

LOSS OF O, Si, S AND K FROM THE LUNAR REGOLITH, R. N. Clayton, T. K. Mayeda and J. M. Hurd, Enrico Fermi Inst., Univ. of Chicago, Chicago, Illinois 60637.

Variations in isotopic compositions in lunar soils have been reported for several light elements: H, C, N, O, Si, S, K. Of these, hydrogen, carbon and nitrogen are clearly dominated by the effects of addition of material to the soils from extralunar sources, as indicated by the much higher concentrations of these elements in the soils relative to igneous rocks. Several mechanisms have been proposed to account for the isotopic variability in the remaining four elements. It is the aim of this paper to present a unified model to account for all of the observations.

Oxygen, silicon, sulfur and potassium all have three or more isotopes in nature (all stable except for  $K^{40}$ ), so that measurements of two independent isotope ratios can be made for each element to determine whether the observed fractionations are due to mass-dependent processes, such as chemical reactions or diffusion, or to some other processes specific to particular nuclides, such as nuclear reactions. Epstein and Taylor<sup>(1)</sup> reported that variations in  $Si^{29}/Si^{28}$  were  $1/2$  as great as those in  $Si^{30}/Si^{28}$  in the same samples. Rees and Thode<sup>(2)</sup> showed that analogous mass-dependent relations hold for variations in  $S^{33}/S^{32}$ ,  $S^{34}/S^{32}$  and  $S^{36}/S^{32}$  ratios. In the present work, measurements of  $O^{17}/O^{16}$  and  $O^{18}/O^{16}$  on partially reacted portions of soil 14163 also indicate a 1:2 relationship in magnitude of the isotope effects. A similar test for potassium can be made in principle<sup>(3)</sup>, but it is very difficult due to the low abundance of  $K^{40}$ . At least in the case of oxygen<sup>(4)</sup> the mass-dependent relationships probably rule out significant complication of the isotope effects by addition of extralunar material. All of the data on these four elements can be understood in terms of processes acting on indigenous lunar materials.

Other general observations of isotopic variability in O, Si, S, and K are as follows:

- (1) All have very uniform composition in lunar crystalline rocks, indicating no earlier low-temperature processing.
- (2) All show enrichments of the heavy isotopes in soils relative to rocks.
- (3) The magnitude of heavy isotope enrichment in O and Si are correlated with one another and with various measures of soil maturity<sup>(1,5,6)</sup>, such as noble gas content, metallic iron, particle tracks, etc.
- (4) There is some evidence for surface correlation for the effects in O and Si<sup>(1,5,6,7)</sup> and S<sup>(8)</sup>.
- (5) There is no heavy-isotope enrichment in O, Si and K in glasses, such as Apollo 15 green glass<sup>(3,9)</sup> and Apollo 17 orange glass<sup>(6,9)</sup>, which appear to have been exposed, while molten, to the lunar vacuum, but which have not been exposed for a long time on the surface.

Various models have been proposed to account for some of these observations, involving thermal volatilization or reaction with solar wind protons at high or low temperatures. It has not been established which mechanisms are dominant. The key to understanding the effects observed in these four elements may lie in the recent observations of sizable isotope effects in potassium<sup>(3)</sup>. In this case, the chemistry of the element involved seems

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to allow no reasonable mechanism other than thermal volatilization, a process observed to occur in the laboratory under moderate conditions<sup>(10)</sup>. However, observation 5 above implies that significant volatile loss with concomitant isotopic fractionation requires temperatures in excess of liquidus temperatures. Such temperatures are locally attainable in the regolith in micrometeorite impacts<sup>(11)</sup>. Laboratory studies have shown that potassium and sulfur have rather similar volatilities in lunar materials<sup>(10,12)</sup>, so that processes vaporizing significant amounts of potassium should also vaporize some sulfur.

Since there is a net enrichment of  $K^{41}$  and  $S^{34}$  in soils relative to crystalline rocks, material balance requires a depletion somewhere else. Analyses of  $K^{41}/K^{39}$  are too few to rule out the possible existence of a low- $K^{41}$  reservoir on the moon, but such a possibility seems much less likely for sulfur. A more probable explanation is that the  $S^{32}$ -rich and  $K^{39}$ -rich material has been lost from the moon, presumably in the same high-temperature event which vaporized these elements. An estimate of the minimum loss of material can be made, assuming isotopic fractionations given by the inverse square root of the mass ratio, and assuming a Rayleigh fractionation<sup>(13)</sup> in the vaporization process. The isotopic enrichments, for various values of the residual fraction  $f$  are given in Table 1.

Table 1  
Isotopic Enrichments in Vaporization Residues.  
 $f$  = Wt-fraction of residual element

	1.0	0.9	0.8	0.7	0.6	0.5
$\delta K^{41} (‰)$	0	2.6	5.5	8.8	12.7	17.4
$\delta S^{34} (‰)$	0	3.2	6.7	10.7	15.4	20.9
$\delta Si^{30} (‰)$	0	3.6	7.6	12.2	17.5	23.8
$\delta O^{18} (‰)$	0	6.0	12.8	20.6	29.6	40.4

Typical values of  $\delta K^{41}$  for Apollo 15, 16 and 17 soils are +5 to +8‰<sup>(3)</sup>, implying potassium losses on the order of 20-30%. Values of  $\delta S^{32}$  range up to +10‰<sup>(2,14,15,16)</sup>, implying sulfur losses in this same range. It is difficult to demonstrate losses of this magnitude from available elemental analyses of rocks and soils, particularly for potassium, due to ubiquitous admixture of a potassium-rich KREEP component to the soils.

Loss of oxygen and silicon by volatilization in micrometeorite impacts is also feasible, as shown by the vapor pressure measurements of DeMaria et al.<sup>(17)</sup> A net loss of about 1% would account for the observed overall enrichments of about 0.5‰ in  $\delta O^{18}$  and 0.3‰ in  $\delta Si^{30}$ . The experiments of Epstein & Taylor<sup>(1,5,6)</sup> have shown that these overall enrichments are due to very much larger enrichments located in some small part of the soil which is especially reactive with fluorine. It is not easy to see how such isotopic enrichments could occur in thin surface films as a residue of a vaporization process. Furthermore, measurements in the present work of  $\delta O^{18}$  in separated glassy agglutinates from soils 14163, 15270 and 66081 show that the agglutinates are no richer in  $O^{18}$  than the whole soil from which they came. It is therefore proposed that these highly fractionated materials have been deposited on the soil grains from a vapor which was derived by micrometeorite

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impact, the fractionation having taken place in the lunar "atmosphere".

Most aspects of the model presented here are in accord with the discussion of Gibson et al.<sup>(10)</sup> and Barnes et al.<sup>(3)</sup> in emphasizing the loss of portions of some elements from the soils and from the moon by impact vaporization. In this model, no significant role is seen for low-temperature chemical interactions with solar wind-derived material in producing the isotopic variations.

## References:

- (1) Epstein, S. and Taylor, H. P. Jr., (1971). Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2, Vol. 2, pp. 1421-1441. MIT.
- (2) Rees, C. E. and Thode, H. G. (1972). Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3, Vol. 2, pp. 1479-1485. MIT Press.
- (3) Barnes, I. L., Garner, E. L., Gramlich, J. W., Machlan, L. A., Moody, J. R., Moore, L. J., Murphy, T. J., Shields, W. R. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1197-1207. Pergamon.
- (4) Clayton, R. N., Grossman, L. and Mayeda, T. K. (1973). Science 182, 485-488.
- (5) Epstein, S. and Taylor, H. P. Jr., (1972). Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3, Vol. 2, pp. 1429-1454. MIT Press.
- (6) Taylor, H. P. Jr. and Epstein, S. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1657-1679. Pergamon.
- (7) Clayton, R. N., Onuma, N. and Mayeda, T. K. (1971). Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2, Vol. 2, pp. 1417-1420. MIT Press.
- (8) Rees, C. E. and Thode, H. G. (1974). Lunar Science V. The Lunar Science Institute, Houston.
- (9) Clayton, R. N., Hurd, J. M. and Mayeda, T. K. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1535-1542. Pergamon.
- (10) Gibson, E. K. Jr., Hubbard, N. J., Wiesmann, H., Bansal, B. M., Moore, G. W. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1263-1273. Pergamon.
- (11) Gault, D. E., Hörz, F. and Hartung, J. B. (1972). Proc. Third Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 3, Vol. 3, pp. 2713-2734. Pergamon.
- (12) Gibson, E. K. Jr. and Moore, G. W. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1577-1586. Pergamon.
- (13) Lord Rayleigh (1896). Phil. Mag. 42, 493-498.
- (14) Kaplan, I. R., Smith, J. W. and Ruth, E. (1970). Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 1, Vol. 2, pp. 1317-1329. Pergamon.
- (15) Kaplan, I. R. and Petrowski, C. (1971). Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2, Vol. 2, pp. 1397-1406. MIT Press.
- (16) Smith, J. W., Kaplan, I. R. and Petrowski, C. (1973). Proc. Fourth Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2, pp. 1651-1656. Pergamon.
- (17) DeMaria, G., Balducci, G., Guido, M., and Piacente, V. (1971). Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta, Suppl. 2, Vol. 2, pp. 1367-1380. MIT Press.