in seawater, with a typical DOC content of ~ 1 mg/liter (34), was appreciable only for Cu (3 to 10 percent total Cu chelated). Because MBSW speciation was computed on the basis of an estimated 20 percent complexation for EDTA (Table 1), a much stronger metal chelator than natural organic ligands (29, 35), it is unlikely that complexation to dissolved organics is an important mechanism in reducing free ion concentrations in MBSW. Work by Balistrieri et al. (36) and Hunter (37) indicated that metals may be scavenged by particulates coated by a film of surface-active organic matter. If the surface chemistry of such coated particles controls the adsorption properties of marine particulates (36), one might expect the stability of metal complexation with these particle films to follow the Irving-Williams order. Thus metal complexation by organic films on marine particulates may be another mechanism for trace metal removal from MBSW.

Crist et al. (38) found that bonding between metallic ions (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Zn<sup>2-</sup>  $Mg^{2+}$ , and  $Na^+$ ) and algal cell walls of Vaucheria followed the Irving-Williams order. This trend would enhance effects due to Cu and Zn overabundance and Co and Mn deficiency. In trace element studies with Chaetoceros socialis cultures and natural phytoplankton communities, Sunda et al. (39) observed that additions of FeCl<sub>3</sub>, MnCl<sub>2</sub>, and the chelators EDTA and NTA (nitrilotriacetic acid) to 800-m seawater collected off the North Carolina coast stimulated phytoplankton growth. A physiological interaction was suggested in which Cu interferes with Mn uptake by competing for nutritional sites. North (40) observed growth stimulation by Macrocystis juveniles (macroscopic plants of  $\sim 1$  g wet weight) with Mn additions to 300-m seawater, collected 3 miles off Newport Bay, California, in batch cultures. Microscopic Macrocystis sporophytes were also produced in 12 to 14 days in flowing 300-m or surface seawater from the same site (41). These observations support trace element deficiency over Cu-Zn growth inhibition.

The results presented here are consistent with the idea that inhibition of the growth of marine organisms observed in cultures prepared with deep seawater is due to inherent toxic Cu and Zn free ion activities; they also suggest that there are Co and Mn deficiencies in southern California deep seawater.

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SCIENCE, VOL. 216, 11 JUNE 1982

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13 October 1981; revised 15 December 1981

### Localization of Calcium in Amyloplasts of **Root-Cap Cells Using Ion Microscopy**

Abstract. An ion microscope has been used to demonstrate that the calcium ion is present in the amyloplasts of root-cap cells of corn, pea, and lettuce. The localization of calcium in the gravity-sensing organelle suggests a possible role of calcium in the gravity-sensing mechanism of plant roots.

Calcium has been implicated in plant geotropism and associated processes in several ways. (i) As growth curvature commences, calcium has been found to move to the upper or concave side of the stem or coleoptile (1). (ii) The transport of auxin, which must be involved in the lateral redistribution of growth, is dependent upon calcium (2). (iii) The application of inhibitors of the calcium-binding protein calmodulin results in an erasure of geotropic sensitivity (3).

The initial process involved in gravitysensing in higher plants is the lateral displacement of amyloplasts upon reorientation of a plant organ with respect to gravity. In roots this sensing function is carried out in the root cap, which contains abundant amyloplasts; when the root cap is removed, geotropic response is lost until new amyloplasts have been formed (4). The mechanism by which gravity-induced amyloplast movement might be transduced into a physiological gradient that would lead to curving growth is notably lacking. A relevant first question would be whether the calcium requirement for geotropism might be related to the amyloplast sensing mechanism. The intent of this study has been to examine the possibility that the redistribution of amyloplasts by gravity might bring about some redistribution of calcium in the gravity-sensing cells of the root cap.

With the ion microscope, a directimaging, secondary-ion mass spectrometer, it is possible to carry out the mass

analysis of a tissue section with a lateral resolution of 1  $\mu$ m. As a direct-imaging microscope with a broad range of elemental coverage and high sensitivity, it provides a direct analysis of an element's distribution in relation to tissue anatomy (5). Ion microscopy has been shown to be applicable to studies of the distribution of calcium and potassium in the motor cells of sensitive plant (*Mimosa pudica* L.) leaves (6). We have used the Cameca IMS-300 ion microscope to examine root-cap cells in corn (*Zea mays* L.), pea (*Pisum sativum* L.), and lettuce (*Lactuca sativa* L.) seedlings.

We produced the ion images by bombarding flat thin sections (0.5 to 1  $\mu$ m) with an O<sub>2</sub><sup>+</sup> primary beam at an energy of 5.5 keV and a beam density of approximately 10<sup>-5</sup> A/cm<sup>2</sup>. We prepared sections by using three different modes of preparation to confirm the results. The first method consisted of the chemical fixation of root tips for 1 hour at room temperature in 5 percent glutaraldehyde in 0.03M Pipes buffer (1,4-piperazinediethanesulfonic acid) at pH 6.8 (7). Root tips were washed with 0.15M Pipes buffer and then fixed for 1 hour in 1 percent osmium tetroxide in the same buffer. After dehydration in ethanol (70 to 100 percent) and propylene oxide, the tissue pieces were embedded in low-viscosity resin (8). In the second mode of section preparation, 4 percent tannic acid was added in Pipes buffer to precipitate calcium. We then followed the same dehydration and embedding steps as for the first method. In the third mode, to prevent loss and redistribution of ions during chemical fixation (9), cryosectioning was used. Pieces of root tips were mounted on silver pins and fast-frozen in liquid nitrogen slush (10). Frozen sections approximately 1 µm thick were cut with a dry glass knife (-80°C) and transferred with a hair onto a thin tantalum disk. After several sections had been collected, they were flattened by pressing for approximately 20 minutes in the cryo-





Fig. 1. Corn root tip (×300) showing multiple amyloplasts (A) in the lower parts of cells of the root tip. Darkly stained walls are thickened toward the periphery. Cells slough off, and slime (S) becomes more diffuse at the surface. A separate thickened layer surrounds the root proper. Fig. 2. Ion micrograph of the extreme tip of the corn root cap. The image is due to the presence of calcium. Slime (S), cell walls, nuclei (N), and amyloplasts (A) are bright. The cells were fixed with glutaraldehyde and tannic acid. Fig. 3. Ion micrograph of the pea root cap with calcium located in the cell walls, nuclei (N), and amyloplasts (A). The cells were fixed in glutaraldehyde.

chamber. Sections were then transferred to a freeze dryer for 8 hours at  $-80^{\circ}$ C. The chamber was allowed to warm gradually to room temperature (approximately 3 hours) under a stream of dry nitrogen. Dried sections were then stored under vacuum until analyzed in the ion microscope.

A light micrograph of the corn root tip is shown in Fig. 1; the amyloplasts occur mainly in a region of about 10 to 15 cells anterior to the compact root tip proper. Ion micrographs of corn root-cap cells (Fig. 2) show marked accumulations of calcium in the cell walls and in the slime layer surrounding the root cap. Intracellular calcium can be detected in the nuclei of most cells, and at the greatest density in the amyloplasts of cells in the middle region of the root cap.

Comparable ion micrographs of the pea root caps (Fig. 3) indicate that calcium is present in the amyloplasts. Similar observations have been made for the root caps of lettuce. Calcium was detected in amyloplasts and cell walls with all three methods of preparation, including cryosectioning.

The detection of calcium in the rootcap amyloplasts of three different species suggests that calcium may be generally associated with this organelle and strengthens the possibility of a calcium involvement in the geotropic function of the amyloplast. Attempts to measure the zeta potential (the difference in potential between the fixed layer of solvent held to the surface of a solid and the bulk solution) of amyloplasts from corn root (11) have indicated that there is a marked negative charge on the surface of the amyloplast; the presence of calcium could be related in part to the negative surface charge on the organelle. Calcium is also well known to have regulatory effects on membrane properties and to be an integral component of numerous biological communication systems such as those involved in nerve impulses, endocrine gland functions, hormonal functions in animal systems, and the regulation of membrane permeability to water and to solutes (12). In plants, calcium is involved in several dynamic functions associated with the permeation of solutes, including diurnal and seismonastic leaf movements (6, 13), polar transport of auxin (2), and senescence (14). The role of calcium in the secretive activity of corn root-cap cells (15) is also suggestive of a participation in dynamic functions in the gravity-sensing region of the root.

Although the presence of calcium on or in the amyloplast does not establish

that ion as an essential component of the geotropic-sensing system, it adds a new characteristic to our understanding of the gravity-sensing organelle and raises the possibility that calcium is associated with the translation of the gravity-induced movement of amyloplasts into a physiological gradient, leading eventually to geotropic growth.

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   Supported by NIH grant GM 24314 to G.H.M. and NASA grant NAG-W3 to A.C.L.

10 March 1982

# Venus: Halide Cloud Condensation and

## **Volatile Element Inventories**

Abstract. Several recently suggested Venus cloud condensates, including aluminum chloride and halides, oxides, and sulfides of arsenic and antimony, are assessed for their thermodynamic and geochemical plausibility. Aluminum chloride can confidently be ruled out, and condensation of arsenic sulfides on the surface will cause arsenic compounds to be too rare to produce the observed clouds. Antimony may be sufficiently volatile, but the expected molecular form is gaseous antimony sulfide, not the chloride. Arsenic and antimony compounds in the atmosphere will be regulated at very low levels by sulfide precipitation, irrespective of the planetary inventory of arsenic and antimony. Thus arguments for a volatile-deficient origin for Venus based on depletion of water and mercury (relative to the earth) cannot be tested by a search for atmospheric arsenic or antimony.

Soviet spacecraft have analyzed cloud particles in the main Venus cloud laver by means of x-ray fluorescence (XRF) spectroscopy (1). On the basis of these analyses it is claimed that chlorine is present as a cloud constituent and sulfur is not detected. These results are in conflict with the weight of evidence from Earth-based studies (2) and from other spacecraft experiments (3), which strongly suggest that the dominant cloud constituent on Venus is H<sub>2</sub>SO<sub>4</sub> droplets. Satisfactory photochemical models for the production of an H<sub>2</sub>SO<sub>4</sub> aerosol from geochemically plausible primary gases, including COS, H<sub>2</sub>S, and SO<sub>2</sub>, are available (4). Direct evidence regarding the abundances of these species in the lower troposphere is lacking: copious production of COS and so on by reactions between sulfuric acid and the inlet system of the mass spectrometer on the Pioneer Venus large probe leads to masking of the atmospheric sulfur gases,

and abundances up to 100 ppm are possible for COS and H<sub>2</sub>S (5). No composition data are available for the bottom 22 km of the atmosphere, a region which contains not only the best-equilibrated gases, but also over 80 percent of the total atmospheric mass.

The source of a chlorine-bearing aerosol is less obvious. We have pointed out the high volatility of halides and sulfides of mercury, arsenic, and antimony (6) and have shown that the terrestrial crustal abundance of even the rarest of these elements, mercury, would suffice to produce substantial masses of halide cloud condensates on Venus: mercury is so volatile at the surface temperature of Venus that it would reside almost completely in the atmosphere.

More recently, in the context of a model for the formation of the planets in the presence of a steep gradient outward from the proto-sun, we have favored compositional models in which the vola-

tile elements are severely depleted in the accreting Venus relative to the earth. Combined condensation-accretion models with a variety of recent estimates of the accretion sampling functions of the terrestrial planets (7) show a primordial water content on Venus from  $10^{-1}$  to as low as  $10^{-4}$  of the terrestrial value. The failure of the 1978 Pioneer Venus mission to detect even a trace of mercury in the lower atmosphere (5) strongly implies that Venus is deficient in mercury relative to the earth. The severe depletion of the most abundant terrestrial volatile, H<sub>2</sub>O, on Venus is well known and is attributed to either a lack of water in preplanetary solids at the orbit of Venus (8) or massive loss of oceans of  $H_2$  after differentiation and outgassing of the planet (9). Donahue (10) found an enhancement of the D/H ratio on Venus by about a factor of 100 over the terrestrial value, requiring either loss of hydrogen from 100 times the present water inventory or accumulation of deuterium-rich material on Venus. Such a late loss mechanism could not deplete mercury while leaving vast amounts of the lighter and more volatile species  $N_2$  and  $CO_2$ . Thus the observed severe depletion of mercury is more convincing evidence for a volatile-poor high-temperature origin of Venus than is the depletion of water. Other moderately volatile elements, such as arsenic, antimony, bismuth, and germanium, are also potential indicators of the overall volatile content of Venus. In addition, such species, if present in the hot lower atmosphere, would condense at intermediate altitudes to form solid halides, sulfides, and oxide cloud particles.

In the past year, Krasnopolsky and Parshev (11) suggested  $Al_2Cl_6$  as the major cloud layer constituent and Barsukov et al. (12) suggested arsenic and antimony halides and oxides. Mole fractions of at least 10 ppm of condensable gases are required to provide the observed cloud density (13). Are these species plausible cloud constituents? Can useful limits on the abundances of the volatile elements arsenic and antimony be derived from atmospheric measurements?

It is simple to estimate the volatility of aluminum compounds at the mean surface conditions of Venus. Consider coexisting anorthite ( $CaAl_2Si_2O_8$ ), quartz (SiO<sub>2</sub>), and calcite (CaCO<sub>3</sub>) at 750 K and 95 bars in contact with the atmosphere

$$CaAl_2Si_2O_8 + CO_2(g) + 6HCl(g) = CaCO_3 + 2SiO_2 + 3H_2O(g) + 2AlCl_3$$
(1)