# Translocation of Silica and Other Elements from Rock into *Equisetum* and Three Grasses

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 594-B

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

# Translocation of Silica and Other Elements from Rock into *Equisetum* and Three Grasses

*By* T. S. LOVERING *and* CELESTE ENGEL

CONTRIBUTIONS TO GENERAL GEOLOGY

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*Study of the rate and form of silica movement into silica-accumulator plants*

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# TRANSLOCATION OF SILICA AND OTHER ELEMENTS FROM ROCK INTO *EQUISETUM* AND THREE GRASSES

By T. S. Lovering and Celeste Engel

## ABSTRACT

To study the way in which silica moves into typical silica-accumulator plants and the rate at which it is abstracted from soil by such plants, *Equisetum hyemale* (*californicum*), *Arundo donax*, *Phalaris tuberosa*, and *Dactylis glomerata* were grown under carefully controlled conditions in the Earhart Greenhouses at the California Institute of Technology. Crushed raw sterilized basalt, rhyolite, and quartz diorite were used as growing media. The use of blanks to determine evaporation allowed calculation of the amount of water transpired by the plants; the composition of the feed solutions was known; the composition and amount of the plant ash was determined quantitatively. From these data the amount of silica taken by the plants from the rocks used as growing media was calculated as equivalent to 2,000 tons per acre in about 5,350 years—equivalent to all the silica in 1 acre-foot of basalt.

The average amount of the inorganic constituents of the *E. hyemale* sap was calculated from the amount of water transpired and the composition of the total ash of the plants. In sap obtained from the *E. hyemale*, silica was found to be present in almost precisely the amount calculated from the ash analyses and transpiration data. Infrared and other analytical techniques used on the freeze-dried sap residue indicate that the silica is present as part of an organic compound containing (fused?) phenyl rings with the silicon attached to a phenyl group. Magnesium probably moves into the plant as an inorganic sulfate, but most of the other cations are probably carried as parts of one or more complex organic compounds in the sap.

## INTRODUCTION

In 1959, the senior author reported on the probability that vast quantities of silica are taken out of the ground by silica-accumulator plants which sooner or later release the silica in a form vulnerable to physical transport by runoff or wind erosion (Lovering, 1959). Among the many unsolved problems discussed in that publication was that of the form in which silica moved into plants and whether the intake represented simply the silica already in solution in soil moisture or whether the plant in some way took up an increased amount of silica through the biological action of the roots in contact with soil minerals. In an effort to solve this problem and understand the processes by which silica and other elements are translocated into accumulator plants, we carried on a series of experiments in the Earhart Greenhouses of the California Institute of Technology at Pasadena during the interval December 1958 to June 1960. The silica-accumulator plants chosen for study were *Equisetum hyemale* (*californicum*) and the three grasses, *Arundo donax*, *Phalaris tuberosa*, and *Dactylis glomerata*. Although the experimental procedure adopted is certainly subject to improvement, a substantial amount of new information was obtained from this work and is reported herein. We had some difficulty in finding optimum conditions for the *E. hyemale;* for a month or more the plants remained almost dormant because, as it was then discovered by trial and error, the temperature (75° F.) was too warm for them. When placed in a temperature of 60° F, the *E. hyemale* grew magnificently (fig 3).

The senior author bears most of the responsibility for planning the experiment, integrating the data, and writing the paper; the junior author was responsible for the actual selection and preparation of growing media and plants, the day-to-day care and records required, and the harvesting and preparation of the crops for analysis. The individuals responsible for the chemical analyses and infrared spectrograms are noted at the appropriate places in the report.

## EXPERIMENTAL PROCEDURE

The Earhart Greenhouses provide an amazing degree of control over the conditions under which plants are grown; the amount and intensity of light; the hours of light and darkness; the amount of moisture available to the plants; and the temperature of the individual rooms all can be kept constant or varied at will. The air within the plant laboratory is not only filtered, it is run through a Cottrell precipitator which removes all particulate matter before the air itself is washed. All materials within the greenhouses, including the clothes of the workers, are kept sterile, and any plants brought in must first be fumigated. A detailed account of the operation of the Earhart Plant Research Laboratory is given by Went (in Went and others, 1957). It was in the environment provided by this unusual laboratory that we carried out carefully planned experiments on certain silica-accumulator plants.

For growing media three different kinds of rock crushed to minus one-fourth inch were used: fresh vesicular basalt from Pisgah Crater, Ludlow, Calif., bulk density as used being 1.20; fresh rhyolite, from the Victorville-Barstow Old Road, Sidewinder Well, Calif., bulk density as used being 1.70; and weathered quartz diorite (or grus) from La Canada, Calif. The sterile crushed rocks were placed in polyethylene flowerpots, and the fumigated roots and rhizomes of the plants were introduced into these soils to produce the plants for the study. Connected with the bottom of each pot by means of a plastic hose was a 4-liter plastic bottle to catch the drainage from the soils (figs. 1, 2, 3). Water accumulating in these plastic bottles was reused many times, and only sufficient nutrient or demineralized water was added to the plants to supply the moisture lost by evaporation from the soil and transpiration from the plants themselves. A series of blank pots containing the same crushed-rock soils wth a similar arrangement for collecting drainage received water and nutrients whenever those containing plants were given demineralized water or nutrients. Blanks were used to assess the amount of water transpired or evaporated from the plant pots and to determine the amount of silica leached from the soils through the agency of the water and nutrient solutions supplied to the plants without the intervention of the plants themselves.

FIGURE 1.—Arrangement of polyethylene pots and drainage bottles as used in experiment with silica-accumulator plants at the Earhart Greenhouses, California Institute of Technology, Pasadena, Calif.

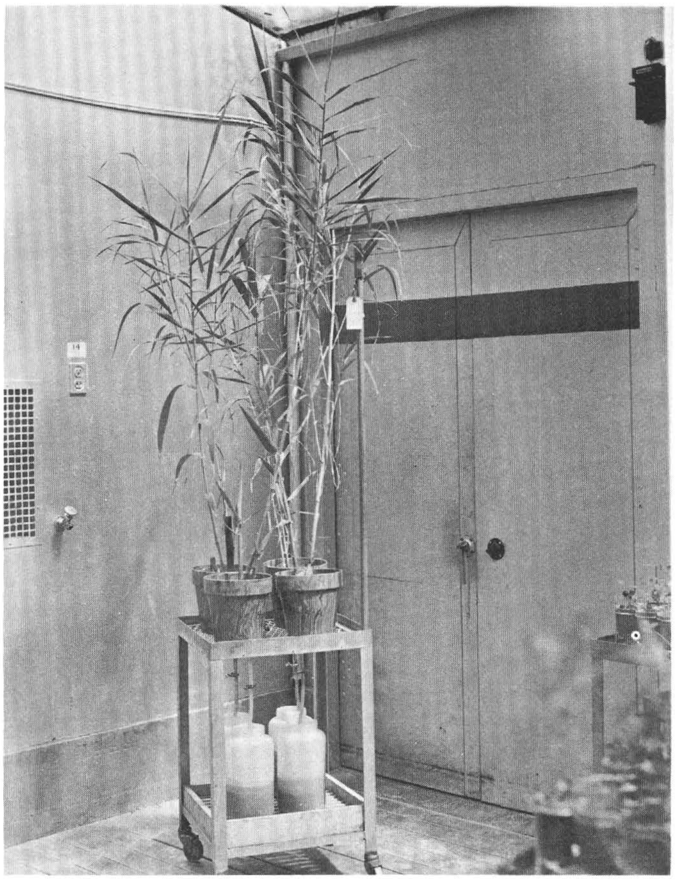

FIGURE 2.—*Arundo donax* on March 28, 1959, showing growth after 105 days.

The leaves and stalks of the plants were harvested two or three times during the experiment, and all the materials so harvested was dried, weighed, ashed, and sampled for quantitative analyses. From the analyses of the solutions fed to these plants and of the residual solutions at the end of the experiment, the total amount of chemical elements or compounds used by the various plants from the supplied solutions was determined, together with the amount that must have been abstracted from the crushed-rock growing media. On the basis of

FIGURE 3.—*Equisetum hyemale* (*californicum*) on July 9, 1959, showing growth after 180 days.

the amount of water transpired by a plant and its bulk composition, the average inorganic composition of the sap of the plant was also determined. A check on the composition of sap from the *E. hyemale* was also made, and the composition was further checked by analyses of sap from *E. hyemale* growing wild. The quantitative data for plants, rock, and solutions resulting from the experiment are given below followed by a discussion of their probable significance.

## QUANTITATIVE DATA ON SOILS, PLANTS, AND WATER

Quantitative analyses made in the rock-analysis laboratories of the U.S. Geological Survey are given for the three different crushed rocks used. The basalt and rhyolite in the pots in which the grass, *Phalaris tuberosa*, was grown were analyzed at the end of the experiment also; comparison of these analyses with those of the original rock suggests gains or losses caused by the plants. Analyses of the crushed rock are given in table 1. The quantity of crushed rock used in the experiments varied with the type of rock used: 3,583 grams of basalt, 5,363 grams of rhyolite, and $\approx$ 5,000 grams of grus.

Because of water losses from transpiration, less water was used for the blanks (those pots that contained no plants). The losses in the blanks were due solely to evaporation. It is, of course, questionable whether the evaporation shown by the blanks was exactly equivalent to that in the pots containing the plants, but presumably the losses through evaporation were nearly equivalent. An exact comparison between the amount of water used by the plants and the amounts used in the blank pots cannot be made because on a few occasions an assistant had watered the plants in an effort to be helpful but had not measured the amounts. From the records that we kept, however, which covered at least 95 percent of all the liquid added to the plants and the blanks, it appears that, on the average, transpiration of water by the plants per pot was from 200 to 300 milliliters of liquid per week. The total amount of water used during the experiment for the different plants and the blanks and the fate of various fractions of the total are shown in table 2, and the compositon of the water is given in table 3.

The amount of the various elements taken from the soil can be closely approximated if we know the composition of the residual solutions in the catchment bottles at the end of the experiment and the composition of the solutions that were fed to the plants during the course of the experiment. The data on the solutions are given in table 3 with the first figure representing the analysis of the solutions in terms of the element and the second figure representing the corresponding oxide. The amount, in grams, available from the total solutions used is given in tables 7 and 8. The data on the residual solutions are incomplete because some of the solutions were discarded after silica had been determined; furthermore algae (including diatoms) developed in the residual solutions and removed some silica. The silica lost from the solution during evaporation from the soil would be deposited at or near the surface. Re-solution of such freshly precipitated silica may have furnished most of the increase noted in the residual solutions from the rhyolite and basalt blanks.

After each harvest of the plants (tops), the harvested material was chopped, dried at 110° C, weighed, ashed, and analyzed (tables 4, 5). From this data the yield (in grams) of the inorganic constituents in the plants was determined (table 6).

## DISCUSSION OF QUANTITATIVE DATA

### *Arundo donax* and *Equisetum hyemale (californicum)* in basalt

The amount of plant harvested for a single pot is shown in table 5. The total amount of liquid used during the period of growth (table 2) was 38.9 liters, which

TABLE 1.—*Composition of rocks used for growing media*

[Analysts: Major constituents for fresh rhyolite, fresh basalt, and quartz diorite, E. L. Munson; spectroscopic analysis, P. R. Barnett. Major constituents for rhyolite and basal D. L. Powers. n.d., not determined]

**Major constituents**

| | Field No. | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | FeO | MgO | CaO | $Na_2O$ | $K_2O$ | $H_2O+$ | $H_2O-$ | $TiO_2$ | $P_2O_5$ | MnO | $CO_2$ | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fresh rhyolite | 22-TL-60 | 66.84 | 15.14 | 2.50 | 0.18 | 0.69 | 2.46 | 3.77 | 4.81 | 1.04 | 0.03 | 0.56 | 0.13 | 0.07 | 1.55 | 0.02 |
| Rhyolite (edge) [1] | 5-TL-61 | 66.70 | 15.12 | 2.50 | .19 | .72 | 2.58 | 3.71 | 4.81 | 1.10 | .06 | .57 | .13 | .07 | 1.56 | .02 |
| Rhyolite (root) [2] | 6-TL-61 | 66.83 | 15.12 | 2.54 | .18 | .68 | 2.48 | 3.70 | 4.81 | 1.09 | .06 | .58 | .13 | .07 | 1.51 | .02 |
| Fresh basalt | 23-TL-60 | 46.67 | 15.84 | 3.29 | 7.20 | 8.63 | 9.09 | 3.79 | 1.79 | .32 | .07 | 2.40 | .57 | .18 | .16 | .04 |
| Basalt (edge) [1] | 3-TL-61 | 46.63 | 15.97 | 3.23 | 7.18 | 8.63 | 9.10 | 3.66 | 1.83 | .27 | .10 | 2.39 | .56 | .18 | .14 | .05 |
| Basalt (root) [2] | 4-TL-61 | 46.52 | 15.80 | 3.23 | 7.27 | 8.88 | 9.07 | 3.64 | 1.82 | .38 | .10 | 2.36 | .56 | .18 | .14 | .05 |
| Quartz diorite (grus) | 21-TL-61 | 61.98 | 17.08 | 2.67 | 1.91 | 2.05 | 4.79 | 3.77 | 2.52 | 1.55 | .51 | .71 | .18 | .07 | .02 | n.d. |

**Minor constituents** [3]

| | Field No. | Ba | Co | Cr | Cu | Ga | La | Nb | Ni | Pb | Sc | Sr | V | Y | Yb | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fresh rhyolite | 22-TL-60 | 0.16 | 0.0003 | <0.0002 | 0.0009 | 0.0017 | 0.009 | 0.003 | <0.0003 | 0.002 | 0.0012 | 0.027 | 0.004 | 0.005 | 0.0005 | 0.033 |
| Rhyolite (edge) [1] | 5-TL-61 | .13 | .0002 | .0004 | .0003 | .0016 | .007 | .002 | <.0003 | .002 | .0010 | .027 | .004 | .004 | .0004 | .027 |
| Rhyolite (root) [2] | 6-TL-61 | .14 | .0002 | .0002 | .0005 | .0016 | .007 | .002 | <.0003 | .002 | .0012 | .026 | .004 | .004 | .0004 | .030 |
| Fresh basalt | 23-TL-60 | .036 | .0037 | .026 | .0057 | .0026 | <.004 | .006 | .015 | <.002 | .0026 | .066 | .026 | .003 | .0003 | .024 |
| Basalt (edge) [1] | 3-TL-61 | .038 | .0034 | .025 | .0057 | .0024 | <.004 | .006 | .014 | <.002 | .0026 | .068 | .023 | .003 | .0003 | .023 |
| Basalt (root) [2] | 4-TL-61 | .036 | .0035 | .030 | .0057 | .0022 | <.004 | .006 | .014 | <.002 | .0026 | .10 | .020 | .003 | .0003 | .024 |
| Quartz diorite (grus) | 21-TL-61 | .14 | .0010 | .0025 | .0018 | .0023 | .011 | <.002 | .001 | .003 | .0012 | .062 | .010 | .002 | .0002 | .016 |

[1] Soil taken from edge of *Phalaris tuberoso* pot at end of experiment.

[2] Soil taken from around *Phalaris tuberoso* roots at end of experiment.

[3] Looked for but not found: Ag, As, Au, B, Be, Bi, Cd, Ge, In, Mo, Pt, Sb, Sn, Ta, Tl, U, W, and Zn.

TABLE 2.—*Water, in liters, used in experiments*

| Material and plant | Time interval (weeks) | Demineralized water | | Nutrient solution | | Total liquid | Liquid in catchment flask | Evaporated plus transpired water | | Evaporation | Water transpired | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Cumulative | Amount per week for interval | Cumulative | Amount per week for interval (ml) | | | Liquid used | Cumulative average per week | | Total | Per week |
| Basalt blank | 45.6 | 14.8 | | | | 14.8 | 2.7 | 12.1 | 0.265 | 12.1 | | |
| Rhyolite blank | 45.6 | 6.8 | | 8 | | 14.8 | 2.7 | 12.1 | .265 | 12.1 | | |
| *Arundo donax* (basalt) | 0-45.6 | 9 | 0-250 | 12.5 | 250-500 | 21.5 | 2.4 | 19.1 | .418 | 12.1 | 7.0 | 0.15 |
| | 46-76.0 | 9 | 0 | 29.9 | 500-750 | 38.9 | 2.03 | 36.9 | .486 | 20.1 | 16.8 | .22 |
| *Arundo donax* (rhyolite) | 0-45.6 | 9 | 0-250 | 11.5 | 250 | 20.5 | 2.0 | 18.5 | .405 | 12.1 | 6.4 | .14 |
| | 46-76.0 | 9 | 0 | 28.0 | 500-750 | 37.0 | 2.02 | 35.0 | .461 | 20.1 | 14.9 | .20 |
| *Equisetum hyemale* | 0-41.0 | 6.5 | 0-250 | 22.5 | 500-1,000 | 29.0 | 2.8 | 26.2 | .640 | 12.1 | 14.1 | [1] .34 |
| | 41-74.0 | 0 | 0 | 42.0 | 500-1,000 | 48.5 | 2.0 | 46.5 | .630 | 20.7 | 25.5 | .35 |
| *Dactylis glomerata* | 0-36.0 | ≈8.0 | | ≈13.0 | | ≈21.0 | ≈2.0 | ≈19.0 | .54 | ≈9.3 | ≈9.7 | ≈.27 |
| *Phalaris tuberosa* | 0-36.0 | ≈8.0 | | ≈13.0 | | ≈21.0 | ≈2.0 | ≈20.19 | .54 | ≈9.3 | ≈9.7 | ≈.27 |

[1] This figure is probably too high, as the *E. hyemale* was dormant the first 4 weeks, which are not included in the 41-week time interval although the water used the first 4 weeks is included in the cumulative amount. The *E. hyemale* was not only slow in getting started, but from the start was watered more copiously than the *A. donax* and the blanks. The data and the laboratory experience suggest that 300 ml per week is a fair approximation of the transpiration of the *E. hyemale*.

TABLE 3.—*Composition, in parts per million, of feed and residual solutions*

[Analysts: Columns 1, 2, and 3, R. A. Wilson; 4, 5, and 11, trace amounts, U. Oda, spectroscopist; 6 and 7, C. A. Horr, chemical analyst, and Nancy Conklin, spectroscopist; 8–11, P and Si, M. J. Fishman, and $SiO_2$, M. W. Skougstad]

| Constituent | | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | | 8 | | 9 | | 10 | | 11 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide | Element | Oxide |
| **Chemical analyses of solutions** | | | | | | | | | | | | | | | | | | | | | | | |
| Si | $SiO_2$ | 5.6 | 12.0 | 6.1 | 13.0 | 5.85 | 12.5 | 5.6 | 12.0 | 5.6 | 12.0 | 9.32 | 20 | 11.18 | 24 | 0.51 | 1.1 | 0.56 | 1.2 | 10.06 | 21.6 | 14.77 | 31.7 |
| Al | $Al_2O_3$ | .00 | | .00 | | .00 | | .3 | .57 | .6 | 1.3 | .2 | .38 | .3 | .57 | | | | | | | | |
| Fe | $Fe_2O_3$ | .001 | .002 | .02 | .030 | .01 | .02 | .5 | .67 | 3.0 | 4.0 | 1.7 | 2.28 | 2.4 | 3.22 | | | | | | | | |
| Mg | MgO | .00 | | .00 | | .00 | | 49.0 | 81.2 | 50.0 | 83.0 | 44.0 | 73 | 26.0 | 43.16 | | | | | | | | |
| Ca | CaO | .24 | .34 | .16 | .22 | .20 | .28 | 201.0 | 281.0 | 91.0 | 127.4 | 52.0 | 72.8 | 54.0 | 75.6 | | | | | | | | |
| Na | $Na_2O$ | 3.2 | 4.3 | 2.5 | 3.4 | 2.85 | 3.85 | 3.9 | 5.3 | 24.0 | 32.3 | 61.0 | 82 | 29.0 | 39 | | | | | | | | |
| K | $K_2O$ | .46 | .55 | .40 | .48 | .43 | .52 | 235.0 | 283.2 | 234.0 | 282.0 | 38.0 | 45.8 | 115.0 | 138.6 | | | | | | | | |
| P | $P_2O_5$ | | | | | | | 31.0 | 71.0 | 62.0 | 142.0 | 2.05 | 4.69 | 4.56 | 10.44 | 1.63 | 5.24 | 1.63 | 5.24 | 9.45 | 21.64 | 11.08 | 25.37 |
| S | $SO_4$ | 1.32 | 3.96 | .29 | .87 | .80 | 2.43 | 64.3 | 193.0 | 67.3 | 201.6 | 38.63 | 116 | 41.29 | 124 | | | | | | | | |
| N | $N_2O_3$ | .00 | | .00 | | .00 | | 140.0 | 321.0 | 115.0 | 312.0 | 15.8 | 121.8 | 50.53 | 389.8 | | | | | | | | |
| Cl | | 1.2 | | 7.0 | | 4.1 | | 4.1 | | 36.0 | | 20.0 | | 1.0 | | | | | | | | | |
| F | | .10 | | .20 | | .15 | | | | | | 8.0 | | 12.0 | | | | | | | | | |
| Mn | MnO | | | | | | | .05 | .06 | .13 | .2 | .00 | | .00 | | | | | | | | | |
| Cu | CuO | | | | | | | .02 | .02 | .016 | .02 | | | | | | | | | | | | |
| Zn | ZnO | | | | | | | .05 | .06 | .012 | .015 | | | | | | | | | | | | |
| B | $B_2O_3$ | | | | | | | .5 | 1.6 | .12 | .39 | | | | | | | | | | | | |
| Mo | MoO | | | | | | | .01 | .01 | .024 | .04 | | | | | | | | | | | | |
| Dissolved solids | | 25.17 | | 24.13 | | | | 1.0 | | | | 506 | | 628.0 | | | | | | | | | |
| Total $SiO_2$: Ionic and particulate (mg)/volume of residual solution (ml) | | | | | | | | No particulate $SiO_2$. | | No particulate $SiO_2$. | | | | | | $\frac{2.338}{1300}$ | | $\frac{51.995}{1100}$ | | $\frac{37.945}{1700}$ | | $\frac{645.970}{900}$ | |
| pH | | 6.0 | | 3.7 | | | | | | | | 7.6 | | 7.3 | | | | | | | | | |

**Spectrographic analysis on residues from evaporation**
[Values are for elements only]

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | | | | | <1 | 0 | 16 | <1 | <1 | <1 | 1 |
| Al | | | | | | 120 | 28 | | | | |
| B | | | | | 200 | 660 | 550 | 1,000 | 500 | 1,000 | 500 |
| Ba | | | | | 10 | 17 | 2 | 20 | 50 | 50 | 150 |
| Co | | | | | <10 | 36 | <10 | 20 | 15 | 10 | 10 |
| Cr | | | | | <5 | <1 | 1.3 | 10 | 10 | 10 | 10 |
| Cu | | | | | 15 | 210 | 39 | 70 | 50 | 50 | 70 |
| Fe | | | | | 2,000 | 1,800 | 1,800 | 5,000 | 7,000 | 20,000 | 15,000 |
| Li | | | | | | | <1 | | | | |
| Mg | | | | | 50,000 | | | 100,000 | 100,000 | 100,000 | 100,000 |
| Mn | | | | | 300 | 20 | <10 | 10 | 50 | 300 | 300 |
| Mo | | | | | 10 | 10 | 3.2 | 15 | 20 | 10 | 15 |
| Ni | | | | | <5 | 66 | 55 | 150 | 150 | 150 | 150 |
| Pb | | | | | <10 | 96 | 22 | 100 | 100 | 70 | 100 |
| Rb | | | | | | | 13 | | | | |
| Sn | | | | | <10 | <10 | <10 | 10 | <10 | 20 | <10 |
| Sr | | | | | <20 | <180 | 26 | 700 | 700 | 500 | 500 |
| V | | | | | 25 | 40 | 0 | 10 | 20 | 10 | 10 |
| Zn | | | | | <200 | <1,000 | <1,000 | <200 | <200 | <200 | <200 |
| Zr | | | | | <10 | <10 | | | <10 | <10 | <10 |

1. Demineralized water from Earhart Laboratory, just after cleaning resins. Sample 402–TL–59.
2. Demineralized water from Earhart Laboratory, just before cleaning resins. Sample 401–TL–59.
3. Average of 1 and 2.
4. Nutrient solution 1, Hoaglands (dilute working solution). Sample 24–TL–60. Major constituents calculated from receipt for original nutrient as diluted to working solution.
5. Nutrient solution 2, Ulrichs (dilute working solution). Sample 25–TL–60. Major constituents calculated from receipt for original nutrient as diluted to working solution.
6. Residual solution from basalt blank (1600 ml). Sample 410–TL–60.
7. Residual solution through rhyolite blank (1600 ml). Sample 411–TL–60.
8. Filtered residual solution from *Arundo donax* grown in basalt (1300 ml). Sample 28–TL–60; residue, 636 milligrams.
9. Unfiltered residual solution from *Arundo donax* grown in basalt (900 ml). Sample 29–TL–60; residue, 556 milligrams.
10. Filtered residual solution from *Arundo donax* grown in rhyolite (1700 ml). Sample 26–TL–60; residue, 676 milligrams.
11. Unfiltered residual solution from *Arundo donax* grown in rhyolite (900 ml). Sample 27–TL–60; residue, 590 milligrams.

TABLE 4.—*Growth time, dry weight, and ash content of experimental plants*

[Analyst, C. E. Thompson]

| Plant, soil, and cutting | Sample | Growth time (weeks) | Dry weight (grams) | Percent ash | Weight of ash (grams) |
|---|---|---|---|---|---|
| *Arundo donax* | | | | | |
| Basalt | | | | | |
| 1st | 5-TL-60 | 33 | 99.25 | 7.8 | 7.74 |
| 2d | 6-TL-60 | 8 | 120.00 | 7.8 | 9.36 |
| 3d | 2-TL-60 | 35 | 131.66 | 5.35 | 7.00 |
| Root | 17-TL-60 | 76 | 58.60 | 4.6 | 2.78 |
| Total | | | | | 26.88 |
| Rhyolite | | | | | |
| 1st | 7-TL-60 | 33 | 97.75 | 7.8 | 7.62 |
| 2d | 8-TL-60 | 8 | 105.50 | 6.8 | 7.17 |
| 3d | 1-TL-60 | 35 | 74.80 | 6.8 | 5.08 |
| Root | 18-TL-60 | 60 | 46.41 | 6.2 | 2.88 |
| Total | | | | | 22.75 |
| *Equisetum hyemale* | | | | | |
| Basalt | | | | | |
| 1st | 9-TL-60 | 41 | 85.50 | 9.4 | 8.04 |
| 2d | 4-TL-60 | 33 | 79.02 | 12.3 | 9.72 |
| Root | | 74 | | | |
| Total | | | | | 17.76 |
| Rhyolite | | | | | |
| 1st | 10-TL-60 | 41 | 76.25 | 10.0 | 7.62 |
| 2d | 3-TL-60 | 33 | 77.10 | 13.2 | 10.18 |
| Total | | | | | 17.80 |
| *Phalaris tuberosa* | | | | | |
| Basalt | | | | | |
| 1st | 12-TL-60 | 26 | 94.75 | 5.6 | 5.31 |
| 2d | 11-TL-60 | 10 | 76.50 | 4.8 | 3.67 |
| Total | | | | | 8.98 |
| Rhyolite | | | | | |
| 1st | 16-TL-60 | 26 | 51.75 | 6.8 | 3.52 |
| 2d | 15-TL-60 | 10 | 56.00 | 4.6 | 2.58 |
| Total | | | | | 6.10 |
| *Dactylis glomerata* | | | | | |
| Grus | | | | | |
| 1st | 14-TL-60 | 26 | 116.25 | 9.2 | 10.70 |
| 2d | 13-TL-60 | 10 | 73.50 | 7.0 | 5.14 |
| Total | | | | | 15.84 |

contained 12 ppm (parts per million) of $SiO_2$, a total of 0.467 grams of $SiO_2$ (table 7). Subtracting the total amount of silica in the residual solution remaining in the catchment bottle at the end of the experiment (0.058 gr $SiO_2$) shows that the total silica available to the plant from water was $\approx$0.41 grams of $SiO_2$. The difference between this figure and the total silica in the plant ash amounts to 2.037 grams of $SiO_2$ (table 7, F) and is the minimum amount that was derived from the crushed-rock growing medium itself. The difference in the analyses of the basalt at the beginning and end of the experiment (table 1) is small—nearly within experimental error of duplication of analyses—but if we accept the figures at face value, the difference in the percentage of silica in the two soils multiplied by weight of basalt in the pots containing the *Arundo donax* indicates that the basalt at the end of the experiment had lost between 1.4 and 5.4 grams of $SiO_2$. The silica in the residual solutions from the basalt blanks is only 20 ppm (12 ppm in the feed solutions) and indicates that more silica was added by evaporation than was dissolved from the crushed basalt by the feed solutions in percolating through 12.5 centimeters of this material. This figure from the basalt blank (20 ppm) is essentially that of the total silica content (22 ppm) of the residual solution in the catchment bottle under the *A. donax* in basalt. The residual solutions from the *Equisetum* and grasses were lost, but the similarity of the analyses of their ash and of the calculated composition of the sap strongly indicates that the figures for the *Arundo* and blank soils probably approximate those of the other plants. We conclude that in addition to the silica carried in the solutions used in watering the plants and in addition to the silica derived from any solvent action of water on the basalt, biological activity of the roots of the *A. donax* and the other plants was instrumental in solubilizing the solid silicates in the rock soil and making available additional silica to the plant. This conclusion is in harmony with the work done on lower forms of plant life by several investigators.

Many years ago Coupin (1922) reported that the diatom *Nitzschia linearis* was not able to use silica glass nor silica gel as a source of silica and that potassium or sodium silicate was poisonous in "larger concentrations" (probably because of their alkalinity); however, the diatom did use silica from kaolin, feldspar, orthoclase, and clay, but the concentrations of silica in the solutions containing these minerals is not given.

In 1942 Vinogradov and Boichenko reported on the decomposition of kaolin by diatoms. They reported that *Nitzschia palea* and *Navicula minuscula* slowly but effectively decomposed a crystal of nacrite (a kaolin mineral). The nacrite started decomposing where it was in contact with the slime sheath secreted by the diatoms, and the decomposition was accompanied by an increase in opacity of the crystal, which gradually swelled and lost its birefringence and began to exfoliate along cleavage planes. As the diatoms continued to solubilize the silica, the crystal became amorphous, irregular in outline, and diminished in size; at the same time alumina was liberated into the aqueous medium while silica was assimilated by the diatoms. According to these investigators, the translocation of silica into the diatoms could take place either with or without symbiotic bacteria.

No attempt was made in the present investigation to determine whether or not symbiotic bacteria act as an intermediary in the solubilizing of the rock-growing media. The work of Vinogradov and Boichenko suggests that the biologic activity of the plants themselves may be sufficient to decompose the minerals in the rock with which the roots or rhizomes are in contact.

Keller and Frederickson (1952) point out that the roots of plants carry a strong negative charge, which

TABLE 5.—*Plant-ash analyses, in weight percent*

**Major constituents** [2]

| Plant ash, soil, and cutting [2] | $SiO_2$ | MgO | CaO | $Na_2O$ | $K_2O$ | $H_2O+$ | $H_2O-$ | $P_2O_5$ | MnO | $CO_2$ | $SO_3$ | Cl | [3] $Al_2O_3$ | [3] $Fe_2O_3$ | [3] $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Arundo donax* | | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | | |
| 1st | 6.22 | 4.50 | 4.68 | 0.23 | 41.25 | 1.32 | 5.61 | 3.35 | 0.05 | 16.55 | 13.04 | 2.08 | 0.05 | 0.10 | 0.003 |
| 2d | 7.69 | 5.03 | 4.35 | .11 | 40.94 | .16 | 5.24 | 3.05 | .05 | 10.67 | 19.46 | 1.41 | .04 | .17 | .003 |
| 3d | 10.62 | 6.18 | 6.90 | .31 | 38.37 | 1.51 | 2.33 | 3.06 | .07 | 6.30 | 20.82 | 1.03 | .28 | .27 | .010 |
| Root | 18.08 | 5.04 | 9.03 | 4.92 | 24.52 | -------- | -------- | 3.36 | .04 | -------- | -------- | -------- | [4] 3 | [4] 1.5 | [4] .3 |
| Rhyolite | | | | | | | | | | | | | | | |
| 1st | 8.19 | 5.03 | 8.17 | .20 | 38.21 | 1.85 | 3.59 | 3.65 | .09 | 12.54 | 14.10 | 3.03 | .11 | .31 | .007 |
| 2d | 9.05 | 5.50 | 5.19 | .22 | 39.18 | 1.82 | 3.32 | 3.70 | .13 | 6.81 | 21.42 | 1.81 | .06 | .21 | .004 |
| 3d | 9.24 | 6.33 | 7.81 | .39 | 36.64 | 1.65 | 2.53 | 4.10 | .12 | 7.25 | 19.98 | 1.72 | .37 | .35 | .01 |
| Root | [5] 54.31 | 1.40 | 9.03 | 3.60 | 11.74 | -------- | -------- | 1.20 | -------- | -------- | -------- | -------- | [3] 7 | [3] 1.5 | [3] .3 |
| *Equisetum hyemale* | | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | | |
| 1st | 9.19 | 4.13 | 14.22 | .54 | 33.45 | 2.41 | 3.70 | 5.40 | .04 | 16.05 | 8.66 | .83 | .02 | .06 | .002 |
| 2d | 12.53 | 4.05 | 19.70 | .23 | 29.31 | 1.00 | 3.66 | 3.86 | .05 | 15.79 | 7.52 | .75 | .07 | .12 | .003 |
| Rhyolite | | | | | | | | | | | | | | | |
| 1st | 7.46 | 5.09 | 15.78 | .44 | 33.06 | 2.37 | 2.53 | 4.24 | .07 | 16.09 | 10.42 | 1.22 | .02 | .06 | .002 |
| 2d | 11.18 | 4.55 | 22.55 | .27 | 27.97 | 1.16 | 2.23 | 3.04 | .07 | 16.13 | 9.00 | .84 | .04 | .09 | .003 |
| *Phalaris tuberosa* | | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | | |
| 1st | 9.29 | 5.98 | 5.46 | 1.78 | 36.44 | 2.90 | 4.28 | 4.17 | .07 | 11.02 | 15.18 | 1.30 | .02 | .07 | .002 |
| 2d | 15.68 | 5.78 | 5.33 | 1.79 | 33.20 | 3.74 | 3.76 | 5.90 | .15 | 7.18 | 14.73 | -------- | .02 | .11 | .002 |
| Rhyolite | | | | | | | | | | | | | | | |
| 1st | 8.75 | 6.39 | 8.40 | .91 | 34.92 | 2.42 | 4.54 | 4.02 | .11 | 12.68 | 14.20 | -------- | .17 | .13 | .005 |
| 2d | 13.36 | 6.96 | 8.34 | 1.08 | 31.16 | 2.74 | 3.98 | 4.72 | .21 | 8.84 | 15.96 | .74 | .04 | .09 | .002 |
| *Dactylis glomerata* | | | | | | | | | | | | | | | |
| Grus | | | | | | | | | | | | | | | |
| 1st | 16.39 | 6.63 | 7.68 | .59 | 32.37 | 2.96 | 5.77 | 4.18 | .23 | 13.00 | 8.50 | 1.38 | .02 | .06 | .002 |
| 2d | 7.33 | 4.94 | 4.42 | .35 | 39.50 | 3.31 | 8.01 | 3.12 | .12 | 21.49 | 7.48 | .92 | .01 | .04 | .001 |

**Minor constituents** [4]

| Plant ash, soil, and cutting [2] | Ag | B | Ba | Be | Co | Cr | Cu | Mo | Ni | Pb | Sn | V | Zn | Za |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Arundo donax* | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | |
| 1st | 0 | 0 | <0.001 | 0 | <0.001 | <0.001 | 0.004 | 0.001 | 0.001 | 0 | <0.001 | 0 | 0.02 | <0.001 |
| 2d | <.001 | <.001 | <.001 | 0 | <.001 | .001 | .003 | <.001 | <.001 | 0 | 0 | 0 | .001 | <.001 |
| 3d | <.001 | <.001 | <.001 | <.001 | 0 | .002 | .001 | <.001 | <.001 | .002 | <.001 | <.001 | .002 | .001 |
| Rhyolite | | | | | | | | | | | | | | |
| 1st | 0 | <.001 | <.001 | 0 | <.001 | .002 | .004 | .002 | <.001 | 0 | <.001 | <.001 | .04 | <.001 |
| 2d | 0 | <.001 | <.001 | 0 | <.001 | .001 | .003 | .003 | <.001 | 0 | <.001 | 0 | .03 | <.001 |
| 3d | <.001 | <.001 | <.001 | <.001 | 0 | .001 | .001 | <.001 | <.001 | .002 | <.001 | <.001 | .006 | .001 |
| *Equisetum hyemale* | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | |
| 1st | <.001 | <.001 | <.001 | 0 | 0 | .001 | <.001 | <.001 | <.001 | .002 | <.001 | 0 | <.001 | .001 |
| 2d | <.001 | <.001 | <.001 | <.001 | 0 | .001 | <.001 | <.001 | <.001 | <.001 | <.001 | <.001 | <.001 | <.001 |
| Rhyolite | | | | | | | | | | | | | | |
| 1st | <.001 | <.001 | <.001 | 0 | 0 | .001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | <.001 | <.001 |
| 2d | <.001 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | <.001 | <.001 | .001 | <.001 | <.001 | <.001 | <.001 |
| *Phalaris tuberosa* | | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | | |
| 1st | <.001 | <.001 | <.001 | 0 | 0 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | <.001 | <.001 |
| 2d | 0 | <.001 | <.001 | 0 | 0 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | <.001 | .001 |
| Rhyolite | | | | | | | | | | | | | | |
| 1st | <.001 | <.001 | <.001 | 0 | 0 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | .001 | .001 |
| 2d | <.001 | <.001 | <.001 | 0 | 0 | .001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | <.001 | .002 |
| *Dactylis glomerata* | | | | | | | | | | | | | | |
| Grus | | | | | | | | | | | | | | |
| 1st | .001 | .001 | <.001 | 0 | 0 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | <.001 | .001 |
| 2d | <.001 | <.001 | <.001 | 0 | 0 | <.001 | <.001 | <.001 | <.001 | .001 | <.001 | 0 | .001 | <.001 |

[1] Standard quantitative analysis, wet methods; analyzed by E. L. Munson, except for Cl by V. C. Smith.

[2] *Arundo donax* growth period for 1st cutting, 33 weeks; for 2d cutting, 3 weeks; for 3d cutting, 35 weeks. *Equisetum hyemale* growth period for 1st cutting, 39 weeks; for 2d cutting, 33 weeks.

[3] Spectrographic analysis, quantitative, on "$R_2O_3$" precipitate from ash analysis, by P. R. Barnett.

[4] Spectrographic analysis, semiquantitative, by P. R. Barnett.

[5] Figure for $SiO_2$ includes $Al_2O_3$ and $Fe_2O_3$; value for $SiO_2$ alone is probably about 45 percent.

TABLE 6.—*Weight, in grams, of major inorganic constituents of plants*

| Plant, medium, cutting, and date | Growth period (weeks) | $SiO_2$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $Al_2O_3$ | $Fe_2O_3$ | $CO_2$ | $SO_3$ | Cl | Ash weight |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Arundo donax* | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | |
| 1st, 7-17-59 | 33 | 0.481 | 0.348 | 0.362 | 0.018 | 3.193 | 0.259 | 0.004 | 0.007 | 1.281 | 1.009 | 0.168 | 7.74 |
| 2d, 9-14-59 | 8 | .720 | .471 | .407 | .010 | 3.832 | .285 | .004 | .016 | .999 | 1.821 | .132 | 9.36 |
| 3d, 5-20-60 | 35 | .743 | .433 | .483 | .021 | 2.686 | .214 | .020 | .019 | .441 | 1.457 | .072 | 7.00 |
| Root (Feb. 1960) | ---- | .502 | .140 | .250 | .137 | .681 | .038 | ---- | ---- | ---- | ---- | ---- | 2.78 |
| Total | 76 | 2.446 | 1.392 | 1.502 | .186 | 10.392 | .796 | .028 | .042 | 2.721 | 4.287 | .372 | 26.88 |
| Yield per year | ---- | 1.675 | .95 | 1.03 | .127 | 7.10 | .54 | .019 | .028 | 1.852 | 2.93 | .24 | 18.38 |
| *A. donax* | | | | | | | | | | | | | |
| Rhyolite | | | | | | | | | | | | | |
| 1st, 7-17-59 | ---- | 0.624 | 0.383 | 0.623 | 0.015 | 2.912 | 0.278 | 0.008 | 0.024 | 0.955 | 1.074 | 0.231 | 7.62 |
| 2d, 9-14-59 | ---- | .649 | .394 | .372 | .016 | 2.809 | .265 | .004 | .015 | .488 | 1.536 | .130 | 7.17 |
| 3d, 5-20-60 | ---- | .469 | .322 | .346 | .020 | 1.861 | .208 | .019 | .018 | .368 | 1.015 | .087 | 5.08 |
| Root | ---- | [1] 1.30 | .042 | .260 | .088 | .339 | .035 | ---- | ---- | ---- | ---- | ---- | 2.88 |
| Total | 76 | 3.042 | 1.141 | 1.601 | .139 | 7.921 | .786 | .031 | .057 | 1.811 | 3.625 | .448 | 22.75 |
| Yield per year | ---- | 2.081 | .78 | 1.095 | .095 | 5.42 | .537 | .021 | .039 | 1.24 | 2.48 | .31 | 15.55 |
| *Equisetum hyemale* | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | |
| 1st, 10-16-59 | 41 | 0.739 | 0.332 | 1.143 | 0.043 | 2.689 | 0.341 | 0.002 | 0.005 | 1.290 | 0.696 | 0.067 | 8.04 |
| 2d, 6-2-60 | 33 | 1.218 | .394 | 1.914 | .023 | 2.849 | .375 | .007 | .012 | 1.535 | .731 | .073 | 9.72 |
| Total (tops) | 74 | 1.957 | .726 | 3.057 | .066 | 5.538 | .716 | .009 | .017 | 2.825 | 1.427 | .140 | 17.76 |
| Tops, yield per year [2] | ---- | 1.38 | .51 | 2.15 | .046 | 3.89 | .50 | .006 | .012 | 1.98 | 1.00 | .10 | 12.48 |
| *E. hyemale* | | | | | | | | | | | | | |
| Rhyolite | | | | | | | | | | | | | |
| 1st | 41 | 0.568 | 0.388 | 1.202 | 0.034 | 2.519 | 0.323 | 0.002 | 0.005 | 1.226 | 0.794 | 0.093 | 7.62 |
| 2d | 33 | 1.138 | .463 | 2.296 | .027 | 2.847 | .309 | .004 | .009 | 1.642 | .916 | .085 | 10.18 |
| Total (tops) | 74 | 1.706 | .851 | 3.498 | .061 | 5.366 | .632 | .006 | .014 | 2.868 | 1.710 | .178 | 17.80 |
| Tops, yield per year [2] | ---- | 1.20 | .60 | 2.46 | .04 | 3.77 | .44 | .004 | .10 | 2.01 | 1.20 | .125 | 12.50 |
| *Phalaris tuberosa* | | | | | | | | | | | | | |
| Basalt | | | | | | | | | | | | | |
| 1st, 7-14-59 | 26 | 0.493 | 0.318 | 0.290 | 0.095 | 1.935 | 0.221 | 0.001 | 0.004 | 0.585 | 0.806 | 0.069 | 5.31 |
| 2d, 9-21-59 | 10 | .575 | .212 | .195 | .066 | 1.218 | .216 | .001 | .004 | .263 | .541 | ---- | 3.67 |
| Total (tops) | 36 | 1.068 | .530 | .485 | .161 | 3.153 | .437 | .002 | .008 | .848 | 1.347 | ≈.10 | 8.98 |
| Tops, yield per year | ---- | 1.54 | .765 | .7 | .23 | 4.55 | .63 | .003 | .011 | 1.22 | 1.95 | ≈.14 | 12.96 |
| *P. tuberosa* | | | | | | | | | | | | | |
| Rhyolite | | | | | | | | | | | | | |
| 1st | ---- | 0.308 | 0.224 | 0.300 | 0.032 | 1.229 | 0.141 | 0.006 | 0.005 | 0.446 | 0.500 | ---- | 3.52 |
| 2d | ---- | .345 | .180 | .215 | .028 | .804 | .122 | .001 | .002 | .228 | .412 | 0.019 | 2.58 |
| Total (tops) | 36 | .653 | .404 | .515 | .060 | 2.033 | .263 | .007 | .007 | .674 | .912 | ≈.025 | 6.10 |
| Tops, yield per year | ---- | .94 | .58 | .74 | .084 | 2.93 | .38 | .010 | .010 | .973 | 1.32 | ≈.04 | 8.81 |
| *Dactylis glomerata* | | | | | | | | | | | | | |
| Grus | | | | | | | | | | | | | |
| 1st, 7-14-59 | 26 | 1.754 | 0.709 | 0.822 | 0.063 | 3.463 | 0.447 | 0.002 | 0.006 | 1.390 | 0.909 | 0.138 | 10.70 |
| 2d, 9-21-59 | 10 | .377 | .254 | .227 | .018 | 2.030 | .160 | .001 | .002 | 1.104 | .384 | .047 | 5.14 |
| Total (tops) | 36 | 2.131 | .963 | 1.049 | .081 | 5.493 | .607 | .003 | .008 | 2.494 | 1.293 | .185 | 15.84 |
| Tops, yield per year | ---- | 3.10 | 1.37 | 1.51 | .12 | 7.91 | .87 | .004 | .011 | 3.59 | 1.57 | .27 | 22.88 |

[1] Assuming $SiO_2$ alone is 45 percent (table 5).

[2] Tops yield per year calculated on 74 weeks' growth time because of delay in getting plants started.

enables them to exchange hydrogen ions for cations in the surrounding soil and rock—the exchange being implemented by the metabolic energy of the plants. The aggressive action of the hydrogen ion makes the plant act as a potential chemical "sink" into which the components of the soil travel to be complexed in the root, utilized by the plant, and removed from the soil system.

Since moisture from the ground goes upward through a plant only by way of the xylem cells, and any silica in the downward moving phloem remains in the plant—chiefly in the growing roots—the total amount of silica in the plant must have moved initially as a constituent of the xylem sap from the roots to where it was incorporated into the plant tissue as opal. A first approximation of the content of silica in the sap can be made by assuming that the total water used, less that in the catchment bottle, was transpired. This assumption gives the minimum possible content of silica; total silica in plant tops divided by total water used equals minimum average silica content of sap; this amounts to 63 ppm for *A. donax* and 42 ppm for *E. hyemale*. If, however, we subtract from the total water used not only the amount in the catchment bottles but approximately the amount lost through evaporation as indicated by the loss from the water used for the leaching of the basalt blanks, the amount transpired by *A. donax* apparently was about 17 liters (16.8 liters) and by *E. hye-*

*male* appreciably less than the 26.8 liters given in table 2, probably about 25.5 liters total. Dividing the total silica (tops and roots) of the *A. donax* (basalt) by 16,800 milliliters indicates that the average silica content of the *A. donax* sap for the whole plant was 145 ppm and for the tops only 115 ppm; for the tops of *E. hyemale* the sap would contain an average of 76 ppm of $SiO_2$ (assuming 26.8 liters transpiration water). As is well known, however, the silica content of the sap of silica-accumulator plants increases with the age of the plants; the average for maize sap (three growth stages) was found by Lowry, Huggins, and Forrest (1936) to be only 73 percent of the maximum content (third-stage growth) (table 9). An accurate analysis of 1 milliliter of sap obtained from *E. hyemale* at the end of the study gave a figure of 107 ppm.

The residual solutions in the catchment bottles were analyzed quantitatively for silica, but the other elements present were determined only by semiquantitative spectographic analysis of the residue from evaporation. In collecting the sap from small-stemmed wild *Equisetum*, some of the silica precipitated on the inside of the stem (see infrared spectrogram, fig. 4, No. 7) and was unavoidably included with the sap. The average composition of the sap can be calculated from the ratio of the total amount of an element in the plant to the total water transpired. The total amount of the various elements translocated from the soil and nutrient solutions into the plant and the relation of the amount present in *A. donax* and *E. hyemale* to that available from the nutrient solutions are indicated in tables 7 and 8.

The raw rock evidently was utilized for elements not supplied by nutrient solution but probably was little affected where adequate amounts of the translocated elements were available to the plants in the nutrient solutions. This is also suggested by table 1 where the difference in the amount of the various elements present in the fresh rocks and in the rock soil at the end of the experiment is shown.

### ***Arundo donax* and *Equisetum hyemale (californicum) in rhyolite***

The assumptions and data given in the quantitative-data section were used to compute the amount of the various elements available to the plants from the original feed solutions and the minimum supplied by breakdown of the crushed rock itself (tables 7 and 8).

Comparing the analyses of the original rhyolite with that at the end of the experiment suggests that the CaO and MgO content of the rock not adjacent to roots has increased slightly. The slight increase probably represents deposition in the rock soil by evaporation of the nutrient solution, which would accord with the oversupply of these elements indicated in tables 7 and 8. However, if biochemical reactions leached silica, a decrease in the density of the rock would result and thus give a somewhat larger weight percent to any unleached constituent. Lacking quantitative analyses of the residual solutions in the catchment bottles for elements other than silica, it is not possible to make a confident choice between the two alternatives.

As with the *Arundo donax*, the *Equisetum hyemale* apparently derived a substantial amount of silica from

TABLE 7.—*Amounts, in grams, and sources of inorganic constituents of* Arundo donax

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|
| A. Constituents available from solutions: | | | | | | | | | | |
| Nutrient 1 [1] | 0.066 | 0.003 | 0.004 | 0.447 | 1.546 | 0.029 | 1.558 | 0.390 | 0.885 | ≈0.023 |
| Nutrient 2 [2] | .293 | .032 | .098 | 2.025 | 3.109 | .788 | 6.881 | 3.460 | 4.075 | .878 |
| Demineralized water | .108 | --------- | <.001 | --------- | .003 | .030 | .005 | --------- | .018 | .037 |
| Total liquid (basalt media) | .467 | .035 | .103 | 2.472 | 4.658 | .847 | 8.444 | 3.850 | 4.978 | .938 |
| A′. Rhyolite media: | | | | | | | | | | |
| Nutrient 1 [1] | 0.066 | 0.003 | 0.004 | 0.447 | 1.546 | 0.029 | 1.558 | 0.390 | 0.885 | 0.023 |
| Nutrient 2 [3] | .264 | .029 | .088 | 1.826 | 2.803 | .710 | 6.204 | 3.124 | 3.674 | .792 |
| Demineralized water | .108 | --------- | .000 | --------- | .003 | .030 | .005 | --------- | .018 | .037 |
| Total | .438 | .032 | .092 | 2.273 | 4.352 | .769 | 7.767 | 3.514 | 4.577 | .822 |
| B. Constituents retained by residual liquid from basalt | 0.058 | --------- | 0.007 | 0.15 | --------- | --------- | --------- | 0.009 | --------- | --------- |
| B′. Constituents retained by residual liquid from rhyolite | .096 | --------- | .021 | .090 | --------- | --------- | --------- | .060 | --------- | --------- |
| C. Maximum net weight available: | | | | | | | | | | |
| Basalt (A–B) | .409 | <.035 | <.096 | 2.322 | <4.65 | <.85 | <8.44 | 3.841 | <4.98 | <0.82 |
| Rhyolite (A′–B′) | .342 | <.032 | <.085 | 2.18 | <4.35 | <.77 | <7.76 | 3.454 | <4.58 | --------- |
| D. Basalt media: | | | | | | | | | | |
| Constituents in *A. donax* ash, tops and root [4] | 2.446 | ≈.040 | ≈.081 | 1.392 | 1.502 | .186 | 10.392 | .796 | ≈4.8 | --------- |
| Tops only | 1.944 | .028 | .042 | 1.252 | 1.252 | .049 | 9.711 | .758 | 4.287 | .372 |
| E. Rhyolite media: | | | | | | | | | | |
| Constituents in *A. donax* ash, tops and root [4] | 3.042 | .24 | .095 | 1.141 | 1.601 | .139 | 7.921 | .786 | ≈4.1 | .405 |
| Tops only | 1.742 | .031 | .057 | 1.097 | 1.341 | .051 | 7.582 | .743 | 3.625 | .448 |
| F. Minimum amount derived from basalt (tops and root) (D–C) | 2.037 | ≈.005 | 0 | 0 | 0 | 0 | >1.95 | 0 | 0 | 0 |
| Tops only | 1.535 | 0 | 0 | 0 | 0 | 0 | >1.3 | 0 | 0 | 0 |
| G. Minimum amount derived from rhyolite (tops and roots) (E–C) | 2.694 | ≈.21 | .010 | 0 | 0 | 0 | >.16 | 0 | 0 | 0 |
| Tops only | 1.394 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

[1] Nutrient solution 1 (Hoagland's), 5.5 liters used, 21 weeks from Dec. 1, 1958, to April 26, 1959 (table 3).

[2] Nutrient solution 2 (Ulrich's), 24.4 liters used, 55 weeks from Apr. 27, 1959, to May 20, 1960 (tables 2 and 3).

[3] Ulrich's nutrient, 22.5 liters used, 55 weeks, from Apr. 27, 1959, to May 20, 1960 (tables 2 and 3).

[4] Al and Fe in root calculated from semiquantitative spectroscopic analysis, percentage of Cl and $SO_3$ in root assumed to be average of that in tops.

TABLE 8.—*Amounts, in grams, and sources of inorganic constituents of* Equisetum hyemale

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $SO_3$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|
| A. Constituents available solutions: | | | | | | | | | | |
| Nutrient 1[1] | 0.066 | 0.003 | 0.004 | 0.447 | 1.546 | 0.029 | 1.558 | 0.390 | 0.885 | 0.023 |
| Nutrient 2[2] | .438 | .047 | 1.42 | 3.060 | 4.640 | 1.177 | 10.293 | 5.183 | 6.132 | 1.240 |
| Demineralized water | .078 | -------- | .001 | -------- | .002 | .025 | .003 | -------- | .016 | .027 |
| Total liquid | .582 | .050 | .147 | 3.507 | 6.188 | 1.231 | 11.844 | 5.573 | 7.033 | 1.290 |
| B. Constituents retained by residual liquid: Basalt media[3] | 0.058 | -------- | 0.007 | 0.210 | | | | 0.009 | -------- | -------- |
| B′. Rhyolite media[3] | .096 | -------- | .021 | .197 | -------- | -------- | -------- | .060 | -------- | -------- |
| C. Maximum net weight of constituents available: | | | | | | | | | | |
| A–B | .525 | -------- | .140 | 3.297 | | | | 5.564 | | |
| A′–B′ | .486 | -------- | .126 | 3.310 | -------- | -------- | -------- | 5.513 | -------- | -------- |
| D. Constituents of *E. hyemale* ash (basalt soil): | | | | | | | | | | |
| Whole plant[4] | 2.33 | -------- | -------- | .84 | 3.28 | 0.32 | 6.45 | .73 | 1.88 | -------- |
| Tops only[4] | 1.957 | 0.009 | .017 | .726 | 3.057 | .066 | 5.538 | .716 | 1.427 | 0.140 |
| D′. Constituents of *E. hyemale* ash (rhyolite soil): | | | | | | | | | | |
| Whole plant[4] | 2.24 | -------- | -------- | .97 | 3.60 | .15 | 6.30 | .65 | 2.20 | -------- |
| Tops only[4] | 1.706 | .006 | .014 | .851 | 3.498 | .061 | 5.366 | .632 | 1.710 | -------- |
| E. Minimum amounts derived from basalt soil (D–C): | | | | | | | | | | |
| Whole plant[4] | 1.81 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tops only[4] | 1.433 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| E′. Minimum amounts derived from rhyolite soil (D′–C′): | | | | | | | | | | |
| Whole plant[4] | 1.175 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tops only[4] | 1.22 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

[1] Nutrient solution 1 (Hoagland's), 5.5 liters used, 21 weeks from Dec. 1, 1958, to Apr. 26, 1959 (tables 2 and 3).
[2] Nutrient solution 2 (Ulrich's), 36.5 liters used, 57 weeks from Apr. 27, 1959, to June 2, 1960 (tables 2 and 3).
[3] Constituents assumed to be the same as for *Arundo donax* (table 7).
[4] Amount of constituents in *E. hyemale* roots calculated on assumption that the proportion of rhizomes and roots to tops in *A. donax* and *E. hyemale* are the same, and that the percentages of an element in the *A. donax* root approximate those of the same element in the *E. hyemale* root and rhizomes for corresponding media.

breakdown of the rocks in which it was grown rather than from the silica dissolved in the nutrient solution. Also, the *A. donax* apparently does not exclude dissolved sulfate whereas the *E. hyemale* apparently did. It is noteworthy that the sulfate is molecularly equivalent to magnesium in *E. hyemale* and to magnesium plus calcium in *A. donax*, and presumably moved into the plants in the form of sulfate. This agrees with the conclusion reached by Thomas, Hendricks, and Bryner (1944) that sulfur moves upward in the stems of plants entirely as a sulfate, but our results do not support their further conclusion that the bulk of the metallic cations are also transported as free ions. The anions found in the plant ash are insufficient to form soluble inorganic compounds in the sap, and the small amount of carbon dioxide found in the *E. hyemale* sap is inadequate to supplement the sulfate and chloride as bicarbonate metal carriers.

## COMPOSITION OF *EQUISETUM HYEMALE* SAP

The composition of saps of various plants has usually been studied with reference to a certain group of constituents, and because saps vary greatly from plant to plant, it is unsafe to generalize from work done on any one plant. Enough plants have been studied, however, to say that the inorganic constituents of plants as well as the nitrogen content is usually measured in parts per million; for example, the sap from maize in untreated soil as reported by Lowry, Huggins, and Forrest (1936) contains an average 181 ppm $SiO_2$ and ranges from 120 to 213 ppm (table 9). The silica content of the 1960 *Equisetum hyemale* sap (107 ppm) is thus comparable to that of the sap of maize; the total load of the *E. hyemale* sap (1960) was 4,520 ppm and was mostly organic. As a saturated solution of silica in contact with silica gel at room temperature is 110 ppm (Krauskopf, 1956, p. 14), the writers at first assumed that the silica in the sap was in the form $H_2SiO_3$, as has long been thought by botanists. An infrared diagram of the freeze-dried 1960 *E. hyemale* sap (fig. 4, Nos. 1–3), however, did not show the absorption bands characteristic of silica gel (fig. 4, No. 6), and led to further investigation.

TABLE 9.—*Composition, in parts per million, of sap from maize*

[The ash and inorganic constituents of the exudate from maize plants collected at different stages of growth. An average of all fertilizer treatments over a 3-yr period (Lowry and others, 1936, table 4, p. 17)]

| Stage of growth | Ash | | $K_2O$ | | CaO | | $P_2O_5$ | | $SiO_2$ | | N | | $SO_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime |
| First | 505 | 500 | 240 | 298 | 78 | 70 | 100 | 105 | 92 | 120 | 245 | 185 | 145 | 99 |
| Second | 563 | 612 | 250 | 289 | 38 | 50 | 116 | 141 | 171 | 210 | 233 | 275 | 172 | 151 |
| Third | 790 | 657 | 233 | 255 | 52 | 20 | 206 | 226 | 218 | 213 | 394 | 321 | 138 | 130 |
| Average | 619 | 590 | 241 | 281 | 66 | 47 | 141 | 157 | 160 | 181 | 291 | 261 | 152 | 127 |

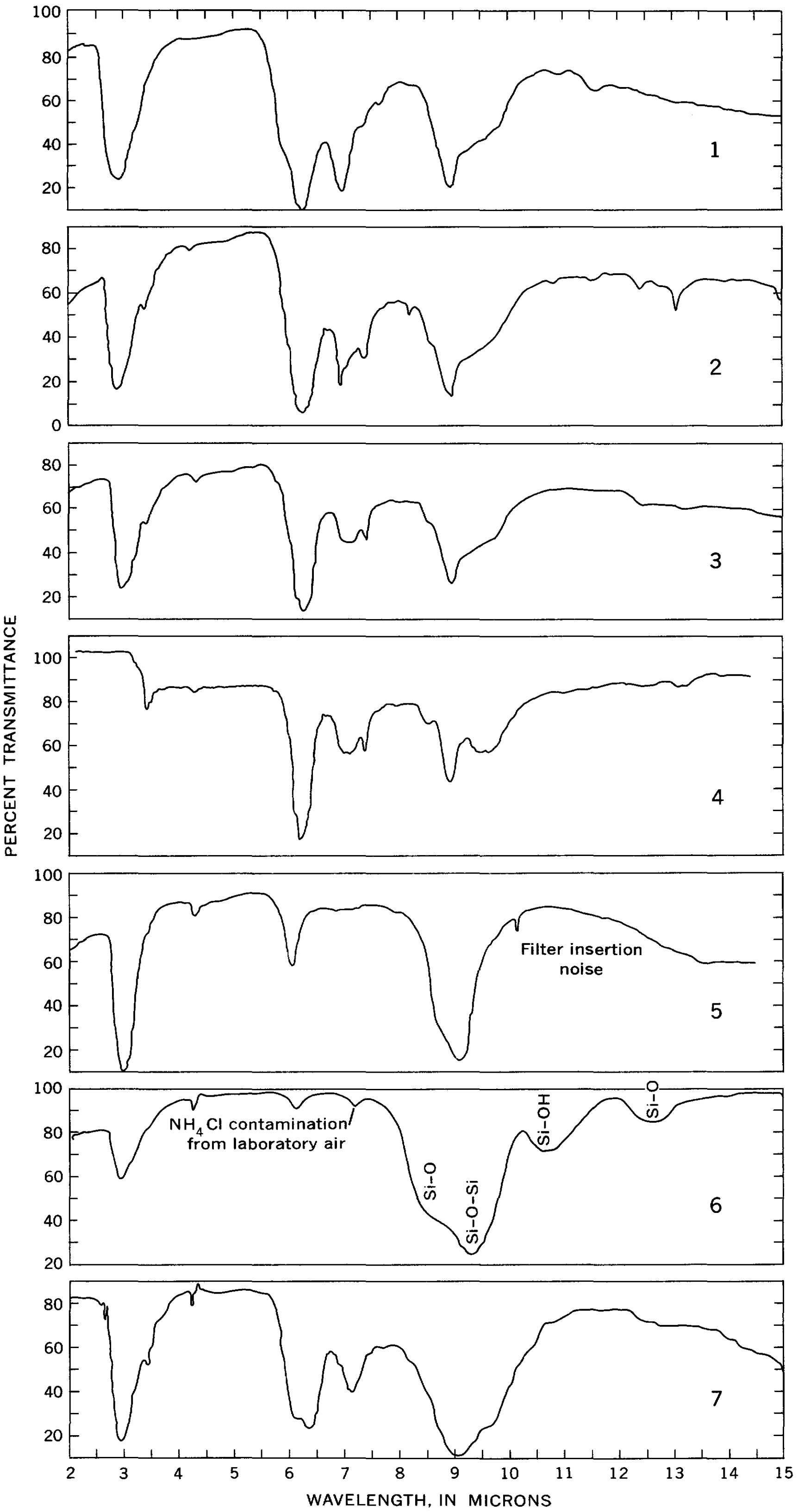

FIGURE 4.—Infrared spectrograms of lyophilized *Equisetum hyemale* sap, epsom salt ($MgSO_4 \cdot 7H_2O$), and "silicic acid" ($SiO_2 \cdot n\, H_2O$). 1. Lyophilized sap of 1960 *E. hyemale* (*californicum*), June 1960 (infrared spectrogram: I. A. Breger, U.S. Geol. Survey), 320 milligrams of KBr. 2. KBr pellet (200 mg) from pellet used for No. 1; repeated in October 1965 (infrared spectrogram: Leo Christianson, Spectran Lab., Denver). 3. No. 2 (200-mg pellet) (infrared spectrogram: February 1966, T. S. Lovering). 4. No. 3 with 0.02 milligrams of $MgSO_4 \cdot 7H_2O$ in 200 milligrams of KBr in reference beam (T. S. Lovering). 5. $MgSO_4 \cdot 7H_2O$, 0.04 milligram in 300 milligrams of KBr (T. S. Lovering). 6. Residue from lyophilized triply distilled demineralized water after 3 weeks contact with silical gel at 52°C; contained 200 ppm of $SiO_2$ (T. S. Lovering). 7. Lyophilized sap from wild *E. hyemale* (*typicum*) November 1965 (T. S. Lovering).

The average content of silica in the *E. hyemale* transpiration stream if calculated from silica content of the second cutting (table 6) and the transpiration stream for the second growth period (33 weeks) is 1.218/11,750=103 ppm, a figure that corresponds to the value found by analysis of the sap, and nearly the same as that calculated for the tops of *Arundo donax*. As shown in table 10, the actual amount silica found in the *E. hyemale* (*californicum*) sap was 107 ppm. Because we were strongly advised by professional botanists to use artificial nutrients, virtually all the nutrient requirements other than silica were supplied by the nutrient solutions. We now believe that this was a mistake and that the plants were given too easy an environment and, therefore, did not break down the mineral in the rocks to the same extent that they would had they been growing wild. To partly test this hypothesis, additional *E. hyemale* sap was obtained in the spring of 1965 from *E. hyemale* (*typicum*) growing wild near Denver, Colo. The sap from the wild plant was collected in early May, and during the collection it was discovered that exudate could be obtained from the broken stems only in the early morning or in the late afternoon. Between these periods the xylem was nearly dry.

The sap collected from the wild plant carried 140 ppm of dissolved Si, equivalent to 300 ppm of $SiO_2$, and contained 0.52 percent freeze-dried residue. In collecting the sap from the small stemmed wild *E. hyemale*, some of the precipitated opal on the inside of the stem was unavoidably included with the sap. The analysis of the sap was made without filtration, however, to avoid possible losses and change of composition during this process. The amount of silica in the sap was determined by diluting it, treating it with hydrochloric acid, and making the usual ammonium molybdenate test. This test gives only the ionic silica present and would not be affected by the particulate opal that had been included. When the sap was freeze dried, however, analysis for total silica (52.6 percent) showed that the dissolved (ionic) silica was exactly 10 percent of the total silica, indicating that in the freeze-dry residue about 47.3 percent (2.7 mg) of the residue was particulate opaline silica. In calculating the composition of the sap, the analysis of the residue has been corrected to allow for this amount of extraneous silica. The original data and recalculated analysis are given in table 10.

The average dissolved material other than silica in the sap from our laboratory *E. hyemale* was approximated by assuming that all the inorganic constituents in the plant ash were transported in the water (11.75 liters) transpired during the second crop period and that the carbon, hydrogen, and nitrogen were present in the same proportion as in the sap of the wild *E. hyemale*, which as originally collected contained about 2,800 ppm of residue exclusive of the un-ionized (particulate) silica in the sap (table 10).

## INFRARED STUDIES OF *EQUISETUM HYEMALE* SAP

An aqueous solution of silica gel was prepared that had approximately 200 ppm of $SiO_2$ in solution, and after it had been freeze dried, an infrared spectrogram of the residue (fig. 4, No. 6) was prepared for comparison with the spectrograms of residues from freeze-dried 1960 and 1965 *Equisetum hyemale* sap (fig. 4, Nos. 2 and 7). It is quite apparent that the spectrograph of the 1960 sap residue and that of the 1965 residue (fig. 4) are remarkably similar except in the vicinity of the 9$\mu$ (micron) absorption peak, which is much broader for the 1965 residue where absorption for particulate silica takes place. The absorptions of Si-O-Si at 9.3$\mu$, of Si-OH at 10.65$\mu$, and of Si-O at 8.5$\mu$, at 12.55$\mu$, and at 12.80$\mu$ (fig. 4, No. 6) are lacking in the 1960 sap residue (fig. 4, Nos. 1, 2, and 3) although the Si-O at 8.5$\mu$ could be represented by a shoulder in the *E. hyemale* infrared curve (fig. 4, No. 2). Certainly there is nothing to correspond to the Si-OH absorption at 10.65 and the very strong Si-O-Si band at 9.3 is clearly lacking. Instead there is a strong absorption at 8.95, which corresponds

TABLE 10.—*Composition, in weight percent, of* Equisetum hyemale sap

| | $SiO_2$ | Si | C | H | N | K | Na | Mg | Ca | P | $SO_3$ | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Equisetum hyemale:* | | | | | | | | | | | | |
| (*typicum*) residue [1] | [2] 52.6 | 24.68 | [2] 22.0 | [2] 2.69 | [2] 2.38 | [3] 4.27 | | | [3] 2.20 | | | |
| Residue recalculated [4] | 5.68 | 2.65 | 41.6 | 5.09 | 4.50 | 8.08 | | | 4.16 | | | |
| (*californicum*) residue [5] | 1.92 | .90 | | | | | | | | | | |
| (*typicum*) sap dissolved solids [6] | .0300 | .0140 | .1162 | .0142 | .0126 | .0226 | | | .0116 | | | |
| (*californicum*) sap [7] | .0107 | .0050 | | | | | | | | | | |
| (*californicum*) sap calculated [8] | .0104 | .0049 | (8) | (8) | (8) | .0203 | 0.0002 | 0.0020 | .0117 | 0.0014 | 0.0063 | 0.0006 |

[1] Residue from lyophilized sap is 0.528 percent of original sap.

[2] Microanalysis by Huffman Lab., Denver, Colo.; oxygen is probably about 26 percent.

[3] Analysis by M, J. Fishman, U.S. Geol. Survey.

[4] Recalculated on assumption that all silica not detected as ionized silica in diluted sap (300 ppm $SiO_2$) is particulate opal contamination (47.3 percent ≈ 47 percent of lyophilization residue).

[5] Residue from lyophilized sap of laboratory grown *E. hyemale* (1960), 0.557 percent of original sap, analysis by F. S. DeRose, U.S. Geol. Survey.

[6] Composition of sap excluding particulate silica, calculated from analysis of lyophilized sap residue and percent of residue in sap.

[7] Fresh sap analysis by J. Breger, U.S. Geol. Survey.

[8] Inorganic constituents calculated from transpired water (11.75 liters) and plant-ash analysis of second cutting. Organic matter plus oxygen=5,570 ppm−480 ppm=5,090 ppm; if content of C+H+N is assumed to be the same percent as in *E. hyemale* (*typicum*) residue recalculated, their combined weight percent in the sap would be 0.2860.

exactly in position to Si-C bonding where the carbon is in a phenyl group.

The infrared spectrogram of the freeze-dried sap from the wild *E. hyemale* (fig. 4, No. 7) shows the presence of opaline silica and contrasts with the infrared spectrogram of the lyophilized (freeze-dried) sap residue from the laboratory grown *E. hyemale*, from which sap uncontaminated with particulate silica had been obtained earlier. Absorption for Si-O-Si at 9.3$\mu$ (stretching), for Si-O at 12.5$\mu$, and for Si-OH at 10.65 have modified the spectrogram characteristic of the uncontaminated sap (fig. 4, Nos. 1 and 2) in which the organic constituents control the absorption spectra.

The most significant, and at the same time the most debatable absorption peak, is the one at about 8.95 which coincides precisely with the absorption peak for the silicon-phenyl ($Si-C_6H_5$) stretching vibration. It also is very close to the strong absorption peak for magnesium sulfate (epsomite) as shown by Omori and Kerr (1963, p. 720) between 8.5$\mu$ and 9.0$\mu$. As the sulfate and magnesium ions are present in essentially molecular proportions in the ash, it seems evident that the sulfate radical is tied to magnesium. To test the possibility that this absorption peak is chiefly caused by magnesium sulfate, the average amount of magnesium sulfate present in the sap was calculated, and the amount that would be present in the freeze-dry residue was added to a potassium bromide pellet in the reference beam of the infrared spectrometer so as to eliminate the absorption bands for this compound. The resulting infrared spectrogram of the 1960 sap (fig. 4, No. 4) shows unequivocally that the absorption band at 8.95 is not caused by magnesium sulfate, the infrared spectrogram of which is shown in figure 4, No. 5, and also indicates that the absorption band at approximately 3$\mu$ may be caused in part by water of crystallization of magnesium sulfate, which remains unevaporated during the freeze-dry procedure.

There are several absorption bands in addition to that at 8.95 which could be caused by the phenyl group; the strong absorption band at 6.25$\mu$ is especially characteristic of the C–C stretching of the phenyl ring; the shoulder at 6.85$\mu$ may also be from a phenyl group, and the small absorption peaks at 9.75$\mu$, 10.55$\mu$, and 12.5$\mu$ are all characteristic peaks for complex molecules made up of fused phenyl groups. The peaks that could be ascribed to the phenyl groups are those at 6.25$\mu$, 6.85$\mu$, 8.95$\mu$, 12.4$\mu$, and 13.1$\mu$. Absorption peaks related to nitrogen-hydrogen bonding should occur at about 3.0$\mu$, but would be hidden by the strong hydroxyl absorption peak at this point. The Shoulder on the hydroxyl absorption peak at 3.37$\mu$ is probably caused by methyl groups. The shoulder on the 6.25$\mu$ absorption peak at 6.10$\mu$ may represent the deformation mode of $NH_2$ and that at 7.05$\mu$ is probably the stretching mode of C–N. In addition to the $Si-C_6H_5$ stretching mode at 8.95$\mu$, it is possible that $Si-CH_3$ absorption bands are represented by the absorption peak at 7.05$\mu$ and the shoulder at 7.80$\mu$, and may be responsible for the band at 12.5$\mu$ which, however, could be caused by a four-substituted phenyl group such as is found in pyridine.

Combined infrared and ultra violet spectra in the residue from lyophilized sap indicate not only that the ionized silicon was bonded to a phenyl group before treatment with hydrochloric acid, but that some 43 percent of the organic material extracted from the residue of the 1965 sap by a water-ethanol solution consists of aromatic type hydrocarbons; if calculated as anisol it would amount to 42.8 percent of the extracted material, according to a report (Dec. 28, 1965) by Dr. Robert Rinehart of the Huffman Laboratory, Denver, Colo. He notes, too, that the infrared spectra of the 1965 sap show the characteristics of silicic and humic acids.

Infrared spectrograms of the 1960 sap leave little doubt that the silica is bound to a phenyl group and is not present as silicic acid but that instead it is part of a complex organic molecule composed in large part of fused phenyl groups with short side chains, resembling in many ways the complex molecular structure of fulvic and humic acids, but probably of much lower molecular weight and certainly not identical with either.

## POSSIBLE COMPLEX STRUCTURE OF ORGANIC CONSTITUENTS OF SAP

Analytical techniques which are dependent on chromotography to determine individual compounds in sap (Bollard, 1953; 1957) invite the destruction of complex high molecular weight molecules; it is thus uncertain when various simple amino acids are reported, whether they were present as part of an original complex molecule or were originally present as the compounds themselves. It is noteworthy that the infrared spectrogram of the two *Equisetum hyemale* saps (fig. 4, Nos. 1, 2, and 7) resemble the infrared spectrograms of fulvic acid (Kononova, 1962, p. 81; Swanson and Palacas, 1965, p. B22). Except for the $Si-C_6H_5$ absorption bond in the *E. hyemale* sap at 8.95$\mu$, the analyses of the *E. hyemale* sap and the fulvic acid are also surprisingly alike (table 11).

Many biochemists believe that, in decaying humus, lignin is the principal precursor of humic acid, but agreement is lacking at present. The water-soluble substances in sap may be tannins and related compounds of lower molecular weight than lignin, and such compounds will precipitate protein complexes in acid solutions that are indistinguishable from humic acid (Waksman and Iyer, 1933).

TABLE 11.—*Analyses, in percent, of fulvic acids and* Equisetum hyemale *sap*

| | C | H | N | O | S | Si | Ash |
|---|---|---|---|---|---|---|---|
| Fulvic acid from heather raw humus [1] | 48. 44 | 5. 49 | 4. 17 | -------- | -------- | -------- | 2. 16 |
| Fulvic acid from gardeners' "turf" soil [1] | 47.25 | 5. 61 | 5.87 | -------- | -------- | -------- | 4.10 |
| Choctawhatchee humate, ultimate analysis [2] | 24. 87 | 4. 31 | 2. 71 | 31. 00 | 0. 59 | -------- | 35. 86 |
| Choctawhatchee humate, ash-free analysis [2] calculated to 100 percent | 39. 18 | 6. 79 | 4. 27 | 48. 83 | . 93 | -------- | -------- |
| Lyophilized *E. hyemale* (*typicum*) sap of 1965, recalculated after excluding all particulate $SiO_2$ [3] | 41. 6 | 5. 09 | 4. 50 | -------- | -------- | 2. 65 | 20. 0 |

[1] Analysis from Kononova (1961, p. 80).

[2] Analysis of fulvic acid obtained from humate collected at Choctawhatchee Bay in northwest Florida, courtesy of Swanson and Palacas.

[3] Analysis of 1965 *E. hyemale* sap calculated to opal-free base, but assuming $SiO_2$, $K_2O$, CaO, and MgO represent ash.

The carbon-hydrogen and carbon-nitrogen ratios are clearly similar in fulvic acid and in the residue from the *E. hyemale* sap. The similarity of the infrared spectrogram, except in the region where silica or sulfate would cause absorption, is striking.

According to Knonova (1962, p. 82) fulvic acids, like humic acids, have structural elements of an aromatic nature, and the presence of phenolic glucosides, hydroxyl groups, and C=C groups is apparently established. In summary, Kononova says, "Fulvic acids possess the same structural units as humic acids—compounds of an aromatic nature, nitrogen-containing substances and reducing substances * * * the aromatic structure in fulvic acids is weakly expressed, there being a predominance of peripheral chains."

Fulvic acid is not a naturally occurring substance; it is itself obtained from humate: humic material is extracted with tenth normal sodium hydroxide for 2 hours, centrifuged, and filtered; the pH of the resulting liquid is decreased to 1.0 with hydrochloric acid; humic acid then precipitates, and the supernatant liquid is separated and its pH is raised to 5 with sodium hydroxide. At this point fulvic acid flocculates, and the floc is centrifuged and vacuum dried. A further increase in the pH will redissolve this floc. The complexity of both the humic acid and fulvic acid is such that as yet the details of their structure are imperfectly known.

The general structure of the humic acid molecule as proposed by Dragunov, Zhelokhovtseva, and Strelkova (1948) and favored by Kononova (1962, p. 65) is shown in figure 5*A*.

Recent work by German biochemists, reported by Heinen (1963), resulted in extraction of organosilicon compounds from rye straw. According to Heinen, W. Engel identified the silicon compounds as a silicon-galactose complex, and found a 1:1 and 1:2 ratio of silicon to galactose in different extracts. L. Holzapfel (in Heinen, 1963) ascribed the silicon to esters of carbohydrates and silicic acid. The suggested structural formulas are shown in figure 5*B*.

Humic acid readily breaks down into a number of compounds commonly found in plants such as the amino acids, pyrocatechol, and protocatechuic acid (Kononova, 1962, p. 58, 59). Conversely humate can be prepared readily from such substances by oxidation and polymerization.

A wide variety of organic compounds useful in plant metabolism could readily be derived from a structurally similar complex compound through the activity of enzymes. It is possible that the organic constituents in the *E. hyemale* sap consist chiefly of a complex molecule of this general type together with minor amounts of inorganic salts. Both the infrared spectrogram of the 1960 sap and the amounts of ionic silica present in the neutral sap (pH 6.95) of the wild *E. hyemale* (300 ppm) and in the exudate from maize (218 ppm) indicate that the sap is highly supersaturated with inorganic silica and that silicon is not present as silicic acid but is instead part of an organic complex. The molecular equivalence of magnesium and sulfate, however, indicate that magnesium is probably transported as an inorganic sulfate in *E. hyemale*, and similarly the molecular equivalence of Ca + Mg to $SO_4$ in *Arundo donax* suggests transport as inorganic salts in *A. donax* sap; the lack of inorganic anions to match potassium shows that it is transported chiefly as part of an organic complex in *E. hyemale* and the grasses.

## CONCLUSIONS

The analytical results allow one to construct a chemical balance sheet which shows the amounts of various elements supplied to the plant by nutrient solutions and the amounts obtained from the rock soil. This chemical balance shows that most of the silica present in the *Equisetum hyemale*, *Arundo donax*, and other grasses must have been derived from the soils in which the plants were grown. Furthermore, it demonstrates that the biochemical action taking place at the roots must solubilize the raw rock with which the roots are in contact so as to allow the transmigration of silica into the plant itself. The silica is moved as part of an organic complex chiefly aromatic in structure, probably related in composition to the fulvic and humic acids obtained

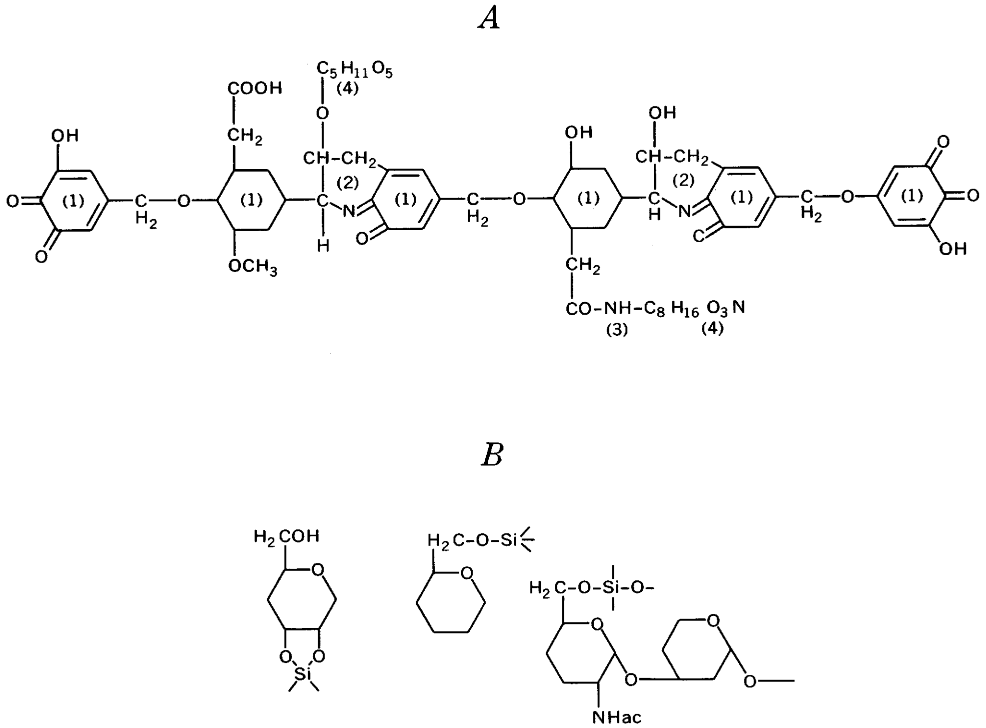

**Figure 5.**—*A*, The structure of the humic-acid molecule (according to Dragunov and others, 1948). (1) Aromatic ring of the di- and trihydroxyphenol type, part of which has the double linkage of a quinone grouping, (2) nitrogen in cyclic forms, (3) nitrogen of peripheral chains, (4) carbohydrate residues. (Sketched from Kononova, 1962, p. 65.) *B*, Structural formulas of organosilicates extracted from rye straw (according to Heinen, 1963).

from normal soils. The complete lack of any humus in the soils used in the experiment indicates that the plants can produce such complex organic compounds through biological activity in the root system. The experimental work also clearly shows that the silica-accumulator plants do not depend on the silica dissolved in ground water for their source of silica but do themselves or with the help of a symbiotic microbiota exercise a profound effect on the silicates present in the soil, solubilizing them, and translocating their silica into the plant, where it is eventually precipitated around the cell walls in the form of plant opal, or "tabashir" (Jones and others, 1966) probably by enzymatic action on the organic complex of which it is a part. This precipitated silica then became available for dispersion in the form of phytoliths on the death of the plant or the plant organ in which the silica was precipitated.

The conclusion reached in the earlier paper by Lovering (1959) on the significance of accumulator plants in rock weathering was that a "forest of silica accumulator plants might extract about 2,000 tons of silica per acre in 5,000 years, which would be equivalent to the silica in one acre foot of basalt." A check on this assumption can be made if we use the figures obtained from the experimental work on *A. donax* and *E. hyemale* as a basis of comparison. The area of the soil in an 8-inch pot was determined as almost exactly 200 square centimeters, and the average amount of silica abstracted by *E. hyemale* (1.38 g) and *A. donax* (1.33 g) per pot per year (exclusive of that taken up by the root) is 1.36 grams $SiO_2$ and approximately 1.675 grams of $SiO_2$ per year for the whole plant (*A. donax*, table 6), or $\approx 0.007$ gram of $SiO_2$ per square centimeter per year for the tops and 0.0084 gram per square centimeter per year for the whole plant; somewhat less for the grass *Phalaris tuberosa*, somewhat more for the grass *Dactylis glomerata* (in grus). One acre is $43{,}560 \times 929.03$ square centimeters, or $40.467 \times 10^6$ square centimeters; multiplying the area of an acre by the amount of silica abstracted per square centimeter gives an approximation of the total amount of silica that might be obtained per acre of silica-accumulator plants equivalent to those used in this study in their capacity to abstract silica from the soil. Thus $40.467 \times 10^6 \times 0.007$ gram$=283 \times 10^3$ grams, or about 620 pounds of $SiO_2$ per acre per year for tops, and 340 kilograms (748 lb) for the whole plant.

There is approximately 2,000 tons of $SiO_2$ per acre-foot in average fresh nonporous basalt, and at the rate of silica accumulation shown by the laboratory plants it would take in years approximately 2,000×2,000 pounds/620 pounds, or 6,440 years for the tops and 5,347 years for whole plants to abstract an equivalent amount of silica from basaltic soil, if natural silica-accumulator plants are comparable to the *E. hymale* and grasses studied in the Earhart Greenhouses. This figure compares very well with the 5,000-year figure derived earlier (Lovering, 1959). The figures do not take into account silica leached from the soil by water percolating through it to the ground-water table however.

Harrison (1934, p. 13) studied the change in composition of surface water that percolated down through about 180 feet of lateritizing basic rock (hornblende schist) in British Guiana; the increase in silica content was approximately 25 ppm. If in addition to the silica abstracted by the plants, we assume a leaching of silica from the rock of 25 ppm, the amount of silica taken from the soil by rainfall comparable to the amount of water added to the *Equisetum* annually can be readily calculated. Approximately 33.6 liters per year per pot was used in growing the *E. hyemale*, equivalent to 168 cubic centimeters per square centimeter of area ($\approx$66 inches of water annually). If it is assumed that the amount of water percolating to ground water is approximately a third of this amount, about 50 milliliters of water per square centimeter of surface would be available for leaching the soil; if it then took up about 25 ppm of $SiO_2$ annually en route to the water table, the silica loss per acre in kilograms annually through inorganic leaching is $25\times10^{-6}\times50\times40.467\times10^{6}\div10^{3}$, or 50.6 kilograms per acre. We can expect, therefore, that approximately 110 pounds of $SiO_2$ per acre is dissolved by ground water under tropical conditions where approximately 20 inches of rainfall (50 cm) reaches the water table annually. If this figure is added to the 620 pounds calculated for tops only on the basis of experiments with silica-accumulator plants, a total of about 730 pounds of $SiO_2$ would be removed annually per acre of silica-accumulator plants, and 2,000 tons would be removed in a total of 5,480 years; if the silica of the whole plant is considered vulnerable to erosion, some 850 pounds per acre could be removed yearly, equivalent to a loss of 2,000 tons in 4,705 years.

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