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Sputtering: Its relationship to isotopic fractionation on the lunar surface

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Abstract—Silicon, oxygen, sulfur and, possibly, potassium show systematic enrichment of heavier isotopes with increasing soil maturity, probably as a result of solar-wind sputtering, but such a pattern is not exhibited by solar wind-implanted species. Apparently sputter-erosion is not penetrating to their implantation depth, about 200 Å. This suggests that sputtering on the moon is being impeded by deposition of vapor condensate following meteoritic impact.

Although neither secular variation in the isotopic composition at the source of regolith carbon, probably the solar wind, nor isotopic fractionation of carbon after implantation in the regolith can be ruled out, carbon isotope systematics currently yield no evidence in support of either process.

INTRODUCTION

It was recognized early that irradiation of the lunar surface by solar wind with energies around 1 KeV per nucleon could sputter material from the surfaces of grains and produce physical and chemical changes in the lunar regolith (Wehner *et al.*, 1963a,b; Hapke, 1966). More recently, interest has revived in this process as a possible mechanism for: (a) producing observed changes in lunar albedo (Hapke, 1973; Gold *et al.*, 1974); (b) reducing indigenous ferrous iron to superparamagnetic metal grains (Yin *et al.*, 1972; Hapke *et al.*, 1975); (c) enriching grain surfaces in heavy elements (Hapke *et al.*, 1975; Pillinger *et al.*, 1976a); and (d) causing isotopic fractionations for some elements in soil samples (Epstein and Taylor, 1971; Pillinger *et al.*, 1976b; Switkowski *et al.*, 1977; Haff *et al.*, 1977). We focus here upon the last of these topics, i.e., the concept that preferential loss of light species from the moon by means of sputtering is capable of explaining observed enrichments in the heavy isotopes of some elements in the lunar surface.

An important detail is that sputtering in the lunar environment is a complex process which may be divided into several stages, each capable of producing its own characteristic fractionation, and that different models have emphasized different stages. Thus, Switkowski *et al.* (1977) considered gravitational sorting of sputtered atoms in ballistic trajectories from the lunar surface; Haff *et al.* (1977) expanded on this idea to include mass-dependent recoil within the sputtered surface; whereas Cassidy and Hapke (1975) and Paruso *et al.* (1978) emphasized preferential sticking of heavy species during redeposition of sputtered material.

Insofar as isotopic fractionation is concerned, the most detailed theoretical treatment of the lunar sputtering process to date is that by Switkowski *et al.* (1977) and Haff *et al.* (1977). They considered establishment of an equilibrium layer on grain surfaces from which atoms are removed by sputtering and to which atoms are added both by diffusion from underlying material and by reimplantation of previously sputtered material which remained gravitationally bound to the moon. A net loss of material from the moon resulted from the fraction of atoms which were sputtered with greater than lunar escape velocity. A general equation was derived for the equilibrium surficial enrichment of the heavier of two components, such as two isotopes of the same element, e.g., ^{34}S and ^{32}S, or two elements, e.g., silicon and oxygen. This expression included a term which depended upon the surface binding energy for the species in question. It was pointed out that, although such binding energies are typically a few eV for normal oxides, the heavily radiation-damaged lunar surface would probably be characterized by somewhat lower values, leading to greater calculated fractionation. A value of 1 eV appeared to be reasonable and gave an acceptable match with observed fractionations, which are typically on the order of a few percent for surficial material. In order to test their model, Switkowski *et al.* (1977) and Haff *et al.* (1977) employed results of analyses for $\delta^{18}O$, $\delta^{30}Si$, $\delta^{34}S$ and Si/O. These data will be discussed in more detail later in this paper; the match between theory and observation is good and justifies the conclusion that "mass fractionation by solar wind is an important phenomenon on the lunar surface" (Haff *et al.*, 1977). We shall take as a working hypothesis that solar wind sputtering is in fact responsible for the fractionations given above and we shall consider the implications of this for other isotopic systems.

Before proceeding, however, it is necessary to point out that other possible mechanisms for producing these isotopic fractionations may exist. One possibility is that, instead of a physical interaction between the solar wind and indigenous atoms, chemical reaction between solar wind hydrogen and elements such as silicon, oxygen and sulfur could produce volatile compounds, SiH_4, H_2O, H_2S, which could be readily lost by diffusion. Faster diffusion of compounds containing the lighter isotopes would then enrich the residue in the heavier isotopes (Kaplan *et al.*, 1970). Similarly, diffusive loss of atomic species at the very high temperatures reached during meteorite impact might result in preferential loss of light isotopes (Clayton *et al.*, 1974). Finally, for relatively volatile elements such as sulfur, diffusion at lunar daytime temperatures may be significant.

Intuitively, it seems unlikely that diffusion of atomic species is capable of explaining the observations. The observed isotopic fractionations for silicon, oxygen and sulfur are comparable, suggesting that diffusive loss of each was also comparable, whereas they differ greatly in volatility, and, at any temperature, they would have been depleted to very different degrees. Examples of fractionation probably produced by diffusive loss will be considered later in connection with the noble gases and will be shown to differ significantly from the silicon, oxygen and sulfur systematics. Diffusive loss of products of reaction with solar wind hydrogen cannot be so easily dismissed as a fractionation mechanism. Fortunately, an observational test may be applied to this hypothesis, as fractionation should in that case be restricted to elements which form volatile hydrides. The key elements for this test are calcium and potassium, although results to date have not wholly resolved this question, as will be discussed later.

A complication may arise in assessing the role of volatility in establishing isotopic fractionation patterns as the behavior of an element during ion sputtering may closely resemble its behavior during thermal volatilization (Housley and Grant, 1977).

In what follows, we review the evidence for isotopic variations among lunar samples, except for nuclear (spallogenic or radiogenic) effects. The systematics of those fractionations believed to be due to sputtering are investigated with the objective of establishing the "signature" of the sputtering process. Similar systematics are then sought among other elements in order either to characterize other fractionation processes or to identify the cause of unknown fractionations. An immediate goal is the interpretation of isotopic variations in regolith carbon.

A concept which will feature prominently in this discussion is that of regolith maturity. The approach adopted here is to regard maturation as a continuous process leading to a homogeneous soil, each component of which has had a similar history of surface exposure. This is a conscious over-simplification; in reality virtually all soils are heterogeneous, consisting of components characterized by different exposure histories. For example, sub-mature soils, such as those from Station 13, Apollo 16, are invariably mixtures of mature, "country" regolith with relatively fresh ejecta from recent craters, e.g., North Ray Crater (Heymann *et al.*, 1975). However, although attempts have been made to model heterogeneous maturation quantitatively, either through the evolution of grain size parameters (e.g., Mendell and McKay, 1975; Lindsay, 1975), or by identification of major components of characterizable maturity (e.g., Heymann *et al.*, 1975; Heymann, 1978; Pillinger *et al.*, 1977), those models do not yet have sufficient predictive capability to enable them to be generally applied to interpretation of analytical data such as the carbon isotope systematics considered here.

OBSERVED ISOTOPIC VARIATIONS

Silicon and oxygen

Because isotopic analyses of silicon and oxygen are frequently conducted on the same aliquots and because the two elements show very similar effects, it is convenient to consider them together. Relative to their parental rocks, bulk soils are slightly enriched in the heavier isotopes of these elements, but these effects are greatly magnified if the silicon and oxygen are removed progressively from soil samples by partial fluorination (Epstein and Taylor, 1971; Taylor and Epstein, 1973). The same authors also showed that these enrichments correlated with soil maturity, as indicated by contents of solar wind hydrogen and noble gases, and that enrichment in $^{30}Si/^{28}Si$ was twice as large as that in $^{29}Si/^{28}Si$, demonstrating that the effect was produced by a mass-dependent process. Clayton *et al.* (1974) showed similarly that enrichments in $^{18}O/^{16}O$ were twice those in $^{17}O/^{16}O$. Maximum enrichments of about 25‰ in $\delta^{30}Si$ and 50‰ in $\delta^{18}O$ were observed in the first cut of material removed by fluorination, the enrichments decreasing as more material was stripped. This was initially interpreted as a purely surficial effect, although subsequently it was shown that partial fluorination attacked agglutinates, i.e., formerly exposed surfaces, as well as existing surfaces (Pillinger *et al.*, 1976b). Because the depth resolution of the partial fluorination technique is poorly controlled, the maximum measured enrichments represent lower limits to the values characteristic of the actual surfaces.

Sulfur

Soils are enriched, relative to rocks, in $^{34}S/^{32}S$ and this enrichment is surface correlated (Rees and Thode, 1974) and also correlated with soil maturity as measured by contents of agglutinates or solar wind nitrogen (Kerridge *et al.*, 1975a). This last relationship is illustrated in Fig. 1 and shows that bulk enrichments can reach 12‰ relative to rock values, although enrichments of about 17‰ may be observed in grain size fractions (Rees and Thode, 1974), leading to a lower limit of about 20‰ for actual surface enrichments. That the enrichment in $^{34}S/^{32}S$ resulted from a mass-dependent process was demonstrated by Rees and Thode (1972), who showed that enrichments in $^{36}S/^{32}S$ and $^{33}S/^{32}S$ were twice and half, respectively, those in $^{34}S/^{32}S$.

Thus isotopic variations in sulfur closely resemble those in silicon and oxygen, both qualitatively and quantitatively, even though sulfur is, compared with the other elements, much less abundant, significantly more volatile and of partly (up to about 30%) meteoritic origin (Kerridge *et al.*, 1975a). As mentioned earlier, the observed fractionations in these elements match well the predictions of models of sputter-fractionation (Switkowski *et al.*, 1977; Haff *et al.*, 1977). It should be noted that the proportion of total sulfur which is surficial, and therefore vulnerable to sputter-fractionation, is much greater than for silicon and oxygen. This does not preclude direct comparison of predictions and observations because the relevant experimental data pertain only to the surficial fraction in each case. However, it is clear that some process, presumably vaporization and recondensation, is responsible for transfer of some initially volume-correlated, indigenous sulfur onto surfaces of grains, and it is possible that this process could be accompanied by some isotopic fractionation. Therefore the observed surficial enrichment in ^{34}S may represent the sum of two fractionation processes, which could cause a discrepancy between the observed isotopic composition of surficial sulfur and that predicted by a model involving only sputter fractionation.

Because sputtering efficiency is a function of atomic mass and surface binding energy and does not depend upon chemical reactivity, fractionations should not vary greatly for the common rock-forming elements, provided that they are exposed on grain surfaces. Consequently, the presence or absence of mass-

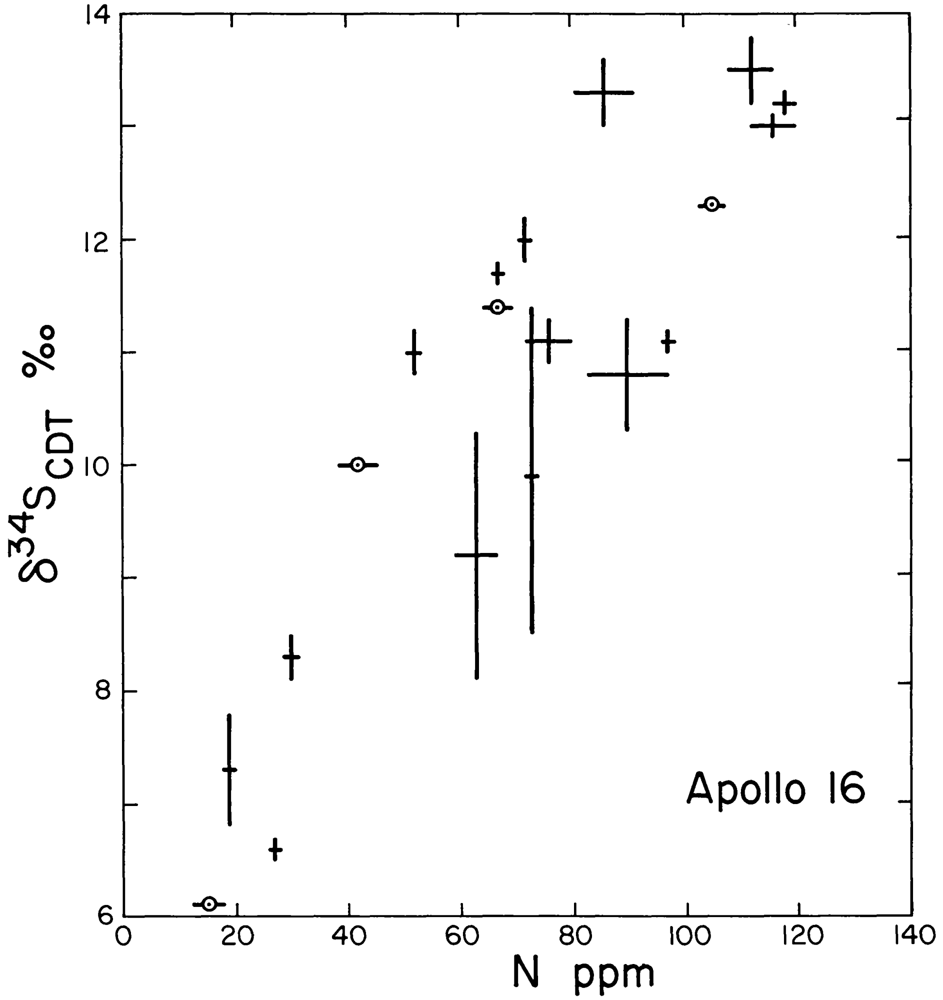

Fig. 1. Enrichment of ^{34}S relative to ^{32}S correlates very strongly with soil maturity, measured by content of solar wind-implanted nitrogen. Rocks at the Apollo 16 site are characterized by $\delta^{34}S$ values around +1.8‰ relative to Canyon Diablo troilite, so that maximum observed enrichments in bulk samples are about 12‰. From Kerridge *et al.* (1975a).

dependent isotopic variations in elements such as calcium and potassium, which are comparable in mass to silicon and sulfur but which do not form volatile hydrides, can provide a useful test of the sputter-fractionation hypothesis. Results of such analyses are therefore considered next.

Calcium and potassium

In order to extract the calcium associated with isotopically fractionated silicon and oxygen, Russell *et al.* (1977) used aqueous leaching of material previously activated by partial fluorination following the technique of Epstein and Taylor (1971). Enrichments of about 3‰ were found for $^{44}Ca/^{40}Ca$ which, though significantly above their limit of detectability, were an order of magnitude smaller than the analogous effects in silicon and oxygen. Although this result may represent a problem for the sputter hypothesis, a number of other possible explanations cannot be excluded at this time. These include the possibility that the leaching procedure does not in fact extract the most heavily fractionated calcium or, alternatively, that it is diluting fractionated calcium with normal material dissolved from easily soluble phases (Russell *et al.*, 1977). That sputtering can, in fact, produce fractionations of about 10‰ in $^{44}Ca/^{40}Ca$ was demonstrated by Griffith *et al.* (1978) in simulation experiments using terrestrial fluorite and plagioclase. These experiments reproduced only the processes occurring within the sputtered zone and did not simulate sorting within the lunar gravitational field or possible fractionation during redeposition. Consequently, significantly larger fractionations, possibly some tens per mill, might be expected for sputtering under lunar conditions. The experiments of Griffith *et al.* (1978) therefore support the idea that sputtering can generate mass fractionations to the degree observed for silicon, oxygen and sulfur, but fail to explain why such an effect is not observed for calcium.

Because isotopic analysis of potassium is effectively restricted to the two isotopes ^{39}K and ^{41}K, corrections for instrumental and chemical fractionations are more difficult than for calcium and resulting data have significantly greater uncertainty. Nonetheless, Barnes *et al.* (1973), Garner *et al.* (1975) and Church *et al.* (1976) have reported enrichments of up to about 13‰ in $^{41}K/^{39}K$ for some bulk soils and respect to rocks. There is a tendency for this enrichment to increase with soil maturity. Thus, the potassium isotope systematics resemble those of silicon, oxygen and sulfur, although the magnitude of the experimental uncertainties prevents the data from being used as a rigorous test of any fractionation model. It is worth noting that there is evidence that some potassium is surface correlated in analysis of grain size fractions (Evensen *et al.*, 1973), so that, like sulfur, it may be subject to fractionation during mobilization onto grain surfaces as well as after emplacement on surfaces.

Noble gases

The foregoing elements have had in common the fact that they are predominantly indigenous in origin, an exception being sulfur which is partly meteoritic. The remainder of our discussion deals with solar wind-implanted elements, as most of those analyzed to date exhibit isotopic variations which may stem from fractionation on the lunar surface.

It is well known that the light noble gases of solar wind origin are depleted in lunar soils relative to either the heavier gases or more retentive species such as carbon and nitrogen. It is generally agreed that this depletion resulted from diffusive loss of gas (Huneke, 1973; Signer *et al.*, 1977), probably from the heavily radiation-damaged margins of soil grains (Ducati *et al.*, 1973). Mineral-specific retention factors have also been shown to be related to activation energies for diffusion, rather than to differences in sputter rate (Signer *et al.*, 1977). It is

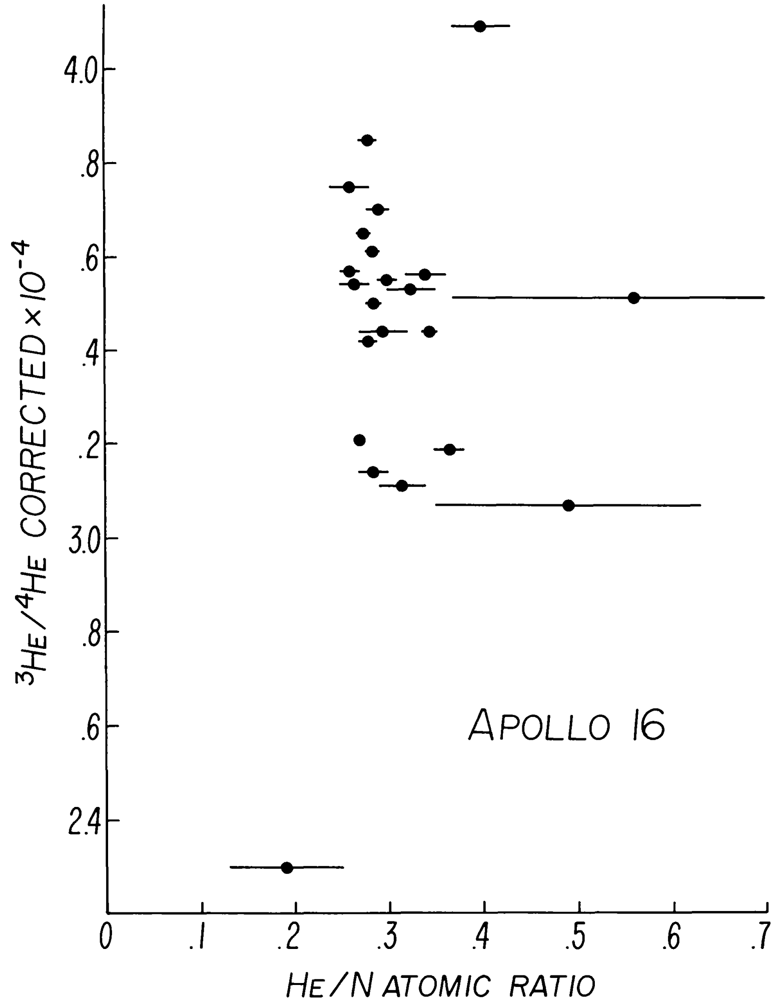

Fig. 2. The ^{3}He/^{4}He ratio, corrected for spallation, does not appear to be related to degree of helium depletion, as measured by the He/N ratio. Helium isotopic data from Bogard and Nyquist (1973), Eberhardt *et al.* (1976), Heymann *et al.* (1975), Hintenberger and Weber (1973) and Kirsten *et al.* (1973).

therefore of interest to compare the systematics believed to result from thermally driven diffusion with those described earlier for sputter fractionation.

We have shown previously that the He/N ratio decreases systematically with increasing maturity (see Fig. 2 in Kerridge *et al.*, 1976). It might therefore be supposed that this depletion of helium would be accompanied by a decrease in the ^{3}He/^{4}He ratio, although the observed variation in He/N represents a small increment compared with the overall depletion relative to the solar ratio. Because most isotopic fractionation probably occurs during the earliest stages of irradiation (Huneke, 1973), it is possible that any maturation-dependent fractionation could be obscured. In fact, Fig. 2 shows that there is no systematic relationship between ^{3}He/^{4}He and He/N ratio. It is possible that secular changes in isotopic composition of solar wind helium may be masking a lunar surface fractionation pattern. However, Geiss (1973) has pointed out that, though such a secular

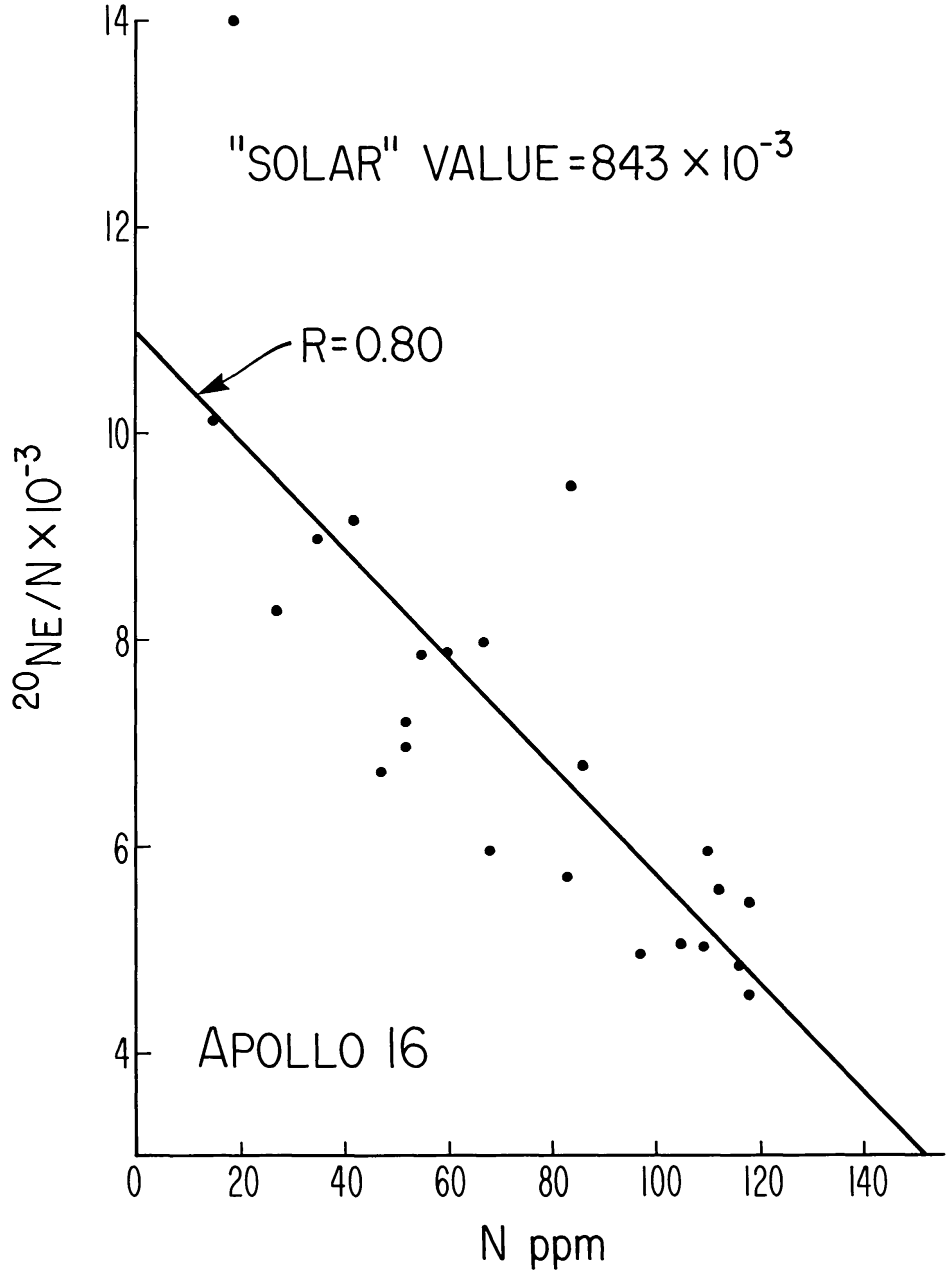

Fig. 3. The ^{20}Ne/N ratio decreases systematically with increasing nitrogen content, indicating progressive depletion of neon with increasing soil maturity. Neon data from sources cited in Fig. 2. "Solar" value for ^{20}Ne/N from Cameron (1973).

increase in ^{3}He/^{4}He may be inferred from comparison of soil analyses with old breccias, soils themselves do not show a systematic change with age. It is also possible that short term variations in the ^{3}He/^{4}He ratio of the solar wind could be masking a fractionation trend (Geiss, pers. comm.).

Similarly, the Ne/N ratio systematically decreases with maturity (Fig. 3) indicating progressive depletion of neon possibly accompanied by mass fractionation of the neon isotopes. Although a comparison of the isotopic composition of

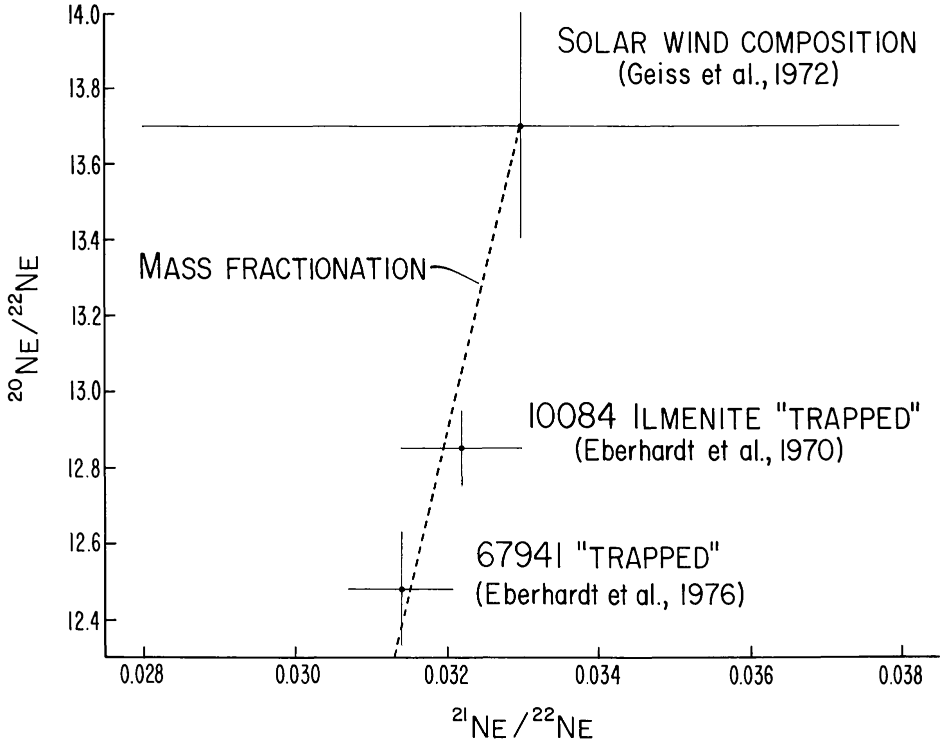

Fig. 4. The isotopic compositions of neon trapped in both a retentive sample, 10084 ilmenite, and a "leaky" sample, plagioclase-rich 67941, lie on a mass-fractionation line through the measured solar wind composition, although observational uncertainties are considerable.

solar wind neon (Geiss *et al.*, 1972) with that of neon trapped in a retentive mineral, ilmenite (Eberhardt *et al.*, 1970), and with neon trapped in a poorly retentive, plagioclase-rich, sample, 67941, (Eberhardt *et al.*, 1976) reveals a trend which is consistent with mass-fractionation (Fig. 4), experimental uncertainties do not permit a unique determination of the trend line. The isotopic compositions plotted in Fig. 4 represent the true trapped components from which spallogenic neon has been subtracted by means of the Eberhardt technique (Eberhardt *et al.*, 1970). Such precise determinations of the trapped composition are available for only a few samples: too few for a reliable test of a possible dependence of this composition upon maturity. If bulk analyses are used in their place, the quantity of data increases but no consistent pattern of decreasing ^{20}Ne/^{22}Ne with increasing maturity emerges (Fig. 5); in fact, a suggestion of the opposite trend may be discerned. Again, it is possible that a real fractionation pattern may be masked by either secular variations or experimental uncertainty. Note the size of some of the error bars in Fig. 5 which reflect inter-laboratory discrepancies, and also the fact that observed variations in ^{20}Ne/^{22}Ne span a range of about 100‰, a factor of five greater than observed for, say, ^{34}S/^{32}S.

None of the light noble gases, therefore, yield the kind of systematic dependence of isotopic composition upon maturity which characterizes sulfur, silicon and oxygen. The closest approach to such a dependence may be found in

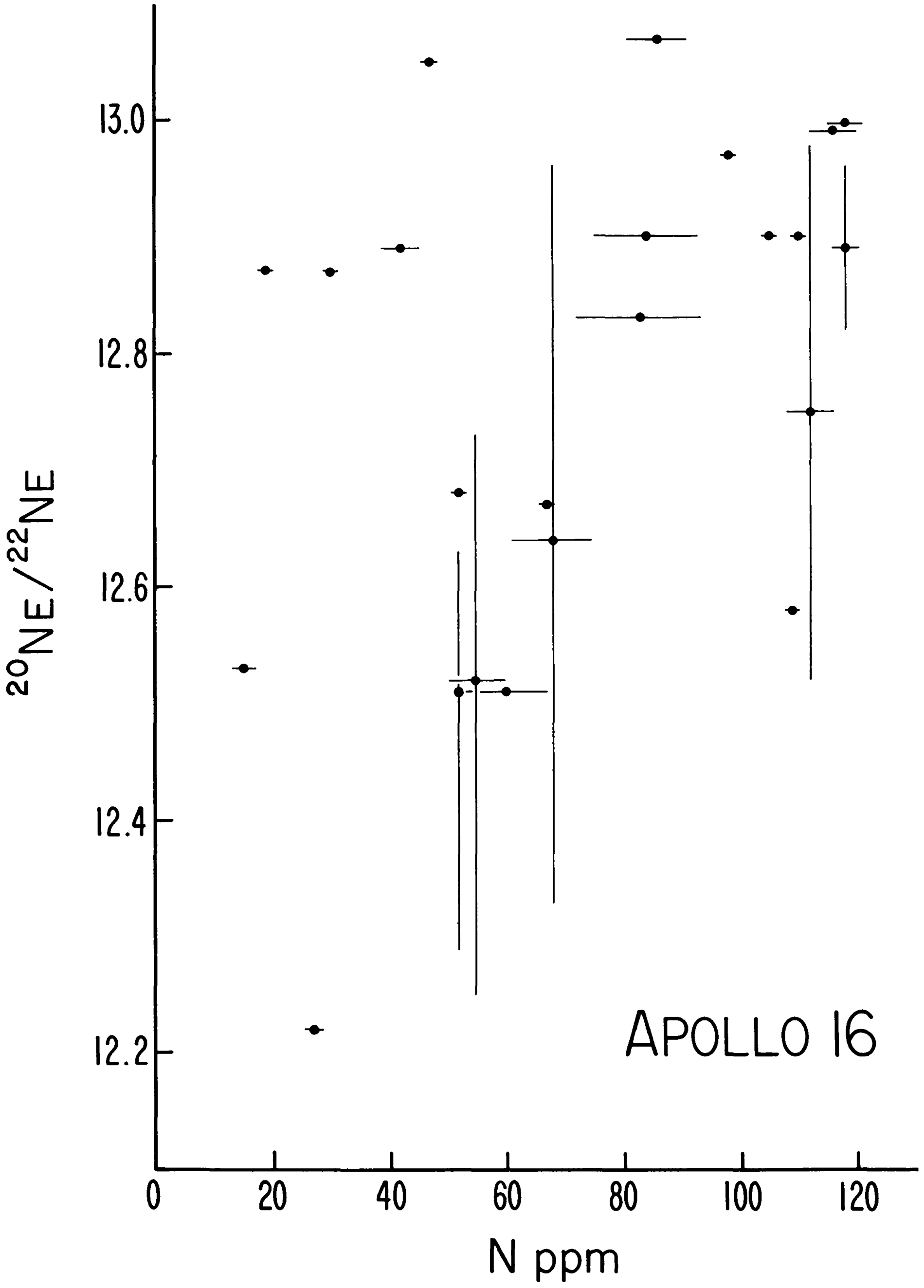

Fig. 5. Analysis of ^{20}Ne/^{22}Ne for bulk samples yields values which show no systematic dependence upon nitrogen content, i.e., soil maturity. Error bars for neon data reflect inter-laboratory discrepancies. Neon isotopic data from sources given in Fig. 2.

the relationship between the ^{20}Ne/^{36}Ar ratio for bulk samples, and maturity, in the form of nitrogen content (Fig. 6). This reveals a statistically real trend for the ratio to decrease with increasing maturity, but the correlation coefficient is only −0.67 compared with 0.89 for the relationship between δ^{34}S and nitrogen content (Fig. 1). If, indeed, depletion of the light noble gases is caused by diffusive loss, as seems likely, this process does not apparently progress uniformly with sample

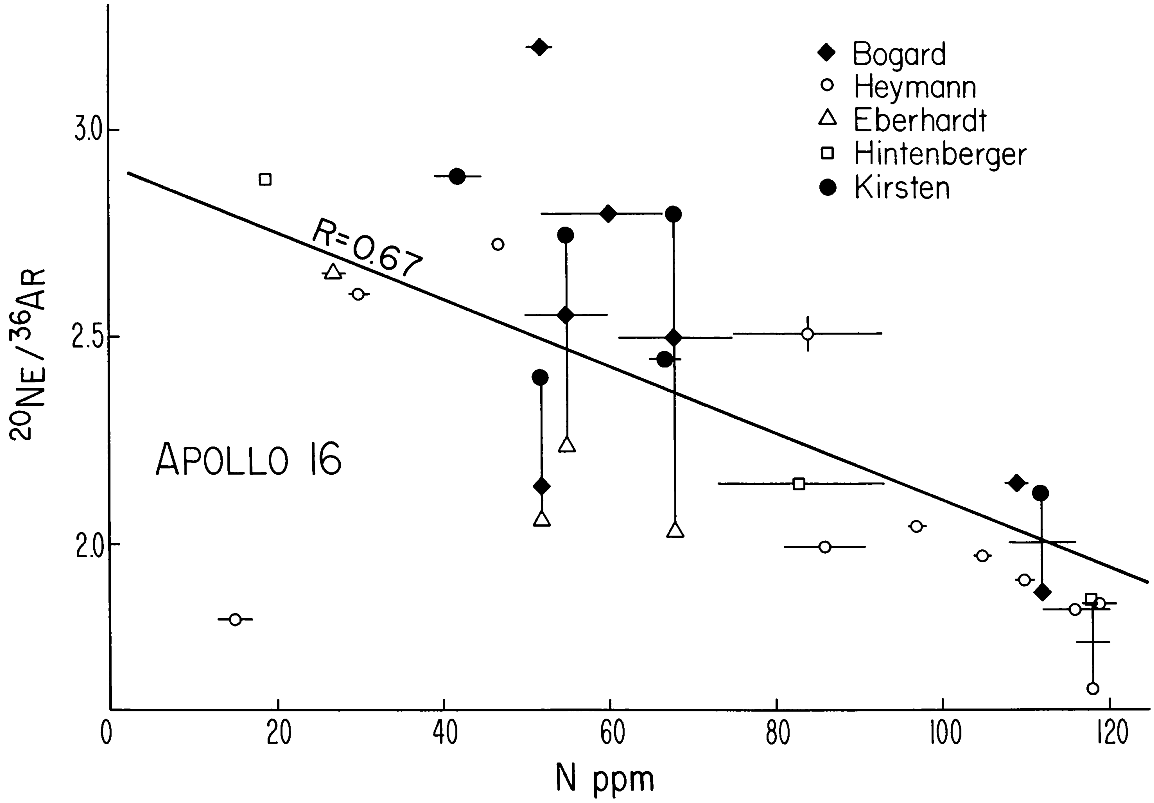

Fig. 6. The $^{20}Ne/^{36}Ar$ ratio decreases systematically with increasing soil maturity, although scatter in the data is significant. Noble gas data from sources given in Fig. 2.

maturation but appears to proceed more randomly. This suggests that the isotopically selective loss of gas from a sample is dominated by a small number of heating events, presumably involving unusually large meteorite impacts.

Mass fractionation trends have been reported for the isotopes of trapped krypton and xenon (Bogard *et al.*, 1974); however, it is not clear whether this fractionation occurred after implantation in the lunar surface or at some earlier stage. Insufficient data exist at present to enable these effects to be investigated by the methods employed above.

Nitrogen

Although variations of about 25% have been reported for the $^{15}N/^{14}N$ ratio of nitrogen apparently implanted in lunar soils by the solar wind, it is generally agreed that these variations represent a secular change in the source composition and do not reflect post-implantation fractionation (Kerridge, 1975; Becker and Clayton, 1975; Becker *et al.*, 1976; Kerridge *et al.*, 1977). The secular trend (see Fig. 2 in Kerridge *et al.*, 1977) consists of an increase in $^{15}N/^{14}N$ by at least 25% over an uncertain time interval, probably about 1 to 4 Gy. The correlation between $^{15}N/^{14}N$ ratio and time of implantation is good but shows some scatter

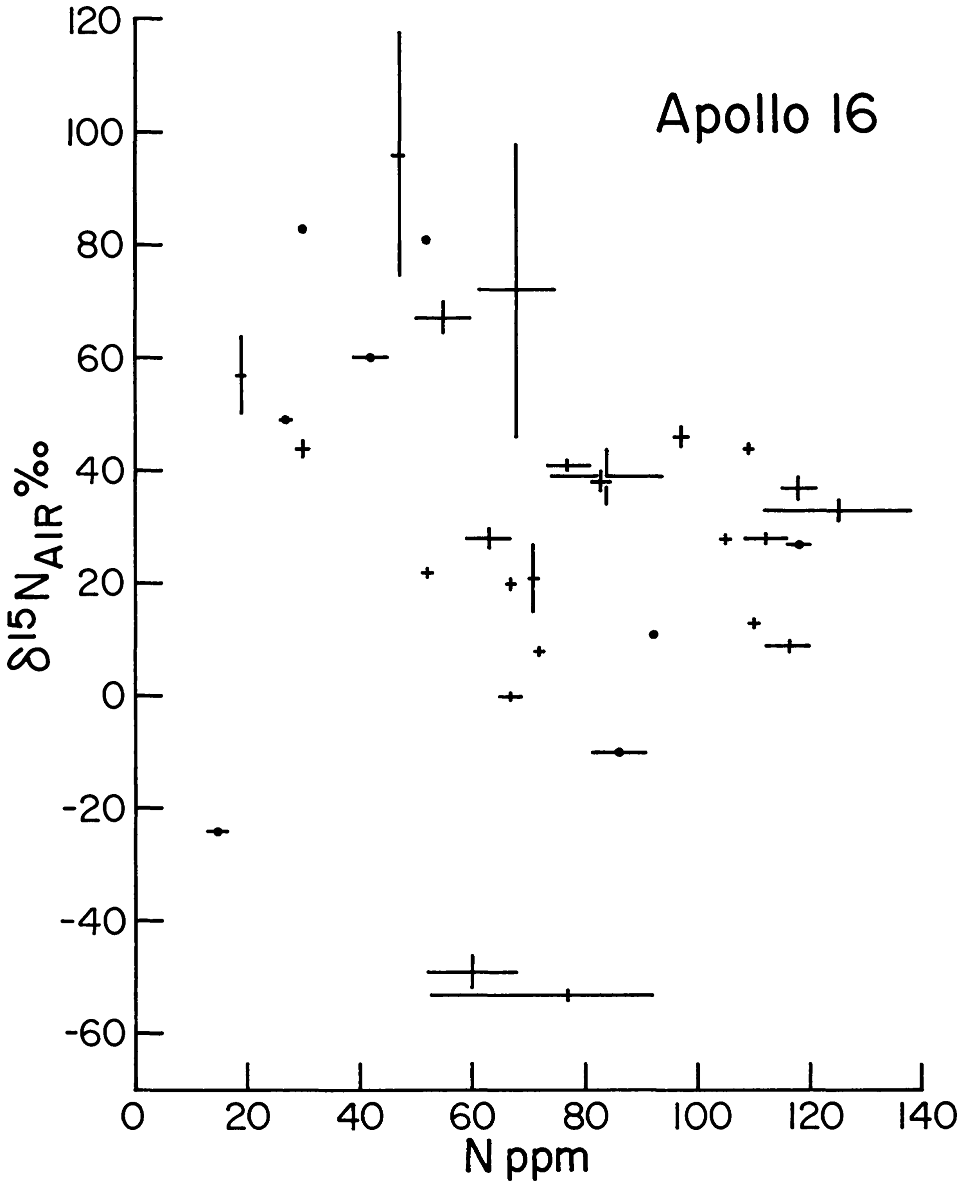

Fig. 7. No systematic variation of $\delta^{15}N$ with soil maturity, given by nitrogen content, may be discerned. This conclusion also holds true for subsets of data chosen to minimize the effects of the secular variation in $\delta^{15}N$, see text.

and the possibility must be considered that this scatter reflects subsequent fractionation. However, Fig. 7 shows a lack of any systematic relationship between $\delta^{15}N$ and maturity, as indicated by nitrogen content. This lack of a trend persists even if subsets of data are selected within which the secular trend is minimized. This is done by taking samples within a narrow range of implantation age and searching for a systematic relationship between maturity and deviation from a linear dependence of $^{15}N/^{14}N$ upon implantation age. There is no evidence at all that the $^{15}N/^{14}N$ ratio of implanted material has changed after implantation. This observation constitutes a serious constraint on any theory involving the processing of solar wind-implanted material.

Carbon

Although it is universally agreed that most carbon in regolith samples is of extralunar origin, it is still not clear whether the solar wind is the sole important source of carbon or whether other sources such as meteorites are also significant. So far as actual abundances are concerned, the solar wind flux is adequate to supply all the extralunar carbon observed in soils. However, additional sources cannot be ruled out, particularly if substantial loss of carbon occurs, either during or following implantation. Jull and Pillinger (1977) have argued that, if solar wind nitrogen is 100% retained during agglutination, observed C/N ratios in soils would allow solar wind carbon in the regolith to be depleted by a factor of two relative to solar abundance. The retentiveness of carbon is not known and although it is likely that carbon could enter into solid solution in the metallic iron known to be present in soils (Jull *et al.*, 1976), this could account for less than 10% of the total carbon.

Variations of about 30‰ have been reported for the $^{13}C/^{12}C$ ratio in lunar soils and these have generally been attributed, at least in part, to selective loss of ^{12}C from the lunar surface (Kaplan *et al.*, 1970; Epstein and Taylor, 1972; Kerridge *et al.*, 1974; DesMarais *et al.*, 1975). Other possible explanations for the observed isotopic variations include addition of extra components, such as meteoritic carbon, and variation in the isotopic composition at the source of one or more of the components. A relatively simple model involving addition of only solar wind to indigenous carbon and subsequent mass fractionation induced by proton stripping provided a fair match with observed data, although it appeared that the solar wind flux was barely able to supply sufficient material (Kerridge *et al.*, 1974). Further failings of this model are considered later. A qualitative model interpreting observed variations in $^{13}C/^{12}C$ in terms of a combination of sputter fractionation and diffusive loss during agglutination has been proposed by Pillinger *et al.* (1976b). Switkowski *et al.* (1977) suggested that sputter-fractionation would lead to an approximately 10‰ increase in $^{13}C/^{12}C$ in surficial carbon.

There is some evidence that the concentration of implanted carbon on the surfaces of grains reaches an equilibrium, quasi-saturation value, attributable to concurrent implantation and sputter-erosion (DesMarais *et al.*, 1975; Filleux *et al.*, 1977, 1978), although total carbon contents could exceed the equilibrium value as a result of cycling of implanted surficial carbon into agglutinates (DesMarais *et al.*, 1973; Kerridge *et al.*, 1974). By analysis of grain size fractions, DesMarais *et al.*, (1975) concluded that, although the finest grains were relatively depleted in ^{13}C, surficial carbon was characterized by $\delta^{13}C$ values which were 6 to 14‰ heavier than bulk analyses; but Epstein and Taylor (1975) inferred from mass balance calculations following analysis of partially fluorinated samples that a small carbon component, enriched by 100 to 200‰ in ^{13}C, resided on grain surfaces. However, subsequent investigation of partially fluorinated residues (Pillinger *et al.*, 1976b) showed that they were effectively devoid of agglutinates and heavily depleted in hydrolysable carbon, known to be greatly concentrated in agglutinates (Cadogan *et al.*, 1973). In view of the fact that agglutinates contain a major fraction of the total carbon in a sample, being enriched by factors of 2 to 4 over non-agglutinate material (DesMarais *et al.*, 1975) it follows that partial fluorination must remove more carbon than inferred from the mass balance calculations; consequently, the isotopic composition of the stripped carbon cannot be as extreme as appeared at first. This conclusion is supported by results of Becker *et al.* (1976) who showed that similar partial fluorination experiments removed about 25% of the nitrogen and it is likely, though not certain, that carbon and nitrogen are similarly sited. We conclude that the evidence for a surficial component of "superheavy" carbon is not convincing at this time.

We have recently presented carbon abundance and isotopic data for a suite of 31 soils from the Apollo 16 landing site (Kerridge *et al.*, 1978; see also Kerridge *et al.*, 1975b). We have argued elsewhere (Kerridge *et al.*, 1974) that the effectively uniform major element composition and useful range of crater ages make this the optimum Apollo landing site for the study of regolith maturation. The soils analyzed were chosen to span as wide a range of maturity as possible, using parameters such as nitrogen content, FMR intensity (I_s/FeO) and agglutinate content. Nitrogen abundances and $\delta^{15}N$ values and helium contents were determined simultaneously with the carbon data. Figure 8 illustrates the close relationship between abundances of carbon and nitrogen, with results from individual replicates plotted separately. The raw data correlate with a coefficient of 0.92. Because of the omnipresent danger of terrestrial contamination in analysis of such small quantities of carbon, we chose to try to estimate the incidence of such contamination. Experience has shown that contamination increases the C/N ratio and decreases the $\delta^{13}C$ value, tending towards a value of −30‰ relative to the PDB standard. Consequently we adopted a trial and error procedure whereby, for each analysis characterized by a high C/N ratio, the amount of "excess" carbon, compared with aliquots of comparable nitrogen content, was related to its measured $\delta^{13}C$ value, again compared with the same neighboring aliquots. Twelve analyses were identified in which the "excess" carbon was calculated to have a $\delta^{13}C$ value of about −30‰, thus most plausible being due to contamination. These analyses are identified in Fig. 8 by open symbols; the remaining data, solid symbols, we term "preferred" data. We emphasize that these data were not selected merely to improve the apparent fit to the trend line in Fig. 8, but were chosen on the basis of an independent, objective criterion, namely isotopic composition. In view of the prevalence of terrestrial contamination in such analyses we believe that some such critical approach is desirable; however, this view was challenged at the Conference as "throwing the baby out with the bath water," so until this issue is settled it is perhaps desirable to present, side by side, interpretations based both upon total data and upon selected data. Thus, although our conclusions here will be illustrated using "preferred" data, we have determined that none of them would be affected by employing total data in their stead.

As noted above, regolith samples display a significant range of $\delta^{13}C$ values and it is of interest to see if these data fit into any of the fractionation patterns

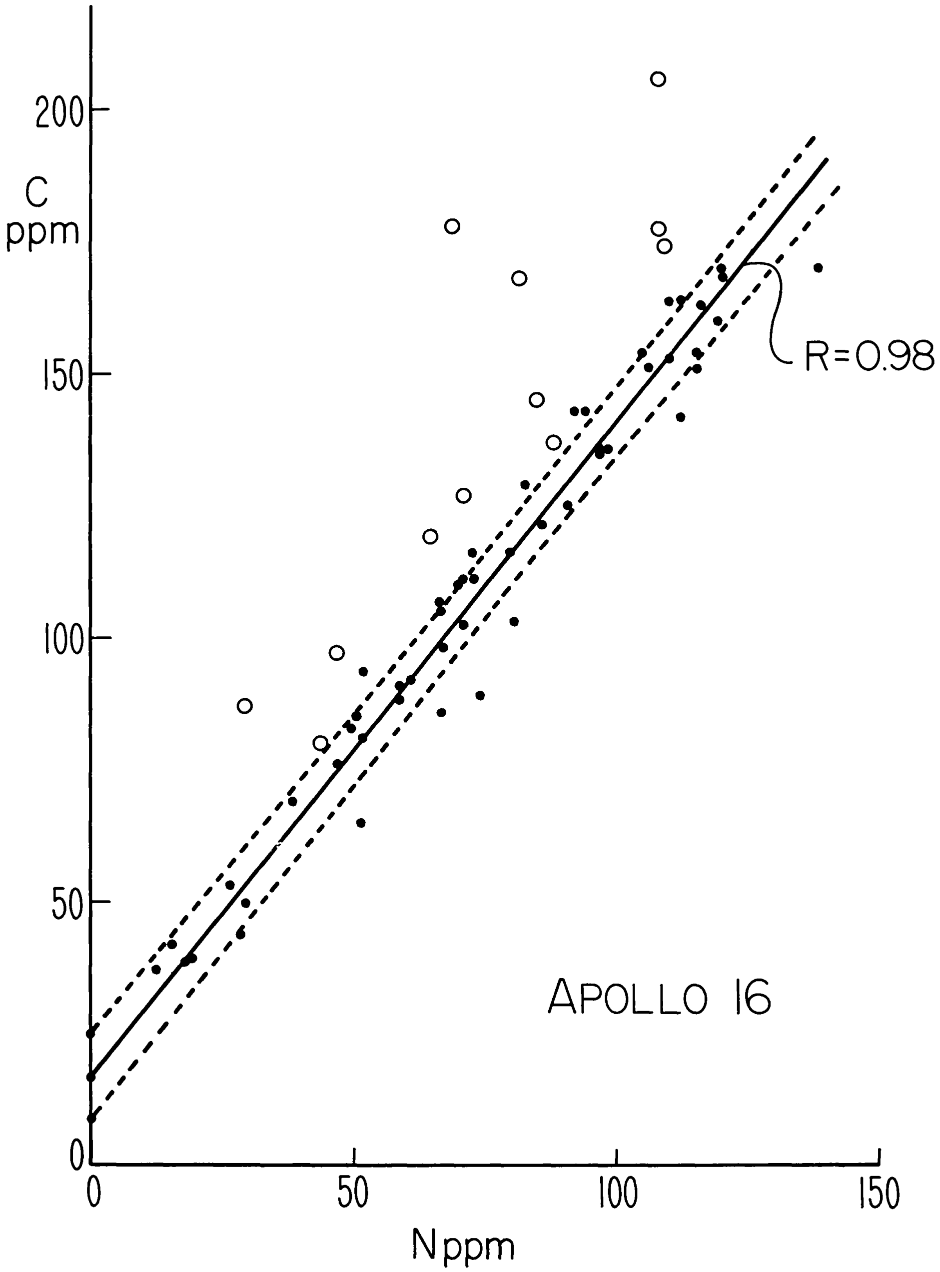

Fig. 8. Carbon and nitrogen abundances for 62 replicate analyses of 31 samples correlate strongly. Open symbols represent data believed to have been affected by terrestrial contamination (see text). Solid symbols, "preferred" data, yield the least squares regression line illustrated with 1σ uncertainty limits. From Kerridge *et al.* (1978).

described earlier. In Fig. 9 we plot $\delta^{13}C$ against carbon content. Because of the extremely strong association between carbon and nitrogen contents (correlation coefficient equal to 0.98 for the preferred data used here), carbon content may be regarded as a reliable measure of maturity, analogous to nitrogen content. Figure 9 also permits comparison with the predictions of our model (Fig. 1 in Kerridge

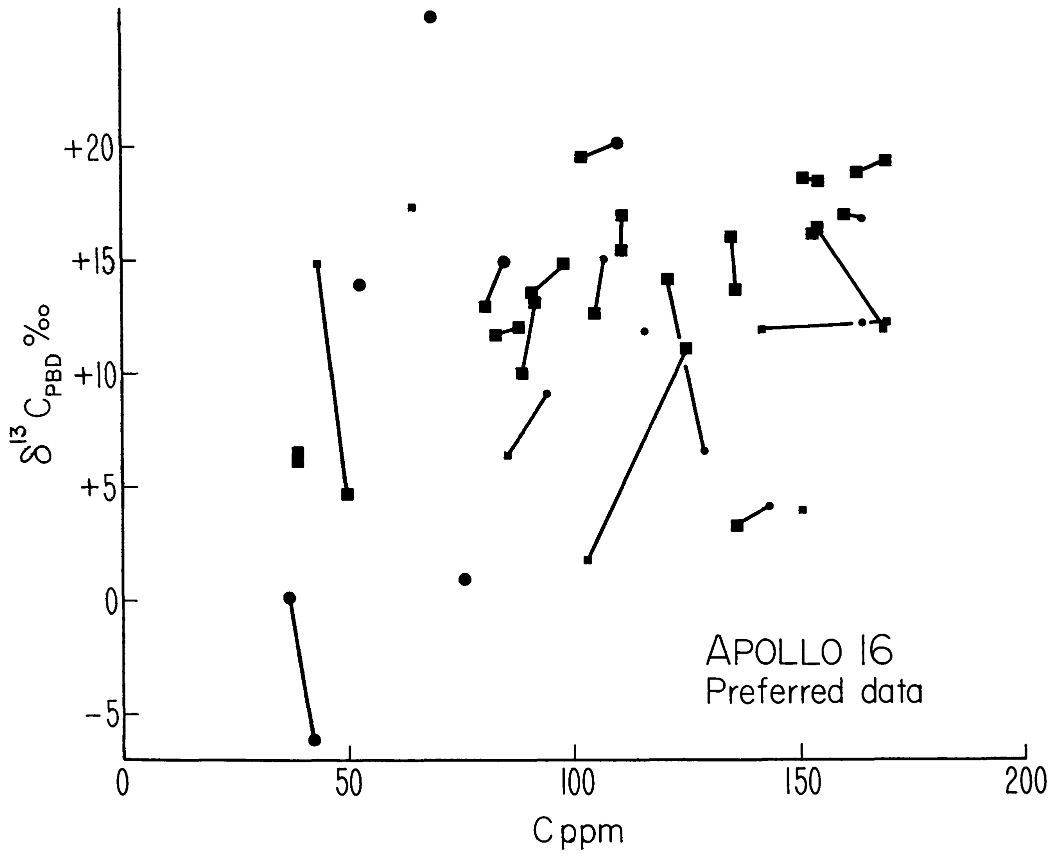

Fig. 9. No clear systematic relationship may be discerned between $\delta^{13}C$ and C content for soils, using "preferred" data. This conclusion also applies if all data are used, or if only those data falling within 1σ of the trend line in Fig. 8 are used (large symbols here). Square symbols represent points on the carbon-poor side of the trend line in Fig. 8; round symbols, carbon-rich. Tie lines join replicate analyses. From Kerridge *et al.* (1978).

et al., 1974) and shows, in fact, that the data do not support that model, which will not be considered further here. More generally, the data show no convincing evidence for a systematic dependence of $\delta^{13}C$ value upon maturity, of the kind found for sulfur, oxygen and silicon. This suggests strongly that, if carbon is being fractionated on the lunar surface, it is by a different process from that responsible for those other elements. As the evidence is in favor of sputter-fractionation for sulfur, silicon and oxygen, it follows that sputtering is unlikely to be the cause of observed variations in $^{13}C/^{12}C$ in the regolith.

The observed association between carbon and nitrogen abundances is so close that a common origin seems highly likely, although independent, exposure-related origins could conceivably mimic such an association. In view of the secular change in isotopic composition of the source of the nitrogen, described above, it is worth searching for evidence of a corresponding secular change in $\delta^{13}C$. Figure 10 shows, however, that no clear relationship exists between $\delta^{15}N$ and $\delta^{13}C$. A hint of a possible positive trend may be discerned, and during

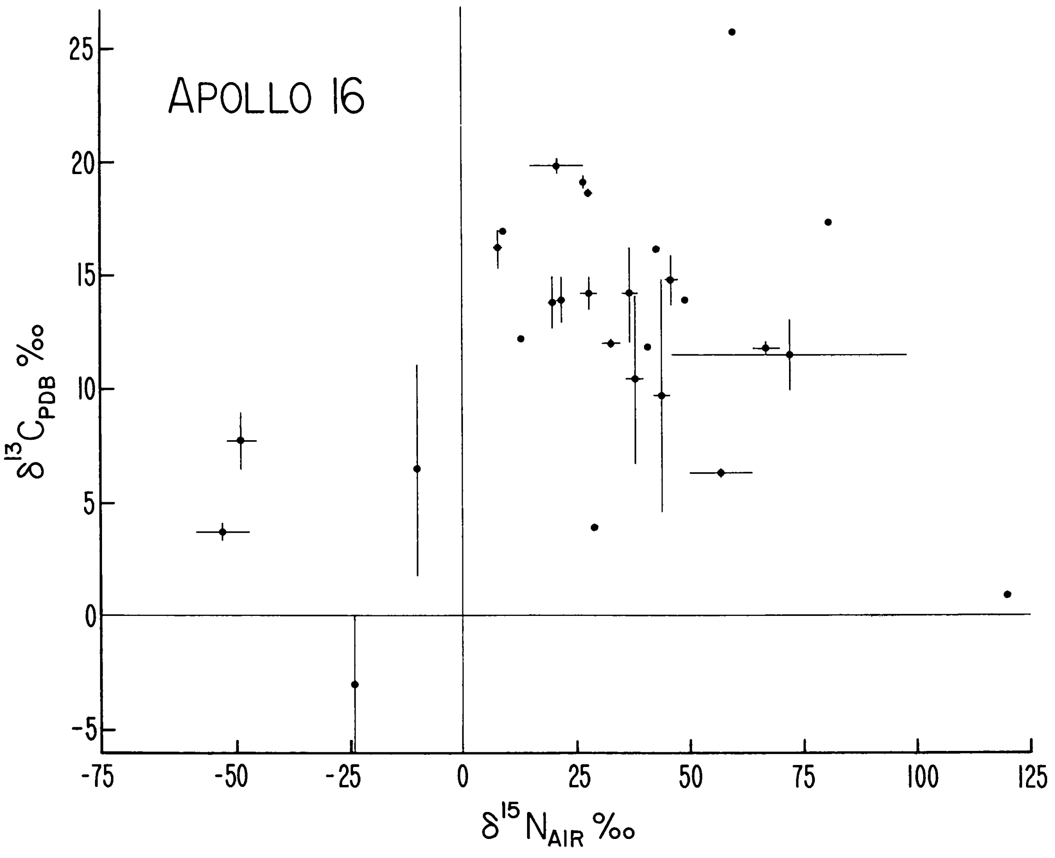

Fig. 10. Although a hint of a positive trend may be discerned in this plot of $\delta^{13}C$ against $\delta^{15}N$, using "preferred" data, it does not show convincing evidence for an actual secular variation in $\delta^{13}C$.

discussion at the Conference, R. H. Becker suggested that combined data for all landing sites revealed significant evidence for such a trend. We are unconvinced by these trends and therefore do not believe that there is currently any evidence for a secular change in $\delta^{13}C$ at the source(s) of the carbon. The possibility that the observed systematics are due to a combination of both secular change and exposure-related fractionation seems unlikely because outlying points in either Fig. 9 or Fig. 10 are not generally characterized by extreme values on the other plot. Nonetheless, it is probably premature to deny the possibility that a secular change may have occurred in the $^{13}C/^{12}C$ ratio of the solar wind.

Although it is intuitively unlikely that the behavior of carbon should resemble that of the noble gases, it is worth comparing the carbon data with the fractionation pattern characteristic of the light noble gases. As noted above, the parameter which seems most faithfully to be reflecting the mass fractionation undergone by noble gases on the lunar surface is the $^{20}Ne/^{36}Ar$ ratio, so in Fig. 11 we plot this ratio against $\delta^{13}C$ value. Again, no trend is discernible, suggesting that diffusive loss is unlikely to be the cause of the isotopic variations in carbon.

We are forced to conclude at this time that there is no evidence that carbon is

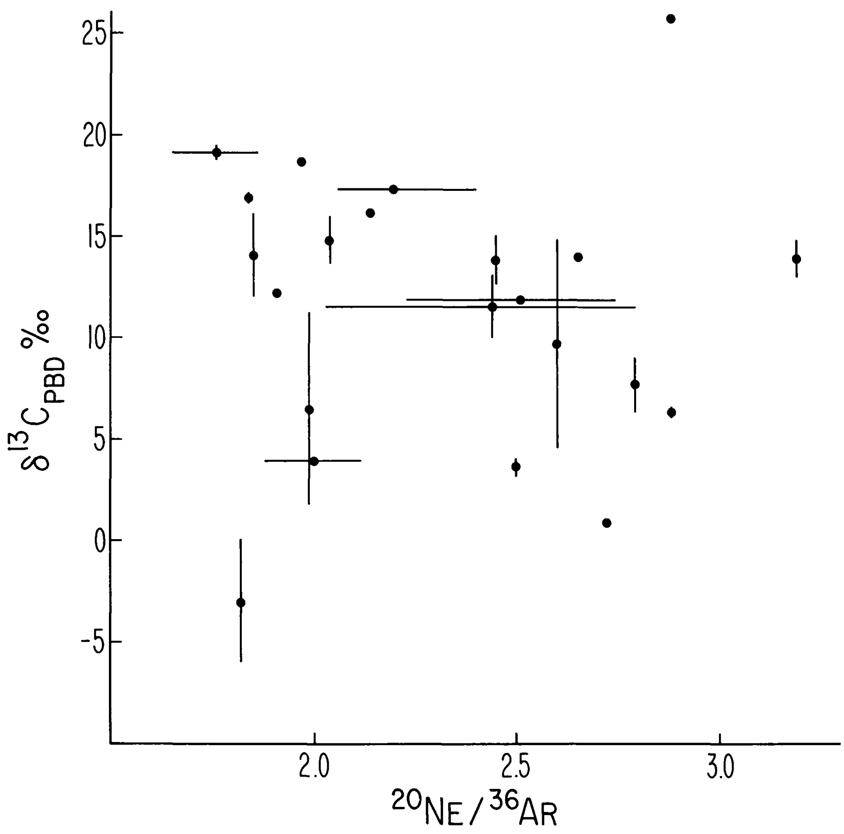

Fig. 11. The isotopic composition of carbon, "preferred" data, is not clearly related to the depletion of trapped neon relative to trapped argon, believed to be due to diffusive loss following solar wind implantation in soil. Noble gas data from sources cited in Fig. 2.

being isotopically fractionated on the lunar surface. If such fractionation is, in fact, occurring, but masked by other effects, then it is highly unlikely that it is caused by solar wind sputtering. At present it is not even clear whether there is any net loss of solar wind carbon from the moon during or following implantation, as the observed C/N ratio, 1.39 from Fig. 8, lies within the uncertainty limits for the solar spectroscopic value, though lower than the nominal value (Cameron, 1973).

It should be emphasized that scenarios involving multiple, independent processes can readily be constructed to "explain" *qualitatively* the carbon abundance and isotopic data (e.g., Pillinger *et al.*, 1976b). However, we believe that a true, quantitative model is more likely to be achieved via the instructive failings of oversimplified but *quantitative* models, than by attempting to insert numbers into a qualitative scenario.

In general, the striking differences in isotope systematics between the silicon-oxygen-sulfur suite, on the one hand, and the solar wind-implanted elements, on the other, suggest strongly that different fractionation mechanisms are active in the two cases. If, as seems likely, solar wind sputtering is responsible for the effects in the former elements, it is therefore unlikely to be the cause of fractionations among the solar wind elements. Even if sputtering is not fractionating silicon, oxygen and sulfur, it is unlikely to be affecting the solar wind elements. This follows because a major fraction of the sulfur is deposited upon grain surfaces and therefore lies directly above the species implanted by the solar wind. It is thus implausible that sputtering could excavate solar wind elements without disturbing, i.e., fractionating the surficial sulfur. Our conclusions about the fractionation of solar wind-implanted species agree with independent reasoning by Huneke (1973), Ducati *et al.* (1973) and Signer *et al.* (1977) which has identified diffusive loss as the likely cause of mass fractionation among trapped noble gases of solar wind origin.

It appears, therefore, that sputtering is not affecting those elements implanted by the solar wind in the outer 200 Å or so of lunar soil grains. Because there is no reason for indigenous atoms to be sputtered preferentially to implanted ones, it follows that the front of sputter erosion is not penetrating in general to solar wind-implantation depths. The lowest value estimated for the solar wind sputtering rate is about 0.02 Å/y (McDonnell, 1977) so that a depth of about 200 Å would be reached in less than 10^4 y. Either this time is greater than the lifetime of a grain against burial or agglutination or the effective sputtering rate on the lunar surface is lower than that found by simulation. The former explanation is unlikely because of the observed surface concentrations of solar wind elements, e.g., carbon (Filleux *et al.*, 1978), which require exposure time for individual grains at least a factor of two greater than the upper limit given above.

Consequently we conclude that the lunar surface sputtering rate is being effectively slowed down below the laboratory simulation values by the operation of some other process. That process is probably the deposition on grain surfaces of material vaporized during meteorite impact. It is well known that mature lunar soils contain at least 1% by weight of meteoritic material (Anders *et al.*, 1973) and, although much of this material is probably incorporated into agglutinates, a proportion is likely to be deposited directly onto grain surfaces. This was suggested by Boynton and Wasson (1977) in view of distributions of volatile and siderophile elements in grain size fractions. It is important to note, in addition, that in the vapor from which such meteoritic elements condense, target atoms would predominate over those from the projectile. Consequently, the concentration of vapor-deposited material on grain surfaces is considerably greater than estimated from concentrations of meteoritic elements alone. It does not appear practical at present to quantify this process but a very rough estimate may be made, taking 1% as the content of meteoritic material in a soil, assuming that 90% of this goes into agglutinates and 10% into a vapor deposit within which it is diluted by about 10 times its weight of indigenous, target material. This leads to a surface deposit about 200 Å thick, a figure which is comparable to the solar wind implantation depth. It is also comparable to the amount of material which must be lost from the system in order to generate the observed oxygen isotope fractionation, assuming Rayleigh fractionation. Clayton *et al.* (1974) pointed out that enrichment of bulk soils in ^{18}O by about 0.5‰ required loss of about 1% of total oxygen. Taking 800 cm^2/g as the surface area of a mature lunar soil, this corresponds to loss of a surface layer about 200 Å in thickness. The dimensions of this surface layer correspond closely to those measured by Dran *et al.* (1970) for the amorphous rims of micrometer-sized soil grains. However, it is not suggested that vapor deposition is producing these rims because it has been demonstrated that they result from solar wind-irradiation damage (e.g., Bibring *et al.*, 1973). Nonetheless, it is likely that a surficial vapor deposit would be promptly metamictized by the solar wind irradiation, to become effectively indistinguishable from amorphous indigenous material.

CONCLUSIONS

1. Isotopic fractionations exhibited by solar wind-implanted elements in lunar soils are of variable magnitude and do not show the systematic dependence upon maturity characteristic of fractionations observed in silicon, oxygen and sulfur.
2. It seems likely that fractionations in silicon, oxygen and sulfur are caused by solar wind sputtering but, whether or not this is the case, sputtering does not appear to be responsible for fractionating the solar wind elements.
3. The active sputtered zone is therefore probably not reaching to the depth within grains where most solar wind-implanted species reside.
4. It follows that the rate of erosion by solar wind sputtering is probably being impeded by deposition from vapor produced during meteorite impact and it is possible that these two processes are close to being in dynamic balance on the lunar surface.
5. Carbon isotope systematics give no evidence for either secular variation in isotopic composition of solar wind carbon or fractionation of carbon isotopes on the lunar surface. However, neither possibility can be excluded at this time.
6. Diffusive loss of light noble gases may be dominated by a small number of major degassing events, presumably large impacts.

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