erased some tracks. The Hg arriving at the surface with a low velocity may not be retained, since it may be ejected before it has had time to diffuse into the surface. The situation is complex; nevertheless, simple consideration of the Hg cosmic abundance (2.3 atoms per 10^6 Si atoms) and a solar wind flux of 10^8 protons cm^{-2} sec^{-1} will provide the 10^{11} atoms or 10^{-10} g cm^{-2} of Hg lost from the surface over 10^6 years.

Exterior and interior samples from rocks 12052, 12053, and 12022 were measured. Of these, orientation and burial depth of only rock 12022 are known with some confidence. Most of this rock was buried, and our samples appeared to come from just at or below the surface of the soil. Rocks 12052 and 12053 were moved before being photographed; hence their orientation is not known. The lower part of rock 12052 appears to have been partially buried (*14*). Neither rock 12052 nor rock 12053 appears to have been buried as deeply as rock 12022.

If the core results are used as a guide, the rock results can be explained as follows. Our exterior samples of rocks 12052 and 12053 were buried and contain more surface-related Hg than do the interior samples. A possible explanation is that the interior of a crystalline rock exposed to the sun will be warmer than the buried surface in contact with the soil. The Hg that has migrated to the surface might be trapped at the cool interface of the rock and the soil. Rock 12022 was so deeply buried that the whole of the submerged part may have been at about the same low temperature; hence, the amount of Hg adsorbed on surfaces in the interior is about the same as that at the soil-rock interface. If this can be verified, the surface-related Hg might also be helpful in establishing the orientation of a rock.

G. W. REED
J. A. GOLEB
S. JOVANOVIC

Chemistry Division,
Argonne National Laboratory,
Argonne, Illinois 60439

References and Notes

1. G. W. Reed, S. Jovanovic, L. H. Fuchs, *Science* **167**, 501 (1970).
2. The elements for which surface-related concentrations have been reported are the rare gases by the Lunar Sample Preliminary Examination Team [*ibid.* **165**, 1211 (1969)]; ^{40}Ar by D. Heymann and A. Yaniv [*Geochim. Cosmochim. Acta* **2** (Suppl. 1), 1261 (1970)]; N and C by Moore *et al.* (*11*); Bi, Tl, In, and so on, by Keays *et al.* (*12*); Pb by L. T. Silver [*Geochim. Cosmochim. Acta* **2** (Suppl. (1), 1533 (1970)]; Rn by A. L. Turkevich, J. H. Patterson, E. J. Franzgrote, K. R. Sowinski, T. E. Economou [*Science* **167**, 1722 (1970)]; and the halogens by Reed *et al.* (*1*).
3. G. W. Reed and S. Jovanovic, *J. Geophys. Res.* **72**, 2219 (1967).
4. J. A. Goleb, *Appl. Spectrosc.*, in press.
5. Lunar Sample Preliminary Examination Team, *Science* **167**, 1325 (1970).
6. R. H. Manka and F. C. Michel, *ibid.* **169**, 278 (1970).
7. G. Kuiper, Ed., *Atmospheres of the Earth and Planets* (Univ. of Chicago Press, Chicago, ed. 2, 1952), p. 366; see also "Apollo 12 Preliminary Science Report" (*14*, p. 97). Values may range down to 10^{-12} torr (R. H. Manka, personal communication).
8. P. Eberhardt *et al.*, *Geochim. Cosmochim. Acta* **2** (Suppl. 1), 1037 (1970).
9. K. Marti, G. W. Lugmair, H. C. Urey, *Science* **167**, 548 (1970).
10. R. L. Fleischer *et al.*, *ibid.*, p. 568.
11. C. B. Moore, C. F. Lewis, E. K. Gibson, W. Nichiporuk, *ibid.*, p. 495.
12. R. R. Keays, R. Ganapathy, J. C. Laul, E. Anders, G. F. Herzog, P. M. Jeffery, *ibid.*, p. 490.
13. E. J. Öpik, *Annu. Rev. Astron. Astrophys.* **7**, 473 (1969).
14. Lunar Sample Preliminary Examination Team, *NASA Rep. SP-235* (1970).
15. Supported by the U.S. Atomic Energy Commission and by NASA contract T-76356. We thank many of our colleagues for fruitful discussions; especially N. Sugarman and H. R. Heydegger of the University of Chicago and M. Perlman of Brookhaven National Laboratory.

7 December 1970

■

Selenium and Sulfur in a Greenland Ice Sheet: Relation to Fossil Fuel Combustion

Abstract. *In the combustion of fossil fuels, selenium is mobilized in the atmosphere to a much lesser extent than is sulfur. This difference is ascribed to the chemical behavior of their respective tetravalent oxides. The ratio of selenium to sulfur in glacial ice is characteristic of terrestrial matter, and these elements may find their way to ice sheets by the formation of volatile compounds in biochemical processes.*

The combustion of fossil fuels (coal, lignite, oil, and natural gas) mobilizes a variety of chemical species from the continents to the atmosphere, where they are subject to translocation. Recent investigations of glacial material have indicated that the amount of sulfur that enters the atmosphere from fossil fuel combustion is of the same order of magnitude as that which has resulted over historic time from the oxidation of organic matter and from volcanic activity (*1*). To determine whether the same is true of selenium was the purpose of this investigation. Selenium is a member of the group VI A elements in the periodic table, to which sulfur also belongs. Such an investigation might, therefore, also contribute to an understanding of the atmospheric chemistry of selenium as compared with sulfur. The value of measuring the concentration of closely related elements in geochemical studies is well recognized and, in relation to the current study, could extend our insight on the origin of sulfur in permanent snowfields.

Glacial samples are productive for studies of man's input of matter to the atmosphere. Various strata, which can be dated by a variety of techniques such as firn stratigraphy, isotopic analyses of oxygen, and ^{210}Pb geochronologies, contain in essentially unchanged condition both the waters and the accumulated solids that precipitated from the atmosphere.

The availability of dated glacial samples from Greenland (and a single sample from Antarctica) with known sulfate contents provided the materials for this investigation. The selenium content of these samples was determined by measurement of neutron induced ^{81}Se.

The samples were from the Camp Century area of the Greenland ice sheet (77°10′N and 61°07′W) and from a virgin area 80 km east southeast of this location. They were collected by C. C. Patterson of the California Institute of Technology for his investigations on Pb (*2*). The older samples of the Greenland ice sheets were recovered from the walls of an inclined shaft at Camp Century; the younger samples (1952–65) were taken from the walls of open trenches at the virgin site.

The single sample from Antarctica was recovered from an inclined shaft at the New Byrd Station.

These samples were collected and handled with extreme care to reduce the possibility of contamination. They were melted and stored in sealed polyethylene containers in 1966. The procedures and precautions involved in sample collection have been described in detail (*2*).

Fourteen samples were analyzed: eleven in duplicate, two in triplicate, and one was analyzed once. The sample volume ranged from 1 to 4 liters. The precise sample size was measured gravimetrically.

Each sample was transferred from its original polyethylene container to a round-bottom quartz flask, which had been previously leached with hot concentrated nitric acid. To the sample were added 10 ml of concentrated nitric acid and ^{75}Se spike (6×10^3 count/min) that contained less than 0.06 ng of selenium carrier.

The flask was placed in a heated mantle and attached to a condenser through a quartz elbow; the volume was reduced to 20 ml. The solution was transferred to a 50-ml Teflon beaker and then evaporated to one drop within a glass enclosure. The enclosure was maintained under slight positive pressure with a sweep of purified nitrogen gas. The residual drop was transferred with small portions of double-distilled water to a polyethylene vial in preparation for irradiation. The final volume was 1.1 ml. The γ-ray activity of the samples was compared with that of standards to determine the Se yield to this point.

A series of blanks was prepared: 20 ml of distilled water, 10 ml of concentrated nitric acid, and the ^{75}Se spike. These constituents were contained in a 50-ml Teflon beaker and processed from that point as described above.

Comparators consisted of 1 ml of $0.16N$ nitric acid containing 1 μg of Se and the ^{75}Se spike. The samples, comparators, and blanks were irradiated for 30 minutes in a thermal flux of 1.8×10^{12} neutrons cm^{-2} sec^{-1}, in the Lazy Susan of the Triga Reactor at the Gulf Energy and Environment Service facility in San Diego. After irradiation, 1 ml of sample or of blank and 0.50 ml of comparator were radiochemically purified by the procedure of Bowen and Cawse (*3*). Two modifications of this procedure were introduced to decrease the processing time. The changes involved dissolution of the first isolated Se metal precipitate in 2 ml of concentrated nitric acid with the aid of heat. Then the second reduction was effected by the addition of 10 ml of a saturated solution of hydroxylamine hydrochloride. Precipitation was accelerated by the application of heat. This final precipitate was filtered onto a glass fiber disk, which was then mounted on a brass planchet; β-rays of ^{81}Se were counted frequently for 5 hours in a gas-flow proportional counter.

After the counting period, the samples were demounted, dissolved in 2 ml of concentrated nitric acid, filtered, and diluted to a definite volume. The ^{75}Se activity was measured on a portion of the sample, a value from which the yield of the selenium carrier (which had been added prior to radiochemical purification) could be determined. For a number of samples and a series of comparators, the carrier yield was also determined by a colorimetric procedure (*4*).

Table 1. Selenium and sulfur concentration in glacial samples. A single analysis was performed on the 1960 sample; the 1859 and 1965 (winter) samples were analyzed in triplicate, and all others in duplicate. The 1724 sample was recovered from Antarctica; the others, from a Greenland ice sheet. All dates in column 1 except the first are A.D.

Deposition of sample (year)	Se (ng/kg)	S (μg/kg)	Se/S $\times 10^4$
800 B.C.	25.5 ± 1.6	56.3	4.5
1724	14.1 ± 1.6	26.0	5.5
1815	13.4 ± 2.6	26.7	5.0
1859	10.1 ± 1.1	34.7	2.9
1881	7.6 ± 0.3	21.7	3.4
1892	8.0 ± 0.2	26.0	3.0
1946	22.0 ± 2.3	37.7	5.9
1952	11.0 ± 0.2	35.7	3.1
1960	8.9	41.0	2.2
1964 (fall)	5.1 ± 0.5	38.7	1.3
1964 (Dec.)	9.7 ± 1.1	72.7	1.3
1965 (winter)	14.2 ± 2.2	98.0	1.5
1965 (spring)	8.0 ± 0.2	71.0	1.1
1965 (summer)	8.7 ± 0.3	53.7	1.6

In the reduction of the sample volume to one drop and in its transfer to the irradiation vial, a loss of about 10 to 15 percent of the Se was experienced.

Blanks were devoid of detectable quantities of ^{81}Se.

The counting of samples was begun 12 to 14 minutes after irradiation. At that time about 45 count min^{-1} ng^{-1} are realized. After substraction of a long-lived component from the decay data, the resolved ^{81}Se gave an average half-life of 18.6 minutes, which is the accepted value for this radionuclide, and the radiochemical purification was therefore regarded as effective. The standard deviation from this mean was only several percent.

Analyses of the Se carrier yield by γ-ray measurement and by colorimetry agreed within several percent.

These factors combined to give a reliable assay for the Se content of the glacial samples. The average error in the replicate determinations of these samples was 9.0 percent (Table 1).

The Se content in glacial material of different ages extending in time from 800 B.C. to A.D. 1965 appears in Table 1. Included in the table are the S content and Se/S ratios for these samples. The pre-1960 samples have Se/S ratios varying between 2.9 and 5.9×10^{-4}; the post-1960 samples range in value from 1.1 to 1.6×10^{-4}. The 1960 sample appears to be transitional in value (2.2×10^{-4}).

The Se/S ratios in petroleums have been recently determined to range between 0.31 and 1.22×10^{-4} (*5*), and coal samples had an average value of 2.9×10^{-4} (*6*). Most crustal rocks have a Se/S ratio of the order of 1×10^{-4}. Similar values occur in snow, dust, and rain in the environs of the Massachusetts Institute of Technology. In general, the Se/S ratio in material of terrestrial origin is of the order of 10^{-4} (*7*), in sharp contrast with concentrations in seawater, for which this value is 10^{-7} (*8*). The relationship of Se and S in the glacial samples analyzed points to a terrestrial origin in both Greenland and Antarctica.

Several inductions concerning the atmospheric chemistries of Se and S can be derived from the glacial results and from the geochemical data given above. Fossil fuel combustion has not yet resulted in the long-range transport of Se as it has for S. The Se content has been relatively constant, but the S concentration in these glacial ices increased markedly in most of the post-1960 samples. This observation suggests a dilution of the Se by the S that was introduced from fossil fuel burning. As was previously noted (*1*, *2*), the incorporation of atmospheric constituents into glacial matter is seasonally related; the lowest values occur in the fall. This study also reflects this effect (see Table 1). Therefore, while the absolute value of S in the 1964 fall sample is low, the Se/S ratio is of a magnitude that indicates S enrichment relative to Se.

The increase in S in glacial snows since 1960 has been uniquely attributed to fossil fuel combustion (*1*). The combustion of coal has been recognized as the primary source of S pollution. In 1960 an estimated 21 million tons of SO_2 pollution could be attributed to the combustion of coal and fuel oil, of which coal contributed 85 percent (*9*). Since the analytical values available for this fuel have a Se/S ratio similar to that of the pre-1960 glacial values, it appears that Se simply is not moved about the atmosphere after its input from fossil fuel burning.

Where and how do the differences in the geochemical behaviors of S and Se come about? It may be rewarding to examine a little more closely the two processes most probably responsible for the mobilization of these elements about the earth's surface: high-temperature fossil fuel burning and low-temperature biological reactions. In high-temperature oxidation Se burns in air to form the white solid SeO_2. The SeO_2 is so readily reduced that even specks of oxidizable dust in the air react with it to form red elemental Se (*10*). On the other hand, S is oxidized to the relatively stable SO_2. Whether the high-temperature process is man-made or is natural, as in volcanic activity, this difference in chemistry between the elements would be manifest.

On the other hand, the low-temperature biological processes produce compounds of S and Se that are volatile. As organic compounds (whose identity is not yet established), Se is volatilized from land plants (*11*). Volatile organic Se compounds are also released in the process of plant degradation (*11*) (possibly as H_2Se). In either case, the very low concentrations in the atmosphere may survive against oxidation long enough to be transported in a similar manner as the gaseous S compounds H_2S and SO_2.

In summary, man initiates the translocation of compounds of S over great distances through fuel combustion, whereas Se is mobilized to a much lesser extent, perhaps owing to the differences in the chemical and physical properties of the tetravalent oxides.

HERBERT V. WEISS
Naval Undersea Research and Development Center, San Diego, California 92132

MINORU KOIDE
EDWARD D. GOLDBERG
Scripps Institution of Oceanography, University of California, San Diego, La Jolla 92037

References and Notes

1. M. Koide and E. D. Goldberg, in preparation.
2. M. Murozumi, T. J. Chow, C. Patterson, *Geochim. Cosmochim. Acta* **33**, 1247 (1969).
3. H. J. M. Bowen and P. A. Cawse, *Analyst (London)* **88**, 721 (1963).
4. K. L. Cheng, *Anal. Chem.* **28**, 1738 (1956).
5. Y. Hashimoto, J. Y. Hwang, S Yanagisawa, *Environ. Sci. Technol.* **4**, 157 (1970).
6. K. K. S. Pillay, C. C. Thomas, Jr., J. W. Kaminski, *Nucl. Appl. Technol.* **7**, 478 (1969).
7. Y. Hashimoto and J. W. Winchester, *Environ. Sci. Technol.* **1**, 338 (1967).
8. D. F. Schutz and K. K. Turekian, *Geochim. Cosmochim. Acta* **29**, 259 (1965).
9. D. Beinstock and F. J. Field, *Air Pollut. Contr. Ass.* **10**, 121 (1960).
10. I. Rosenfeld and O. A. Beath, *Selenium* (Academic Press, New York, 1964), pp. 41 and 301.
11. B. G. Lewis, C. M Johnson, C. C. Delwiche, *J. Agr. Food Chem.* **14**, 638 (1966).
12. Supported in part by the U.S. Atomic Energy Commission, Division of Biology and Medicine, under grant AT (11-1)-34, Project 84, to the University of California. We thank C. Patterson of the California Institute of Technology, who graciously provided the glacial samples.

18 January 1971

Hydroxyl Orientation in Muscovite as Indicated by Electrostatic Energy Calculations

Abstract. *The electrostatic energy of the* $2M_1$ *muscovite structure,* $KAl_2(Si_3Al)O_{10}(OH)_2$*, has been calculated as a function of the orientation of the hydroxyl group (O–H distance = 0.97 angstrom). The minimum in the electrostatic energy occurs when the OH bond makes an angle of 18° with the cleavage plane and an angle of 31° with the* b*-axis (in the* a-b *plane), which is 2.5° away from the orientation of the transition moment as determined from infrared measurements on single crystals. If the* K^+ *ion is excluded from the calculation, the O–H bond makes an angle of 53° with the cleavage plane. This indicates the strong influence that the interlayer cation exerts on the hydroxyl hydrogen in mica structures.*

The role of the hydroxyl group in micas has recently attracted much attention, particularly in the trioctahedral mica biotite (*1, 2*). Juo and White (*2*) have shown, by examining the pleochroism of the O–H stretching frequencies from oriented biotite films, that the OH orientation depends on the oxidation state of the octahedral iron. The interpretation of the infrared absorption spectra of layer silicates is very complex, and, except for studies of single crystals, one can determine only whether the OH bond is perpendicular to the cleavage plane or inclined. What is needed is a simpler method of determining OH orientation with respect to the other atoms in the crystal structure. Giese *et al.* have shown (*3*) that the hydroxyl hydrogen in diaspore (α-AlOOH) and goethite (α-FeOOH) is found in a position at which the electrostatic energy of the crystal is a minimum, or nearly so. In this report I present evidence that the hydroxyl hydrogen in the mica muscovite, $KAl_2(Si_3Al)O_{10}(OH)_2$, also occupies such a position.

The electrostatic energy of an ionic crystal can be calculated from (*4*)

$$\Phi_0 = -\frac{e^2}{2}\sum_{s=1}^{N}\sum_{t=1}^{\infty}\frac{Z_s Z_t}{r_{st}}$$

where e is the charge on the electron, N is the number of atoms in the unit cell, Z is the ionic charge of the atoms in the unit cell, and r_{st} is the distance between the sth and tth atoms.

A procedure with more rapid convergence was described by Bertaut (*5*) and used by Baur (*6*) to locate hydrogen atom positions in hydrated salt structures. The computations reported here were made with a modified version of Baur's computer program.

The orientation of the hydroxyl group in muscovite has been discussed by several authors on the basis of infrared absorption data from single crystals. Serratosa and Bradley (*7*) suggested that the O–H bond makes an angle of 15° to 20° with the cleavage plane and is directed toward the unoccupied octahedral site. Tsuboi (*8*) and Sutherland (*9*) favored an orientation pointing away from the octahedral layer. The most reliable study is that of Vedder and McDonald (*10*), who give an orientation of the O–H transition moment as making angles of 16° and 30° with the cleavage plane and the *b*-axis, respectively, in the *a-b* plane. They are very careful to point out that the actual OH bond need not coincide with the transition moment. The question of whether the bond points away from or toward the octahedral layer is not answered as clearly as one would wish (*11*). Their data suggest an orientation away from the octahedral layer.

I made my initial electrostatic energy calculations, using the atomic positional parameters of Radoslovich (*12*), the full ionic charge for each ion, and an assumed O–H distance of 0.97 Å. The OH vector was rotated about an axis approximately perpendicular to the cleavage plane, and the hydrogen ion positional parameters were calculated every 30° with reference to an arbitrary but constant origin. The angle between the rotation axis and the OH vector was varied in increments of 20°. In this manner a sampling of all possible hydrogen positional parameters was made and the electrostatic energy was calculated for each. The minimum value was determined by interpolation of these data points. The positional parameters (in fractions of the cell edge) for the hydrogen ion for the minimum energy are $x = 0.337$, $y = 0.640$, and $z = 0.059$. The OH bond makes angles of 8° and 40.5° with the cleavage plane and the *b*-axis, respectively, in the *a-b* plane and it points away from the octahedral layer. This orientation is approximately 11° away from the orien-