfonate (BC). Their experimental protocol duplicated a previous use of BC to determine the ability of low density lipoprotein (LDL) to reduce Cu(II) (2). Both groups stated that BC could be used to quantitate Cu(I) because of its lack of interaction with Cu(II). However, the references they cited to support this statement do not make such an assertion. In fact, not only is it well known that BC binds to Cu(II) to give the bis complex  $(\text{BC})_2\text{Cu(II)}$ , but BC thereby also makes Cu(II) a nearly 0.5-V stronger oxidizing agent than usual (3). This results from the 2,9-dimethyl substitution on the phenanthroline ligand sterically preventing planar tetracoordination and forcing instead a Cu(I)-preferring tetrahedral-like coordination on Cu(II). In the presence of BC,

Cu(II) has been observed to oxidize "biological" buffers such as HEPES (4) and PIPES (5), a reaction which we demonstrated to reflect oxidation of the tertiary amine center in these buffers (6). The main purpose of this comment is to call attention to the fact that BC is not an innocent indicator of Cu(I) and that any protein oxidation observed in using it could well represent a methodologic artifact.

On the basis of the expected stability constants, one can calculate that at the concentrations of Cu(II) and excess BC used in the above two studies (1, 2), 99.5% of the Cu(II) will exist as  $(\text{BC})_2\text{Cu(II)}$  (7) before addition of protein. Thus, in these studies, APP and LDL are being exposed to a predominantly highly oxidizing, non-physiologic form of Cu(II). Certain Cu(II)-coordinating ligands and protein sites that are capable of competing with BC for binding to Cu(II) can displace one or both BC ligands, thereby abrogating the unusual ox-