ADVANTAGES OF METAL AMINO ACID CHELATES IN FOLIAR ABSORPTION

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SUMMARY

Albion® Metalosates®, as the foliar version of Albion Metal Amino Acid Chelates, are manufactured to allow for increased absorption from leaf surfaces. They are formed according to sound chemical principles of reacting ingredients in proper proportions and under proper conditions to achieve chelation. Their formation as amino acid chelates can be demonstrated through standard chemical properties and chemical instrumentation widely acknowledged to be capable of measuring chelation. The metal Metalosates contain inherent charge characteristics which are capable of traversing the various layers of cuticle and cell walls without being bound by them. They also possess characteristics which make them compatible for passing through the plasmalemma by active transport. When split apart at the sites of usage, the metal atoms can assume their niches in the metabolic hierarchy of the plant and the resulting free amino acids are left to be of nutritive benefit wherever they may be needed in the metabolic processes. There are no xenobiotic ligands to metabolize, detoxify or sequester as with synthetic ligands, such as EDTA. Foliar applications of Albion Metalosate Metal Amino Acid Chelates are thus compatible with the inherent anatomy and physiology of plants and constitute a highly bioavailable means for improving crop nutrition and productivity.

INTRODUCTION

Plants are considered the primal sources of chemically reduced carbon compounds--the carbohydrates, oils, proteins, and other molecules harboring energy chiefly in carbon-to-carbon covalent bonds. These compounds provide storable energy for the plants and food for the humans and animals which consume the plants, thus sustaining life on earth. The ability of plants to utilize inorganic sources of minerals from soil along with air, water and sunlight by synthesizing storable food prompted an early tendency to view these substances as the only building blocks allowed for plant health and growth. In reality, plants are capable of absorbing more elaborate organic compounds from the soil, such as urea as a nitrogen source, Vitamin B_6 as an auxin-like growth regulator, and amino acids as protein building blocks.

In addition to the absorption of these more complex molecules from the soil, even this basic route is not the sole avenue for nutrient absorption into plants. The outer cell walls of leaves and stems are built to accept some nutrients and even larger organic molecules (such as, systemic pesticides and herbicides), providing that these compounds meet physical and chemical criteria required to be absorbed. Because of the vast surface areas of leaves, absorption of man-administered chemicals for crop improvement can occur quickly from foliar applications if the compounds are in a form that is readily absorbed into the cells which make up the leaf and which interconnect to other cells in the plant.

One of the first barriers for minerals to surpass on the way into the living cytoplasm of plant cells is the waxy cuticle that covers both upper and lower surfaces of leaves. This layer has a negative charge. If mineral nutrients are given in the ionic form, or in a form that must become ionic to be absorbed, as is the case with sulfates and other ionizable salts, the positively charged metal cations can be attracted to the negative charges on and within the waxy cuticle and be impeded from progressing further. Extra amounts of mineral nutrients given to override the polar attractions of the cuticle become rapidly toxic to the leaf surface, causing burn. Thus, there are both physical and physiological restrictions as to how much mineral fertilizer may be sprayed on leaves when the mineral is in the inorganic salt form. Further into the interior, where the mineral enters the epidermal cell wall of the leaf, cellulose, hemicellulose and pectin in the cell wall carry more negative charges and display high cationic-exchange properties which further impede the progress of mineral cations.

If metal oxides are administered as the mineral source, the metal may exhibit little if any charge because oxygen keeps it tightly bound, but this prevents the metal from being soluble and it still remains unobtainable to the plant. Oxides may possess a high percentage yield of minerals, but if the minerals are unobtainable, there is little nutritional benefit for plants receiving minerals as oxides and the money spent on them is no bargain.

For the efficient foliar uptake of metal nutrients by plants, they need to be neutral in charge, while still retaining a degree of polarity. This polarity assures that the molecules will be soluble in water which also maintains a degree of polarity. In Albion Metalosates, both water solubility and the presence of slight partial charges on the molecule, combine to increase the uptake of the mineral nutrient(s) into the plant. The partial charges are due to the two sets of unpaired electrons on each oxygen atom in the chelate and are less than the equivalent of a full charge electron displacement (as occurs in ionization). These amino acid chelates have unique chemistries which allow the mineral to migrate through the cuticle and cell wall and enter the cytoplasm intact. Once inside the cell, the mineral element can be released for the metabolic needs of plants.

CHEMISTRY OF CHELATES

A. Characteristics of Chelation

In the cytoplasm of plant cells, the metal elements do not exist in a free state. Metals, by chemical definition, are those elements capable of losing and gaining electrons easily, thus easily promoting oxidative and reductive reactions. If such reactions were allowed to proceed inside plants indiscriminately, life would be impossible. The enzymes, carriers, and other molecules in plants which form a working relationship with the nutritive metals do so by harnessing their oxidative/reductive capabilities and making use of these catalytic properties on an as-needed basis. Chelation is a common method used by plants to sequester or transfer the metals and allow their chemical energy to be parceled out for constructive purposes. Although vacuoles may contain free ions and salts of metals, these are not involved in cellular metabolism. In the cytoplasm, the metal elements which take an active part in metabolism must be sequestered in carrier molecules.

A chelate occurs whenever a metal is suspended by more than one bond from different atoms of the same molecular ligand. Once the bonds are made, ring structures are formed with the surrounding molecule. Plants have been utilizing the principles of chelation since

plants have been in existence. What is relatively new is the creation of mineral chelates in biocompatable and bioavailable forms which can be utilized for needed mineral supplementation to plants.

B. Chemical Properties of Chelates

1. Specifications for Chelation. In agricultural settings, the term "chelate" has often been misunderstood or applied in a general or catch-all fashion. Although chelation is a defined chemical entity, the molecules which bind to the minerals (called ligands) may vary widely in their physical, chemical and nutritional properties. For this reason, it is not sufficient to refer to a mineral nutrient as "a chelate." Among these different types of molecules, their nutritional quality depends on the degree of quality manufactured into each product. Proper conditions for chelation to take place must be present. Additionally, the proposed ligand, or chelating molecule, must have chemically reactive sites (moieties) capable of participating in the chelation process. The reactants must also be in the proper mole ratios for chemical combination to occur. Metal atoms lose electrons to become positively charged ions according to set patterns, with each metal producing ions of characteristic charge. Their capacity for chelation depends on compatibility of the proposed ligand to the metal ion and also on thermodynamic allowances for the chelation reaction to take place.

2. Necessity of Proper Mole Ratios. The mole is a concept used in chemistry to assure that adequate numbers of molecules are present in just the right proportions for the needed reaction. One mole is defined as the gram equivalent of the molecular weight of any compound or element. One mole of any compound has the same number of molecules in it regardless of how large or small the molecule is. Likewise, one mole of a single element has the same number of individual atoms as there are molecules in one mole of any other compound. Thus, components used to build larger or different molecules can be combined as equivalents of proper mole ratios, assuring that every part has its partner. Percentages are not molar ratios. Percentages or weight ratios result in products that are only partially chelated, at best, or not at all chelated if the proposed ligand is large with respect to the atomic weight of the metal atom being chelated. The presence of chelation, of course, presumes that the proper synthetic chemistry is also present.

To illustrate, an iron atom has a molecular weight of approximately 56 daltons (rounding off). The average molecular weight of the twenty protein-based amino acids is 137 daltons (there is no 'average' amino acid with this weight among the twenty proteinaceous ones, but this value serves to illustrate an average response). Since a mole is defined as the weight in grams of a compound divided by its molecular weight, one mole of any and all compounds contains the same number of molecules. Proportional combining amounts required for making new compounds can then be balanced appropriately. To form the bicyclic chelate where a single metal ion is suspended between the four chelating bonds of two amino acids, two moles of the average amino acid would have to be used for every one mole of metal atoms. This would equate to 274 grams of the 'average' amino acid. Since percentages are based strictly on weight for weight ratios in the same unit amounts, the percentages of these two constituents (assuming nothing else was in the product) would be 17% Fe to 83% of the 'average' amino acid. If iron were present in the final product at the rate of 10%, then the 'average' amino acid would have to be present as 49%, by weight. A product which claimed 10% Fe and 20% of amino acids as ligands would actually have less than the quantity of amino acids required to completely chelate the metal present, even

if only one molecule of the 'average' amino acid was chelated to each metal atom (providing that the proper conditions for chelation were present in the first place).

Partially hydrolyzed proteins or intact proteins used as ligands suffer an even greater mole ratio handicap. The requirements for adequate mole ratios for true chelation are augmented drastically when partially hydrolyzed proteins or full-sized proteins are substituted as the purported ligands. Since the protein is only 'partially' hydrolyzed or is whole, molecular weights for each molecule can range from thousands of daltons to tens or hundreds of thousands of daltons depending on the degree of hydrolysis. To match mole ratios between a metal atom and even one of these molecules would be a monumental task. One mole of Fe to one mole of partially hydrolyzed protein would equal 56 g Fe to 1,000's to 100,000's of grams of the far larger protein molecule. It can thus be seen how a product claiming 10% Fe with partially hydrolyzed protein as the ligand could not possibly be chelated except in minute trace amounts -- attempts to add the proper amount of ligand would too soon fill up all of the available space -- there would never be room for 'enough' of the ligand. The 10% level could never be physically or chemically achieved for full chelation and actual chelation (if present) would be several orders of magnitude less than the 10% value. In cases where 10% Fe was being claimed next to 20% of partially hydrolyzed protein as a 'chelating' ligand, the actual amount of chelate possible (if manufacturing conditions would allow chelation to occur in the first place) would be far less than the example calculated above using free amino acids.

3. Thermodynamic Resistance to Chelation with Large Ligands. In addition to the chemical incapacities of forming true chelates from the reaction of metals with proteins or partially hydrolyzed proteins of varying and unknown lengths and weights, there are thermodynamic constraints that shrink the likelihood of ever being able to form chelates from these long-chained ligands in the first place. The first concern encountered is that free metals cannot form bonds just anywhere on the long-chain intact or partially hydrolyzed protein molecule -- there must be an available and reactive moiety capable of sharing or donating electrons to each metal atom. All of the 20 proteinaceous amino acids contain a terminal carboxyl group and an α-amino group which allow chelation of metals through these two moieties which result in stable, five-membered chelating rings. Unfortunately for the proposed protein or partially-hydrolyzed protein ligands, the terminal carboxyl groups and an α-amino groups of their constituent amino acids are the very same moieties which are tied up in the peptide linkages, which form the binding backbone of the protein molecule. Unless an amino acid in the sequence of amino acids making up the protein or partially hydrolyzed protein has an extra amino or carboxyl group (or, to a much lesser reactive possibility, a free sulfhydryl group), the only reactive moieties on a multi-amino acid chain are at the extreme ends of the long-chain protein molecule. The likelihood of forming one large macrocyclic compound by chelating a metal atom at either end of the long chain is essentially non-existent. The two ends would need to just happen to meander within reactive distance of each other and then orient with an available ionized metal atom. In addition, the chemical requirements for chelation would have to be present at the precise event of close proximity and correct orientation of the terminal ends to allow a chelating reaction to take place.

In cases where an extra moiety existed on an amino acid closer to the end of a protein chain, chelation would still be energetically difficult to maneuver and the resulting molecule would tend to destabilize, due to the number of atoms in the ring structure and the arm of the rest of the protein molecule stretching out from the ring. Destabilization would result in no lasting chelation. Mineral performance and absorption would thus be similar to that of inorganic sources if proteins or partially hydrolyzed proteins were being claimed as the chelating ligands.

4. Importance of bonding strengths on metal bioavailability from chelates. A chelated compound will take on general properties similar to the ligand(s) which form it, since the ligands are larger molecules and contribute more in terms of chemical and physical properties than the metal. However, the metal chelate is a different molecule than either the metal or the ligand and will have its own unique properties. An example of a property of a chelated molecule that has great bearing on its nutritive capability is the strength of the actual bonds formed between the metal and the ligand. An early chelator which was used for mineral nutrition in plants was ethylenediamine tetraacetic acid (EDTA). The EDTA molecule forms bonds with metals that are very strong as to their stability constants. Plants (and other forms of life) find it difficult to free the metal atoms for metabolic usage. Research conducted by Albion Laboratories, Inc., has demonstrated which relative strengths of bonds should be incorporated into Albion Metal Amino Acid Chelates to assure that the minerals contained in the chelates can be released to appropriate metabolites within the plant cells. Albion Metal Amino Acid Chelates are complete nutrients since, upon cleavage, the needed metals are released and the residual cleaved ligands become normal straight-chained amino acids which can then enter their normal metabolic pools. There are no xenobiotic ligands for the plant to attempt to metabolize, detoxify or sequester to protect itself from toxic buildup -- nor are xenobiotic toxins accumulated into the environment.

C. Advantages of Albion Metalosate Amino Acid Chelates

Advantages of using amino acids as the ligands for chelating nutritive metals include: 1) their easily absorbable, small molecular size; 2) the affinity of the ligands to basic metabolism (the ligands are not synthetic or foreign to living systems, but are actually required by them); 3) since chelation occurs at the proximal sites of the carboxyl moiety and the alpha-amino nitrogen, each amino acid is capable of forming chelates in the same way, since all are alpha-amino acids, and all of such chelates result in stable five-membered rings; 4) their bonding strengths are strong enough for the molecules to remain intact through application and absorption, but not so strong as to resist breakdown for metabolic usage of the metal atoms; 5) the reduction of charge on either the metal atom or the molecule, as a whole; and, 6) ease of passage of the chelate containing the mineral through the cuticle and cell wall barriers and into the cells of the plants.

The negatively charged carboxyl oxygen of each amino acid bonds to the positively charged metal ion, while the lone pair of electrons on the alpha-amino nitrogen are both donated into vacant p- or d-orbitals of the metal atom. This results in twice the number of bonds being allowed in chelation, compared to that which would be expected from the normal valence or oxidation number of the metal atom. Depending on this valence or oxidation number for distinct metal ions, they may be chelated with amino acids in proportions of 1:1, 1:2, or 1:3 molar ratios of metal to amino acids. For instance, a metal atom with a valence or oxidation number of two could accept four bonds from two chelating ligand molecules, while metal atoms with a valence or oxidation number of three could accept six bonds from three chelating ligands, etc. Examples of Albion Metal Amino Acid Chelates (Metalosates) with stable five-membered rings are shown in Figure 1.

D. Proofs of Chelation for Albion Metalosate Amino Acid Chelates

The proofs that Albion Metalosate Amino Acid Chelates are true chelates can be shown both by analytical instrumentation and by operational consequence. The benefits of foliar applications of Metalosates would not accrue if the metal sources were not truly chelated; the minerals would not behave differently than minerals from inorganic sources. They would be no better absorbed than inorganic minerals and no better transferred to tissues and would show no improvements in nutritive capability over inorganic sources. The opposite of these concerns is the actual result.

While such operational proofs of chelation regarding how these compounds are absorbed and utilized by plants are certainly helpful, bottom line proofs of chelation are in the actual viewing or measurement of the bonds of chelation -- the ultimate proof of chelation is chemical proof. Albion laboratories is unique among manufacturers of mineral supplements in making the research and monetary outlays to demonstrate the actual presence of chelate bonds in products manufactured according to its specifications and by its patented processes.

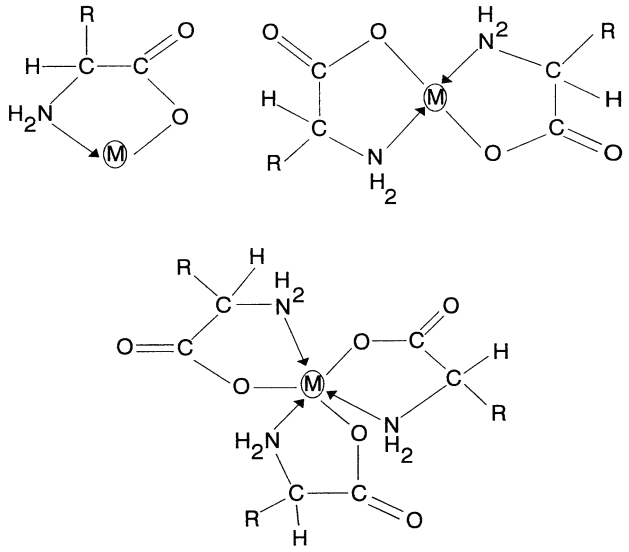

Figure 1. Chelate examples formed between free soluable metals and free amino acids. R-groups represent the molecular extensions of the individual amino acids forming the metal amino acid chelate.

Various instruments and methods have been utilized to demonstrate that Albion Metal Amino Acid Chelates are true chelates. Three have been the most definitive. This is because these are capable of discerning the actual chelating bonds coming into the metals from the ligands and, thus, are able to prove the presence of the heterocyclic rings of the chelates. These three techniques include: 1) electron paramagnetic resonance spectrometry (EPR); 2) X-ray diffraction spectrometry; and, 3) Fourier-transformed infrared spectrophotometry (FT-IR). The following three sections describe results that have been obtained from these instrumental methods.

1. Electron Paramagnetic Resonance Spectrometry (EPR)

When feed-grade powders of Albion Metal Amino Acid Chelates were subjected to cryostatic EPR as both pure compounds and mixed with other nutritional feed ingredients, the resulting upper and lower G-values demonstrated the presence of four bonds on the metal atoms which were splayed out at tetrahedral angles. This spacial orientation is exactly what would be expected for a 2:1 molar (amino acid:metal) chelate. Since the principles of creating chelates at Albion Laboratories are the same for both feed-grade and foliar products (although the processing lines are kept separate), foliar Metalosate Amino Acid Chelates would show the same results.

2. X-Ray Diffraction Spectrometry

When Zinc Glycine Amino Acid Chelate made by the Albion Laboratories method was crystallized and subjected to X-ray diffraction spectrometry, the bonding angles, atom identifications, and orientations of ligand atoms surrounding the zinc atoms all demonstrated the presence of 2:1 molar (glycine:zinc) amino acid chelates. A copy of the plotted configuration from the X-ray spectrometer showing the Zinc Glycine Amino Acid Chelate molecules and their crystalline alignment to each other is shown as Figure 2. It is particularly important to notice the presence of four bonds going into each zinc atom of the 2:1 molar (glycine:zinc) molecules. The oxidation number or valence of zinc is two. The allowance of four bonds entering each zinc atom demonstrates the presence of coordinate covalent bonds which donate both electrons of the bond from the same ligand atom into receptive d- or p-orbitals of the metal atom, which is a key characteristic of the presence of chelation.

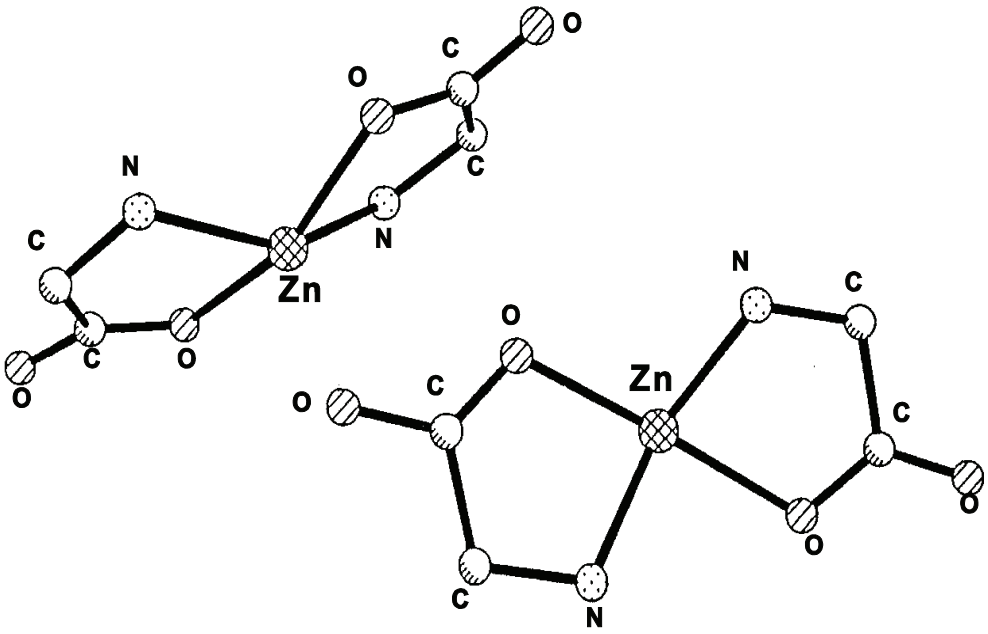

Figure 2 X-ray diffraction plot of 2:1 molar (glycine:zinc) Albion Metal Amino Acid Chelate showing participating elements, bonds, and spatial orientation of the molecules in the crystal.

3. Fourier-transformed Infrared Spectrophotometry (FT-IR)

The Zinc Glycine Amino Acid Chelate product above which had been proven to be a true chelate was used to validate a Fourier-transformed infrared spectrophotometric (FT-IR) method for further proving the existence of true amino acid chelates. Since literature IR spectra were available for known amino acid chelates, these were compared to FT-IR spectra of Metal Amino Acid Chelates produced by the Albion chelation technique. Significant and important absorbency bonds were observed at 3300 to 3400 cm^{-1} (N-H) and at various peaks between 1300 cm^{-1} and 1500 cm^{-1}(COO^{-}) which are specific for individual amino acid ligands. The data complied compared favorably with literature data for further proof that Albion Metal Amino Acid Chelates are true chelates.

E. Stability of Albion Metal Amino Acid Chelates

The products which were analyzed by cryostatic EPR as cited above were subjected to the same test three years after the first analysis. Results again demonstrated the presence of chelated tetrahedral bonds surrounding the metal atoms, which proved that the chelates were still intact.

Additionally, FT-IR methods have been applied to morgue samples of batches of Albion Metal Amino Acid Chelates which are five years old and the retention of chelation of the metals with amino acids has been demonstrated.

Mechanisms of Absorption of Albion Metalosate Metal Amino Acid Chelates

A. Structural and Chemical Anatomy of Leaf Surfaces

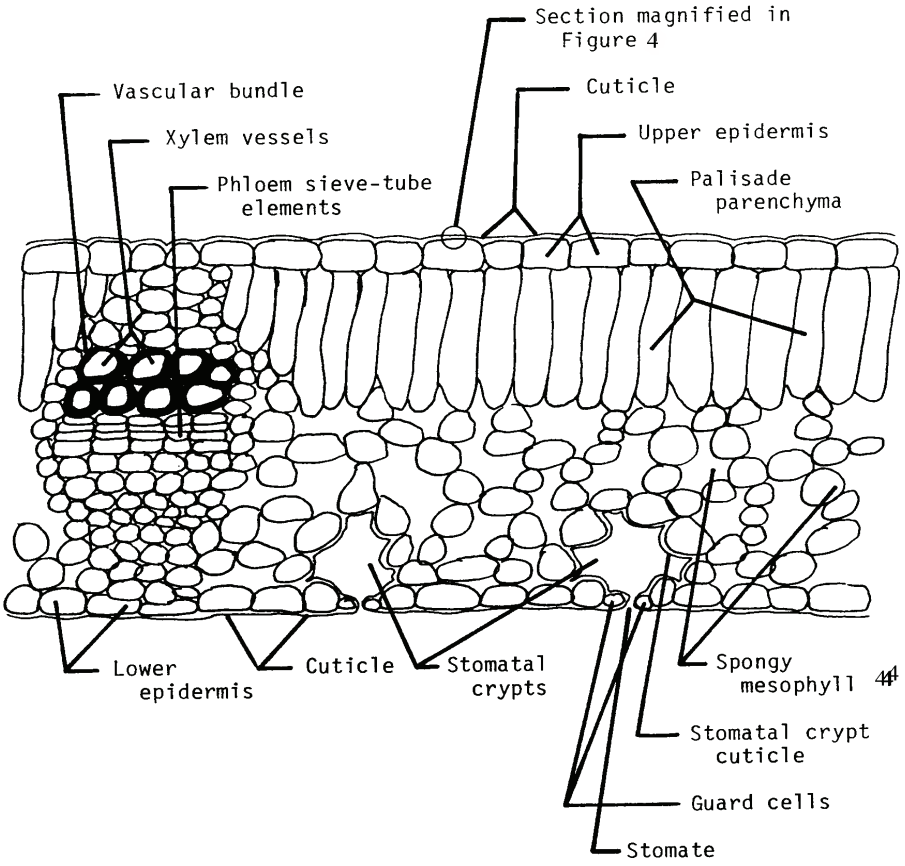

Figure 3. Cross-section of a leaf blade.

A generalized diagram of a leaf in cross-section can be seen in Figure 3. The labels on the diagram designate various areas and cell types. The diagram shows the upper and lower epidermal layers, stomates with guard cells, palisade parenchyma and spongy mesophyll including a vascular bundle sheath which surrounds thick-walled xylem vessels for transporting water into the cells and sieve-tube elements for distributing sugars and other photosynthate products to the rest of the plant.

The circled area including the upper cuticular layer and the cell wall of an upper epidermal cell is shown expanded in Figure 4.

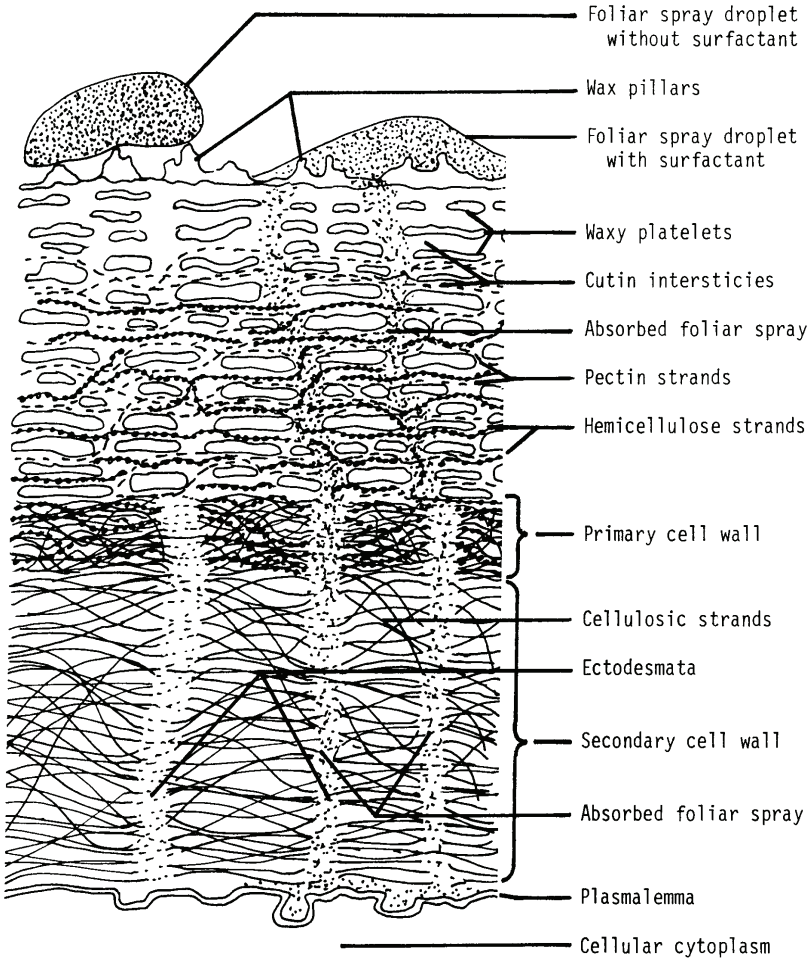

Figure 4. Cross-section of exuded cuticle and outer cell walls of the upper epidermis.

The initial surface cells for both the upper and lower surfaces of leaves are called epidermis. Both the upper and lower epidermal cells secrete elastic cutin and waxy platelets to the atmospheric side of their cell walls. These compounds are further bound by pectin, which is a polymer of methyl-D-galacturonate. Hemicellulose, which comprises a mixture of beta-linked pentoses, chiefly D-xylans, also adds strength to these other three components. The resulting covering is called cuticle and provides a semipermeable barrier on both upper and lower surfaces of leaves. The active ingredients of foliar sprays applied for absorption by leaves must be capable of traversing this waxy, semi-impervious covering.

Both morphological and cellular structures of green leaves maximize the efficiency of photosynthesis. Photosynthesis typically occurs in the palisade parenchyma and the spongy mesophyll tissues, the latter being characterized by open areas for gas exchange and openings to the outside called stomates or stomata. These openings are surrounded on their perimeters by guard cells which, in response to the relative pressure of water within them, expand or contract the size of the openings. When plants are low in water, the guard cells are limp and seal the stomata closed. This prevents the plant from losing even more water through the stomata which join the humid stomatal crypts with the outside drier and/or hotter air. Most stomata are found in the lower epidermis, although a few may occur in the upper epidermis.

Given the propensity of natural openings on the lower surfaces of leaves, one might erroneously presume that the most rapid avenue for getting foliar sprays into the leaf would be through stomata. Difficulties in doing this are both physiological and mechanical. The stomatal crypt is not an unattended gateway straight into the spongy mesophyll. The interior of the crypt is also sheathed with cuticle, although not is thickly as the outer surfaces of the leaf. Foliar sprays must be compatible for passage through cuticle, no matter to which surface of leaves they may be applied. Another impediment to sending foliar sprays into the stomatal openings for absorption is mechanical, since most plants are sprayed from the top. In the case of trees, however, both surfaces of the leaves can be easily sprayed and passage through stomates into stomatal crypts can allow for larger surface areas for foliar absorption. Cuticle and cell wall layers, as described in Figure 4, must still be traversed, however.

Several areas are diagramed in Figure 4: 1) the cuticular layer of the upper epidermis; 2) the cell wall of an epidermal cell, consisting of the primary and secondary walls; 3) the plasmalemma (or plasma membrane), which is the semipermeable membrane surrounding the cytoplasm of the cell; and, 4) the outer edge of the cytoplasm, just inside the plasmalemma. The cuticle is exuded from the epidermal cells and is shown in Figure 4 as everything above the upper surface of the primary cell wall. On the outer surface of the cuticle, waxy pillars may form. These pillars are hydrophobic and can repel water droplets and suspend them above the surface of the cuticle. This is depicted on the upper left portion of the drawing. The droplet on the upper right is shown adpressed to the upper surface of the cuticle. This is allowed when the foliar spray contains sufficient surfactant(s) to lower the normal surface tension of water and allow the droplet to adhere to the cuticular surface. Surfactants are characterized by having some components of the same molecule which are soluble in lipids and others which are soluble in polar solvents like water. The molecules of surfactant thus form a common phase between the waxy cuticular surface and the water-based foliar spray.

Once the droplets of the foliar spray adhere to the surface of the cuticle, the water and the solutes dissolved in it can be imbibed by cutin, which is the elastic, water-compatible substratum of the waxy platelets. Cutin and the pectin and hemicellulose strands, which offer structural support to the cuticle, all display negative charges. Thus, solutes dissolved in the water which are positively charged tend to hang up in the cuticle, while those which are negative are repelled. If neither of these two impediments occur, the water soluble spray contents can enter the interstices surrounding the waxy platelets and migrate to the interior of the cuticle by gradient diffusion.

The primary cell wall is composed of strands of cellulose, hemicellulose, and pectin, while the thicker secondary cell wall to the interior is mostly composed of cellulose. Secondary walls commonly contain lignin for strengthening; primary walls occasionally also contain lignin. In addition to displaying negative charges in similar fashion to the cuticle, both primary and secondary cell walls also have high cation exchange properties which can bind up positively charged ions (cations) passing through them. Gaps occur between the various structural polymers of the cell walls and usually fill with water. The gaps range from 10 angstroms in the primary cell wall to as much as 100 angstroms in the secondary wall. Small molecules may move through the walls in these spaces, but most of the transport through the primary and secondary cell walls occurs through very thin corridors called ectodesmata. These thin channels were once thought to be directly linked to the plasmodesmata which connect the cytoplasms between cells by thin cytoplasmic strands through the cell walls. However, they are now known to be separate entities--materials entering cell walls from the outside must traverse at least one plasmalemma to be admitted into the cytoplasm of the initial cell. Thereafter, plasmodesmata connect the cytoplasms of contiguous cells. Transport through the ectodesmata is by gradient diffusion, although thenegative charges and cation exchange properties of the primary and secondary cell walls may still impede the progress of positively charged metal ions.

The final barrier to the absorption of foliar sprays by leaves occurs at the plasmalemma (also known as the plasma membrane) which surrounds the cytoplasm of the epidermal cell. The plasmalemma is a semipermeable membrane having the classic lipid bilayer form. Pore sizes are limited to four angstroms across which limit intramolecular passage basically to water only. Molecules and ions able to reach this site for absorption require active transport to enter the cytoplasm. Active transport requires energy expenditure to convey substances from the outside of the plasmalemma to the inside. The active transport mechanisms utilized by leaf cells are considered to be the same as those utilized in the root. Of the three mechanisms operative in active transport (molecular carrier transport systems, mechanical widening of pore sizes, and pinocytosis), the mechanism viewed to be the most used is molecular carrier transport. This involves carrier molecules inside the membrane attaching to the nutrients or other solutes on the outside of the plasmalemma, traversing the membrane carrying the attached molecules and releasing the transported molecules on the interior side of the membrane. Energy is expended to effect this molecular transmigration.

B. Facilitated Passage of Metalosates through the Cuticle and Cell Walls of Leaf Epidermal Cells

When a divalent metal atom is chelated with two molecules of amino acids, the two positive charges on the cation are satisfied by the negative charge on each carboxyl oxygen of the two ligands. In terms of the full charges of electrons or protons, this full chelation would produce a metal atom that is neutral. However, the chelated molecule still carries a slight negative polarity, due to the presence of two pairs of unbonded electrons associated with each oxygen atom in the molecule. Although this is not the equivalent of a full charge for one electron, the occurrence of this polarity on the chelated molecule allows Albion Metalosate Metal Amino Acid Chelates to be soluble in water at the levels used for nutritional purposes. This partial negativity also predisposes the Metalosate for improved penetrance of the cuticle--highly polar or neutral compounds do not penetrate or traverse the cuticle as well as compounds that are only slightly polar (less than a full positive or full negative charge).

In cases of hybridization of chelating effect, where not all divalent metal ions are fully chelated at a 2:1 ratio of amino acids to metal or where trivalent metals are chelated at a 2:1 ratio rather than a 3:1 ratio, the compounds are still more equipped to traverse the cuticle and cellulosic cell walls than are inorganic ions. This is due to the ion exchanging capacities of these layers. Any hybridized chelates present have less partial charges to be bound by stratified ion exchanging sites than do free metal ions.

C. Facilitated Passage of Metalosates through the Plasma Membrane of Leaf Epidermal Cells

At the final barrier to reaching the cytoplasm, Metalosates may have an additional feature aiding more rapid absorption. As stated above, solutes presented to the plasmalemma require active transport to traverse the membrane. As noted in the **Introduction** section, the roots of plants have the capacity to absorb amino acids intact.

Since the modes of active transport are considered to be the same at the plasmalemma of leaf epidermal cells as they are at the root level, there may be capacities, and even predispositions to absorbing amino acids intact at the leaf epidermal plasmalemma. In animals, a predisposition has been shown for the intact absorption of Albion Metal Amino Acid Chelates in the jejunum or middle section of the small intestine. This is the area where free amino acids as well as dipeptides and tripeptides are absorbed. Through the use of radiolabelled Albion Metal Amino Acid Chelates, it has been demonstrated that these compounds retain enough of the character of dipeptides and tripeptides to be absorbed intact at the same sites for absorbing dipeptides and tripeptides. Since the mechanisms of active transport in classic lipid bilayer membranes seem to be universal in diverse forms of life and since it has been demonstrated that plants can take up intact amino acids, it is probable that Metalosates are as predisposed to active transport at the plasmalemma as they are at the surfaces of other site-specific membranes. Experiments have shown that when droplets containing Albion Metalosate Metal Amino Acid Chelates are placed on leaves much higher absorption and transport of these mineral nutrients occur than can be obtained when the same concentrations of minerals from inorganic sources are placed on the leaves.

It is important to note that minerals which were purported to be chelated to intact or partially hydrolyzed proteins (if these were able to be made in the first place, owing to the thermodynamic restrictions on such formations) would have severe difficulties traversing the cuticle layer and the primary and secondary cell walls. Even if such compounds were to eventuate to the barrier between the secondary cell wall and the plasmalemma, their progression would stop there. They would need to be cleaved, somehow, for the contained mineral to gain passage across the membrane by active transport. Such long-chained, proteinaceous molecules could only be of benefit, nutritionally, if they released their minerals as metal ions. In this form, these sources have no greater advantage to plant nutrition than do inorganic mineral salts given as nutrients, in the first place, and they meet with additional problems inherent in traversing the cuticle and cell walls.

D. Unique Properties of Albion Metalosate Amino Acid Chelates

At times there are some manufacturers or salespeople who may make the claim that the products which they market are just the same as Albion Metalosate Amino Acid Chelates, no matter which manufacturer produces them. Different producers have different manufacturing processes for their products. Both Albion's techniques and their resulting products are patent-protected and true sameness would be illegal. Some companies make specific claims for specific sources of proteins and/or amino acids used in their products and additional claims for other ingredients. Although these manufacturers infer that their products are like the Amino Acid Chelates made by Albion Laboratories, Fourier-transformed infrared (FT-IR) spectra discern unique differences. Many specific properties and features of molecules contribute to the final FT-IR spectra. In the absence of matching spectra, and in the face of specific patents, the claims made by other companies or their representatives to being the same as Albion's Metalosate Amino Acid Chelates cannot be true and the benefits of high absorption and safety gained through using Albion's Metalosate Amino Acid Chelates cannot be expected.