The great tragedy of science - the slaying of a beautiful hypothesis by an ugly fact.

Thomas Henry Huxley (1825-1895)

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Chapter 6

EFFECTS OF PREHARVEST TREATMENT WITH UNCALCINED KAOLIN ON POSTHARVEST APPLICATION OF COMMERCIAL WAX ON MANGO (*Mangifera Indica* L.) FRUIT

6.1 ABSTRACT

Mango cultivars have wide ranging developmental periods, with fruit reaching physiological ripeness during summer time when severe meteorological conditions prevail. Sunburn damage manifests as necrotic lesions, rendering fruit useless for both local and export markets. Mechanical measures currently employed against sunburn are expensive, time consuming and labour intensive. Alternative solutions must meet with the requirements posed by the target export markets in Europe. Kaolin is a lucrative proposition, but the physiological effect of the clay on mango fruit surfaces has not been investigated. Furthermore, the effect of the clay on the film formation of commercially applied wax formulations is also poorly understood. Results from this study indicate that kaolin affects epicuticular wax development. Persistent kaolin lamellae on fruit surfaces have a negative impact on commercial wax film formation.

6.2 INTRODUCTION

Mango cultivation is a lucrative industry in many parts of the world, being the second most popular tropical fruit crop (FAO, 2002). In South Africa, mangoes are primarily grown in the Eastern parts of the country, with some production in the Western and Northern Cape, in areas below 600 m. Main production farms are geographically situated between the 24° and 26°S latitudinal, and 30° and 31°E longitudinal lines. Environmental conditions in these areas are harsh during the periods of fruit set (Barkstrom, 2004). Typical early summer temperatures average 25 - 30 °C, often exceeding 38 °C in mid-summer, with solar insulation during this time reaching 6,35 kWh/m^2/day. The relative humidity in mid-summer can rise to 85 % with an average of 69.7 % cloud cover during daylight hours.

Continuous exposure to this intense light energy during fruit development annually causes up to 20 % loss of export quality material due to sunburn blemishes and physiological disorders (Le Lagadec, 2003). Huge investments in terms of both strategies for sunscald prevention and human resources are made during each growing season to reduce these losses. Currently, the most widely practiced sunscald prevention strategy in South Africa is the innovative practice of using caps made from aerothene on fruit exposed to afternoon sun (Silimela & Korsten, 2001). However, this practice is labour-intensive and expensive, and not always successful (Le Lagadec, 2003). The possibility of an alternative solution that may address these problems would be pursued enthusiastically, as was the case with kaolin.

Kaolin is a term that refers to rock consisting of at least 90 % kaolinite. It is also used as a general commercial term for material consisting of, amongst other minerals, kaolinite. Kaolin normally occurs in two geological environments (Newman, 1987):

- as a primary or residual ore where it formed *in situ* due to alteration or weathering of a parental rock which is often of granitic composition
- as secondary or sedimentary kaolin ores.

It usually forms a massive, white to light greyish or light yellowish rock in which kaolinite occurs with other more stable minerals such as quartz. A normal requirement is that kaolin ores are beneficiated, during which process impurities such as quartz and mica are removed from the product, and kaolinite is dry- or wet-milled, classified and bagged.

Kaolinite belongs to the phyllosilicate group of minerals because of a laminar physical nature, and simple 1:1 layered crystal structure containing the basic units from which all clay minerals are made (Newman, 1987). From this structure it is clear that kaolinite can be defined as a hydrated aluminium silicate mineral with the general formula $Al_4Si_4O_{10}(OH)_8$ with the following theoretical composition: SiO_2 = 46,5 %; Al_2O_3 = 39,5 %; H_2O = 14 %. From Figure 1 it can be seen that one Si coordinated tetrahedral layer is bound to an Al/Fe coordinated octahedral layer by the sharing of OH groups for apical oxygen atoms in the tetrahedral layer. Si in the tetrahedral layer can be substituted by limited numbers of Al ions while Al in the octahedral layer can be substituted by Fe. Microscopically, the clay often displays subhedral to euhedral, hexagonal grain shapes consisting of many thin platelets arranged face to face, which can be arranged in booklets (Huggett & Shaw, 1997). The length and breadth dimensions of a typical kaolinite platelet far exceed the thickness thereof, while the general dimensions vary greatly, depending on the mode of formation of the clay. Chemically, other elements which could be in solid solution in the kaolinite crystal structure, or which could be adsorbed onto the clay platelets, include mostly Ti and Fe (Newman, 1987). Another hydrated aluminium silicate mineral that is mineralogically and chemically indistinguishable from kaolinite (except if special sample treatment tests are done), but which displays a typical tubular morphology, is halloysite. The presence of such alternative clay structures is typical of uncalcined kaolin.

Some of the most important characteristics of kaolin that makes it very useful in a wide variety of preharvest applications on tree crops are:

- its laminar or plate-like morphology and concomitant large surface area (Huggett & Shaw, 1997)
- high reflectivity (Glenn *et al*., 2002)
- ease of dispersion (Zaman & Mathur, 2004)
- chemical inertness (Newman, 1987).

The potential uses of kaolin on fruit surfaces gained prominence when it was applied as a particle film deterrent against ovipositioning by psylla on pears (Glenn *et al*., 1999; Puterka *et al*., 2000). This success was followed by application of kaolin against codling moth on apples and pears (Unruh *et al*., 2000). Since then, the use of kaolin against insect pests include the suppression of fruit fly infestations on nectarines, persimmons and apples (Mazor & Erez, 2004), and olives (Saour & Makee, 2004). The possibility of using kaolin as sunshield in a sunscald-prevention program was first investigated in studies on the preharvest physiology of apples (Glenn *et al*., 2001; Glenn *et al*., 2002). In 2003 it was applied for the same purpose on the surfaces of pomegranates in Spain (Malgarejo *et al*., 2003). The use of kaolin as a particle film barrier against sunscald on mango fruit were tested in field trials on locations in the Hoedspruit area (24.4°S, 31.0°E) of the Limpopo province of South Africa during the 2002/2003 season (Joubert *et al*., 2002; Le Lagadec & Ueckermann, 2002; Le Lagadec, 2003). Different concentrations of kaolin suspensions (3 % - 15 %) in water were applied by either spraying or dipping, and even the lowest concentration indicated acceptable results (Le Lagadec, 2003). The 2003/2004-production season saw the first commercial application of the clay on mangoes.

At the time of the first commercial application of kaolin on mangoes, limited quantified information existed on the preharvest sunblock properties of kaolin. No studies could be found on its possible effects on fruit physiology, with a single study pointing towards possible repercussions on the packline (Malgajero *et al*., 2004). During postharvest processing of kaolin treated mangoes, immediately following washing and application of the commercial wax emulsion, it was noted that areas with receding wax developed while the wax was still wet. As the applied wax dried, uneven, dull spots created an unacceptable blotched surface appearance. Furthermore, this problem persisted when untreated fruit followed the batches of kaolin-treated fruit that had passed over the packline. Initially, the formulation of commercial wax emulsions was the suspected culprit, but this was dispelled after extensive quality checks were done by the manufacturer of the emulsions. Further investigations then indicated the presence of kaolin on fruit surfaces that experienced uneven wax coating.

The waxing problems exacerbated apprehension about a possible increase in the percentage of fruit developing lenticel damage after waxing. This apprehension was not based on any data or observations, but stemmed from the uncertainty about the nature of the initiators for development of a postharvest condition known as 'lenticel damage'. To determine the effects of kaolin on mango fruit surfaces, this two-fold investigation was undertaken. A study of the interaction of uncalcined kaolin and commercial wax emulsion was accompanied by an assessment of the threat of lenticel discolouration due to kaolin application.

6.3 MATERIALS AND METHODS

6.3.1 Plant material

During the 2003/2004 seasons, mango fruit (cultivar 'Tommy Atkins') produced and packed for export were obtained from Bavaria Fruit Packers, a commercial packhouse near Hoedspruit, Limpopo Province, South Africa. Two packlines were investigated, namely one used strictly for the packing of organically produced fruit, and the other for fruit that are produced and packed conventionally (non-organically). Two designated points on each packline were investigated, namely the elevated exit following the warm water bath, and the rollers after commercial wax application. From the conventional packline, two separate batches of treated samples were collected: one consisting of fruit that were dipped in 3% kaolin slurry and the other of fruit that were sprayed with 3% kaolin suspension. From the packline for organic production only fruit sprayed with 3% kaolin suspension was collected. Three fruit were collected from each sample point and a box with nine fruit from each batch collection point.

Triplicate samples, consisting of 5 fruit each, were also collected from two orchards where trees received preharvest treatments of kaolin that consisted of either dipping in or spraying with 3 % slurry. Fruit from untreated trees were collected as control samples. Table 1 is a summary of the sample collection schedule.

6.3.2 Application techniques of the kaolin-based product

A product consisting of uncalcined kaolin and copper oxychloride was made up to a 3 % suspension and applied as either a spray or slurry into which the fruit was dipped. Spray applications were done with commercial spray apparatus and delivered at 30l /tree, while dipped treatments were done manually by dipping individual fruit into buckets containing the slurry. Fruit that had not yet reached physiological ripeness were used for single-application spray and dip treatments. For the application of multiple spray-treatments in a study on insect control, sprays were delivered from the period when the peduncle to stamen end-length of the fruit was about 15 mm to physiological ripeness, totalling four applications per season.

6.3.3 Preparation of the fruit sample material

All the chemicals were obtained from SPI Supplies (SPI Supplies, West Chester, Pennsylvania). Fruit samples were collected from the orchards or commercial packline during normal operation and processed within 18 hours after collection. Three sections (each >25mm^2) of mango fruit rind were dissected from the shoulder area of each fruit, and processed by plunge freezing it in liquid propane at -180 °C (Reichert KF80, Vienna). Sections were then dried in a high vacuum freeze drier (custom built, Tshwane University of Technology, Pretoria, South Africa) at 1.39 x 10^{-7} mbar and -80 °C for 72 hours. All the samples were duplicated and prepared by standard fixation in 2.5 % glutaraldehyde, followed by OsO_4 post-fixation and critical point drying (Bio-Rad E3000, Watford, England). The two methods were used in parallel in order to eliminate the interpretation of any artefacts present due to the preparation technique. Sections from both preparation techniques were made conductive by exposing it to vapour from a 0.5 % solution of RuO_4 for 30 minutes (Trent *et al*., 1983; Van der Merwe & Peacock, 1999) before viewing in a JSM-6000F high-resolution field emission scanning electron microscope (FE-SEM) (JEOL, Tokyo, Japan).

6.3.4 Material and instrumentation for study of kaolin

Two sets of samples consisting of different types of commercially available kaolin were subjected to basic comparative analytical tests to determine differences in mineral and geochemical properties. The base of one set consisted of locally produced, uncalcined kaolin. The base of the second set was a calcined kaolin product known as Surround®. Samples JH914, JH915 and JH916A consist of kaolin used as mango sunscreen, while JH916 is a carrier for copper oxychloride. JH914 and JH916 are samples of kaolin derived from a South African kaolin producer.

X-ray diffraction analysis (XRD) was done at room temperature, using a powder diffractometer (Siemens D500) (Siemens, Karlsruhe, Germany) in reflection mode with Cu-Kα radiation at generator settings of 40 kV and 35 mA, and at a speed of 0,02° step size per 1 sec. The powder diffractogrammes were run in a 2θ range from 5° to 65°. Phase concentrations are determined as semi-quantitative estimates, using relative peak heights/areas proportions (Brime, 1985). For the geochemical work, a Philips PW1480 X-ray fluorescence apparatus (Philips Analytical, Almelo, Netherlands) was used with a Sc anode for major-element analyses and a Rh anode for trace-element analyses.

Presence of uncalcined kaolin on the fruit surface and embedded in the commercial wax layer was confirmed by FE-SEM using backscatter mode at 20 kV, and a low vacuum JSM-5800LV SEM (JEOL, Tokyo, Japan) with an Energy Dispersive Spectroscopy (EDS) apparatus attached to it. For confirmation of the EDS analysis of kaolin inclusions on the fruit surface, kaolin samples were prepared by scattering a small amount of the powder onto double-sided carbon tape on an aluminium stub. The sample was sputter coated with gold to a thickness of approximately 8nm and viewed in EDS mode at $P < 2.67$ mBar.

6.4 RESULTS AND DISCUSSION

Results of the mineralogical analyses consisted of three parts, namely the semi-quantitative analyses of the mineralogy, including different types of clay minerals, by X-ray diffraction (XRD), analysis of the geochemical composition by X-ray fluorescence (XRF) and the geochemical composition of individual mineral grains such as kaolinite by electron dispersive spectroscopy (EDS). The latter studies confirmed the random presence of several elements in the clay, while features identified by XRD were used in diagnostic determination of the geochemistry of the clay samples investigated. Observations made with FE-SEM were related to the mineralogical results.

6.4.1 Results of X-ray diffraction analysis

Samples JH914 and JH916 consisted of 90 % kaolinite and approximately 6 % mica (Table 2). Mica is another member of the phyllosilicate group of minerals and closely associated with the uncalcined kaolin. JH915 was a sample of imported kaolin (Engelhard, Surround®). The composition of this sample differed from that of JH914 and JH916 because of the presence of 55 % amorphous material. The amorphous mineral component was the result of heat treatment or calcining, during which time moisture in the clay was driven off (Table 2). Typical utilisation of the clay in JH915 included application as an insect repellant, sunscreen and temperature control product on ripening fruit. From the comparison of results in Table 2, it could be seen that, firstly, no amorphous material was present in the local product, the high crystallinity of JH914 implying that the clay had probably not been calcined. Secondly, the mineral component (except for the copper oxychloride, which is an additive and the trace minerals) was similar in both the South Africa derived kaolin and imported product.

6.4.2 Results of X-ray fluorescence

The presence and weight distribution of all the elements in the samples shown in Table 3 were determined by means XRF. The composition of JH914, uncalcined South African kaolin, compared well with the ideal theoretical kaolinite composition. JH915 was a sample of imported, calcined kaolin and the result of the compared mineralogical compositions was given in Table 3. Loss on ignition (LOI) of JH914 was approximately 17.4 %. Comparatively, JH915 had a LOI of only 2.27 %, similar to the mineralogical results in Table 2, indicating that this sample was calcined to less than 3 % total moisture. Silicon, titanium, aluminium, magnesium and manganese oxide concentrations had higher values in JH915 in comparison to JH914 due to normalisation to a calcined basis.

Chemically, other elements which could be in solid solution in the kaolinite crystal structure, or which could be adsorbed on the clay platelets, included mostly Ti and Fe.

6.4.3 Results of electron dispersive spectroscopy

Although EDS results were useful as both quantitative and qualitative data, EDS analysis of the JH-samples were only used as qualitative confirmation of observed kaolin particles inclusions of the wax film. This was because of the absence of standards against which to determine the mineralogy of each sample.

EDS data was used in combination with the visually determined results from the FE-SEM to confirm the texture of analysed samples. These results excluded the contribution of water, oxygen and carbon to the mass ratios represented in Table 4. The following were important in the consideration of the EDS results obtained:

- the chi-squared values of the scans varied between 1.09 and 1.46, which was well below the required value of ten, indicating an excellent fit of the graph (Fig. 2).
- all element weight percentages above 0.5 % were considered to be significant (standard EDS interpretation).
- qualitative results were indicative of the small component analysis of material investigated.

The presence and weight distribution of all the elements in the samples that were investigated were in agreement with results from the raw materials used in the formulation (Tables 2 & 3).

6.4.4 Scanning electron microscopy and other observations

The sun block agent/carrier was found to consist of a finely milled rock containing mostly (>90 %) a hydrated aluminium silicate (kaolinite). The length and breadth dimensions of each platelet far exceed the thickness thereof. Surface dimensions of the studied samples ranged between 0.2 – 0.5 μm, which meant it fell in the very fine category. Lamellae appeared both fragmented and still in the booklets (Fig. 3A & B). Halloysite was observed in the powder samples as well as on the plant surface (Fig. 3A - D). Quartz was also present in subordinate quantities in the sample material, and aggregates of kaolinite/mica/smectite showing rosebud textures, were observed (Fig. 3C). Copper oxychloride in the formulation was observed as fused, cubic crystals attached to the clay particles. Observed crystal sizes meant that these crystals could fit between mango fruit wax crystals comfortably (Fig. 3D, 4A-C).

Dip application of the clay caused irregular colour development (vein-like appearance of fruit colour pattern) (Fig. 5). The kaolin furthermore had serious repercussions on the packline, because apart from contact contamination of the lugs, bulk bins and other fruit, the outmost parts of the clay overload rinsed off in the different water baths (Fig. 6A). Dislodged clay particles from heavily encrusted fruit surfaces remained suspended in the water and could attach to fruit surfaces with available binding sites, creating a carry-over effect that eventually contaminated the complete packline.

Fruit subjected to spray application (Fig. 6B) were less negatively impacted in terms of colour development, while still being protected against sunburn, which included temperature control of developing fruit (Le Lagadec, 2003). However, the kaolin particle film could not be removed completely by any mechanical means and dispersing fractions of the film contaminated water in dump and wash baths (Fig. 6C). Kaolin booklets (Fig. 2) delaminated and fragmented through mechanical wear. The kaolin debris fitted between the complex crystalline structures in the outermost (aliphatic) wax layer (Fig. 3D, 4A -C, and 6D) and would be trapped by mechanical compression of the wax crystals and cohesion forces.

Kaolin-free fruit passing through the wash processes at a later stage were shown to be affected by this particulate debris. Due to the size and pliability of epicuticular wax crystalloids, the fruit surface effectively captured some of the kaolin and associated fragments (Fig. 4 & 6D). Thus, although the fruit surfaces had a clean appearance at the exit of the packing line, a microscopic layer of clay lamellae still adhered to it, either by application or due to the attachment of suspended particles (Fig. 6C). Dynamic reconstitution disrupted plant wax over objects or inclusions on the fruit surface further contributed to the failure of the packline procedures to remove kaolin (Fig. 7A - C). The configuration of reconstituted wax was determined by the physical and chemical characteristics of the obstructions through which wax constituents have to migrate. Low absorption and good permeability of commercial wax polymers meant that the architecture of reconstituted wax crystals did not alter severely (Fig. 7A) after diffusion through this layer. Kaolin lamellae, on the other hands, have high absorptive properties that trap oily substances (Gu *et al*., 2003), which account for the atypical architecture of reconstituted fringing crystals (Fig. 7B & C).

This absorptive quality of kaolin caused particles attached to the fruit surface to form a physical barrier between the natural and commercial wax (Fig. 8A), preventing their integration and subsequent film formation. Although evidence could be found of the commercial wax flowing into spaces between epicuticular wax crystalloids, film formation was either incomplete or absent in most sampled material (Fig. 8B). The amount of commercial wax applied, as indicated by the thickness of its layer, did not affect film formation (Fig. 8C). Close scrutiny of set commercial wax emulsion showed that it did not set homogenously. The solidified emulsion had a granular appearance that was indicative of localized polymerization (Fig. 8D) due to loss of moisture and unsaturated oils to the kaolin lamellae. The loss of these fractions created incomplete coalescence of the emulsion constituents (Yan *et al*., 2003).

As seen from Table 5, kaolin present on the fruit surface also altered the surface tension of the wax substantially, causing insufficient adhesion between the commercial wax and plant (epicuticular) wax. This effect was found on both the organic line where a carnaubabased wax was used and the normal packline where a polyethylene-based wax was used. Areas with preferential adherence corresponded with areas where the difference between the surface tension (dyne.cm^{-1}) of commercial wax and the fruit surface was the largest. Disturbance of the surface tension by any foreign inclusions, in either the commercial wax or the plant wax, would result in an irregular application of the wax emulsion (Fig. 9A - D). An uneven distribution of kaolin and the altered surface tension in coated areas therefore led to unsatisfactory wax application as encountered on the packline. Furthermore, the hygroscopic ability of the clay fractions also had a detrimental capillary effect on the available free water in the commercial wax (Brady *et al*., 1996; Zaman & Mathur, 2004). It is suspected that this withdrawal of capillary water from the particulate fraction of the commercial wax impeded film formation, which led to the wax film having a granular structure, and to disruption of coalescence of commercial wax polymers and plant wax crystalloids (Fig. 10A & B).

A problem that manifested only once the fruit had been packed in cartons, actually originated during processing on the line, when wet, swollen kaolin lamellae had formed inclusions during commercial wax application. Once these lamellae started to dry inside the wax film, they shrank, resulting in the formation of cavities in the wax film layer (Fig. 11A & B). These cavities, together with the kaolin inclusions changed the tensile properties of the wax film, and disrupted the mechanical integrity of the film, making it brittle (Fig. 12A).

Finally, kaolin debris that had entered into lenticels was observed in epicuticular membranes from the sample material studied. Such debris became trapped underneath the commercial wax emulsion that flowed into the lenticel (Fig. 12 B). However, it was not possible to unequivocally relate the discolouration of lenticels to the presence of kaolin debris, as discoloured lenticels without kaolin were also found.

6.5 CONCLUSION

Fruit intended for extended periods of transport are coated with commercial wax formulations. The ultimate goal of commercial wax application on fruit surfaces is to achieve a sound, homogenous wax film that gives an appealing gloss and adequate protection against desiccation and postharvest pathogens during export, without adding physiological stress to the fruit. During the 2003 - 2004 mango production season in South Africa, this objective was obstructed at a cooperative packhouse, when packed fruit presented with an uneven and blotchy wax film. This investigation pointed out that it was due to the presence of uncalcined kaolin on the packlines and in the waterbaths. A number of producers were using a kaolin-rich product as a preharvest sunscreen and anti-fungal agent, and these fruit were part of the scheduled packing at the time that the problems were encountered.

In South Africa, uncalcined kaolin is available as a locally produced preharvest product which is sometimes regarded as being more cost efficient, but is applied more often. Calcined kaolin is imported and applied singularly as a sunscreen. Dip application of the mixture is not recommended, but this method was used by several growers in order to circumvent the overall misting effect and subsequent coating of complete trees by the spray. However, dipping resulted in a very heavy kaolin load on fruit surfaces and uneven colour development of the fruit rind. Nevertheless, regardless of application, persistent adherence of dispersed kaolin lamellae were confirmed, indicating that complete removal of the kaolin lamellae from the surface of the fruit during packing processes is impossible.

The interaction between commercial fruit wax and residual kaolin particles on the fruit surface is crucial, since it affects the integrity of the wax film formed. Persistent particles form a mechanical barrier to the commercial wax and affect the surface tension properties of both the fruit surface and commercial wax. During the period of the incident investigated, several batches of fruit received on the packline were covered extensively in kaolin. Subsequent batches of fruit not treated with kaolin were contaminated by carry-over of persistent clay fractions present on the packline. This resulted in all the fruit on the packlines involved being characterized by irregular application of the commercial wax. These irregularities were due to charge effects by the lamellae that interfered with the cohesion and adhesion properties of the various wax fractions involved (Brady *et al*., 1996). The resultant incompatibility of the surface tensions then manifested as visibly dull areas where the immiscible waxes separate. The phenomenon was more prevalent on organically grown fruit packed on a line dedicated to such fruit. This was due to the formula of the wax emulsion approved for organically produced and packed fruit being far less tolerant of surface tension deviations. Fruit from normal production lines similarly treated with uncalcined kaolin, also exhibited dull areas, but the presentation was far less severe.

Consumer preference has created a growing demand for organically produced crops. Kaolin meets the requirements for this type of produce, and the application of kaolin as a sunscreen may be effective in the orchard (Le Lagadec, 2003). However, the postharvest repercussions for mangoes need to be investigated in more detail. A disruption of the adhesive qualities of the wax applied to organically produced fruit raised alarm to such repercussions. The synthetic wax used on the normal line had less severe adhesion problems, but uneven wax film formation associated with definite kaolin inclusions in the wax film were observed. The specific architecture and size of the wax crystals on the mango fruit surface is an efficient trap for both copper crystals and fractured kaolin lamellae, which can fit between the wax crystals comfortably, affecting its functionality. Epicuticular wax play a role in both light attenuation and light harvesting by the fruit, and therefore the effect of kaolin on the ultimate sugar and acid content of the fruit needs to be investigated.

In this study, no conclusive evidence was found to support or dismiss the anticipated increase in lenticel discolouration by kaolin. Lenticel morphology may determine the probability that kaolin can block up the entrance to the lenticel cavity, which could affect the susceptibility of a cultivar to the development of discoloured lenticels.

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6.7 TABLES

Table 1 Preharvest treatments of mango fruit (cultivar Tommy Atkins) with a locally obtained, uncalcined kaolin-based product

Application		***Point of Collection***
Number of replicate applications	***Method***	
3	None	Tree
1	Spray	Tree
4*	Spray	Tree
1	Dip	Tree
1	Dip	Packline (normal), after warm water bath
1	Dip	Packline (normal), after waxing
1	Spray	Packline (normal), after warm water bath
1	Spray	Packline (normal), after waxing
1	Spray	Packline (organic), after warm water bath
1	Spray	Packline (organic), after waxing

* : This was a experimental treatment to determine the feasibility of multiple kaolin applications to control insect pests during mango fruit development.

Table 2 Semi-quantitative analyses by X-ray diffraction, comparing three kaolin samples and copper oxychloride-bearing kaolin (% weight)

Analyte / ***Sample***	***Anatase***	***Jarosite***	***Crandalite/Fluorencite***	***Kaolinite***	***Mica***	***Cu Oxy-chloride***	***Amorphous matter***	***Total***
JH 914: Sample A (Uncalcined)	-	1	3	90	6	-	-	100
JH 915: Sample B (Calcined)	12	-	-	34	-	-	55	101†
JH 916: Uncalcined + Cu oxy-chloride	-	-	-	77	5	18	-	100
JH 916 A: Control (Uncalcined kaolin)	-	-	-	91	7	-	2	100

*: Chemical Composition of Analytes:

- Anatase = TiO_2;
- Jarosite = $KFe_3(SO_4)_2(OH)_6$;
- Crandalite / Fluorocite = $CaAl_3\ (PO_4\ )_2(OH) \cdot 5H_2O$;
- Mica = $KAl_2(Si_3Al)O_{10}(OH,F)_2$;
- Analcime = $NaAlSi_2O_6 \cdot H_2O$ - Not detected.

†: Decimal margins of error contributing to accrued value ≥100 %

Table 3 Results obtained from X-ray fluorescence analyses, depicting the chemical composition of locally produced kaolin versus imported kaolin (weight %), both of which are used in applications for insect repellent, sunscreen and temperature control on ripening fruit

Element	JH-914 Uncalcined kaolin	JH-915 Calcined kaolin
SiO_2	41.70	51.00
TiO_2	1.02	1.52
AL_2O_3	35.30	43.90
Fe_2O_3	0.86	0.66
MnO	0.01	0.02
MgO	0.40	0.50
CaO	0.42	0.16
K_2O	1.07	0.19
Na_2O	<0.1	<0.1
P_2O_5	0.22	0.11
Cr_2O_3	<0.01	<0.01
V_2O_5	0.01	0.02
Cl	0.02	0.01
S	0.30	0.10
H_2O	1.28	0.49
LOI	17.38	2.27
Total[†]	99.99	100.95

[†]: Decimal margins of error contributing to accrued values of Total ≠ 100 %

Table 4 Quantitation of spectroscopy results of uncalcined kaolin with added Cu-OCl

Accelerating Voltage: 20 KeV	Take Off Angle: 35°
Live Time: 100 seconds	**Average Dead Time: 11.916**
Chi-sqd * = 1.39	

Element	k-ratio (calc.)	Element Wt % †	Wt % Error (1-Sigma)
Al-K	0.2278	32.20	+/- 0.34
Si-K	0.2513	44.17	+/- 0.50
Cl-K	0.0262	4.20	+/- 0.15
K-K	0.0153	2.01	+/- 0.24
Ti-K	0.0158	1.89	+/- 0.16
Fe-K	0.0071	0.77	+/- 0.25
Cu-K	0.1289	14.57	+/- 1.07
Mg-K	0.0012	0.20	+/- 0.09
	Total	100.01§	

*: The chi-squared values of the scans varied between 1.09 and 1.46, which is well below the required value of ten, indicating an excellent fit of the graph.

†: All element weight percentages above 0.5 % are considered significant.

§: Decimal margins of error contributing to accrued values of Total > 100 %

Table 5 Surface tension values of commercially available wax and mango fruit collected from various sampling points on packline not dedicated to organic production

Sampling point	Surface tension * (dynes.cm^{-1})
Fruit, physiologically ripe, untreated	30-34
Fruit at various points along the line:	
After warm water bath	34-38
After Prochloraz application	30
After kaolin application	73
After commercial wax application	23-26†
Commercially available wax	20-21

* : Values were obtained by standard wettability tests conducted in cooperation with SASOL Wax Polymers. Fruit used to obtain the values were not treated or contaminated with kaolin.

† : The wax was applied by hand in these tests, therefore the variable values are due to differences in the thickness and consequently, moisture content of the integrated film of plant wax and commercial wax.

6.8 FIGURE CAPTIONS

Figure 1 Diagram of the relationship between Si and Al in the crystal lattice of kaolinite (after Newman, 1987).

Figure 2 Typical spectrograph obtained from EDS of a sample of uncalcined kaolin.

Figure 3 Micrograph of clay particles from a kaolin powder sample, showing lamellae arranged in a booklet (white arrow) and halloysite particles (tubular structures) (black arrows) (A). Close-up view of booklet structures (white arrows) and tubular halloysite structures (black arrows) (B). Micrograph of uncalcined kaolin containing kaolinite/mica/ smectite aggregates, showing rosebud textures (white arrow) and halloysite structures (black arrow) (C). Tubular halloysite structures (black arrows) were observed on fruit surfaces treated with uncalcined kaolin, while clay particles were sufficiently small to fit between epicuticular wax crystalloids (white arrow) (D).

Figure 4 Small crystals (between 0.2 - 0.5 μm) of Cu oxychloride (white arrow), attached to some clay lamellae (A). Similar Cu oxychloride crystals observed trapped underneath a layer of commercial wax (B). The presence of Cu oxychloride crystals was confirmed by the emission of secondary electrons in backscatter mode at 20 kV (C).

Figure 5 Fruit dipped in kaolin shows streaky and blotchy colouration due to the barrier effect of clay crusts on photosynthesis and colour pigment development.

Figure 6 Crust of kaolin (white arrow) on the surface of a fruit dipped in 3 % slurry. Epicuticular fruit wax crystalloids could be seen in areas where the slurry did not adhere to the fruit surface (black arrow) (A). Surface view of mango fruit sprayed with 3 % kaolin slurry (white arrow), with epicuticular wax crystalloids (black arrow) (B). Kaolin particles (white arrow) from the contaminated packline onto surfaces of fruit not exposed to preharvest treatment of kaolin. The black arrow indicates where brushes scarred the epicuticular wax (C). Transverse section of the epicuticular membrane, showing how particles of kaolin (large white arrow) and halloysite (small white arrow) could fit between the epicuticular wax crystalloids (black arrow) (D).

Figure 7 Epicuticular wax has a self-reconstructing ability, and tends to grow over objects or inclusions on the fruit surface (A - C). The configuration of the reconstituted wax (black arrow in all figures) is determined by the physical and chemical characteristics of the obstruction through which wax constituents have to migrate. Low absorption and good permeability of commercial wax polymers meant that the architecture of reconstituted wax crystals did not alter severely (A). Absorptive kaolin lamellae trap oily substances, leading to atypical reconstituted epicuticular crystalloids (B & C). Halloysite structures were visible (white arrows), confirming the presence of kaolin in the viewed area.

Figure 8 In micrographs A - D, a large white arrow indicates the commercial wax layer, epicuticular wax is pointed out by a small white arrow, a large black arrow shows the distribution of kaolin lamellae, and cutin is indicated by a small black arrow. Although evidence of the commercial wax penetrating between epicuticular wax crystalloids could be found, there was largely no integration of the two wax types during film formation (A & B). The barrier effect of kaolin lamellae on the integration of commercial wax and epicuticular wax did not depend on the amount of commercial wax applied(C). The commercial wax emulsion did not set homogenously, with localized polymerization possibly due to loss of moisture and unsaturated oils to the kaolin lamellae (D).

Figure 9 Features of poor adhesion and incomplete film formation between commercial wax and epicuticular wax was evident in surface views. (A) Poorly formed wax film, with inclusions of kaolin lamellae jutting from the wax layer (arrow) (A - C). A receding wax film (black arrow) left the epicuticular wax exposed (narrow white arrow) (B). The encircled area was enlarged in (C), detailing the commercial wax margin (black arrow), exposed fruit wax crystals (narrow white arrow) and kaolin lamellae (large white arrow). Side view of the commercial wax margin (black arrow), exposed fruit wax crystals (narrow white arrow) and kaolin lamellae (large white arrow) (D).

Figure 10 Micrographs of transverse sections through the wax film and epicuticular membrane, depicting typical separation of the wax emulsion during polymerization (white arrows) (A & B). This separation was due to failed integration of the waxes, as confirmed by the presence of epicuticular wax crystalloids (large black arrows). In micrograph (B), granular polymerization of the commercial wax, a result of water absorption from the wax emulsion by kaolin, was visible (narrow black arrow).

Figure 11 Micrographs of clay inclusions in the wax film, showing cavities left in the wax film after dehydration of the kaolin lamellae caused shrinkage (white arrows) (A & B).

Figure 12 Fruit from packed cartons, indicating damaged coverage of the fruit surface (A). Persistent kaolin fractions (white arrow) created an effective barrier preventing wax film formation between the plant wax (black arrow) and the commercial wax. The resultant brittle covering was ineffective and negates the objective of the fruit coating. In a transverse view of a lenticel (B), kaolin debris (white arrows) was visible below the flow of commercial wax that penetrated the lenticel cavity.

6.9 FIGURES

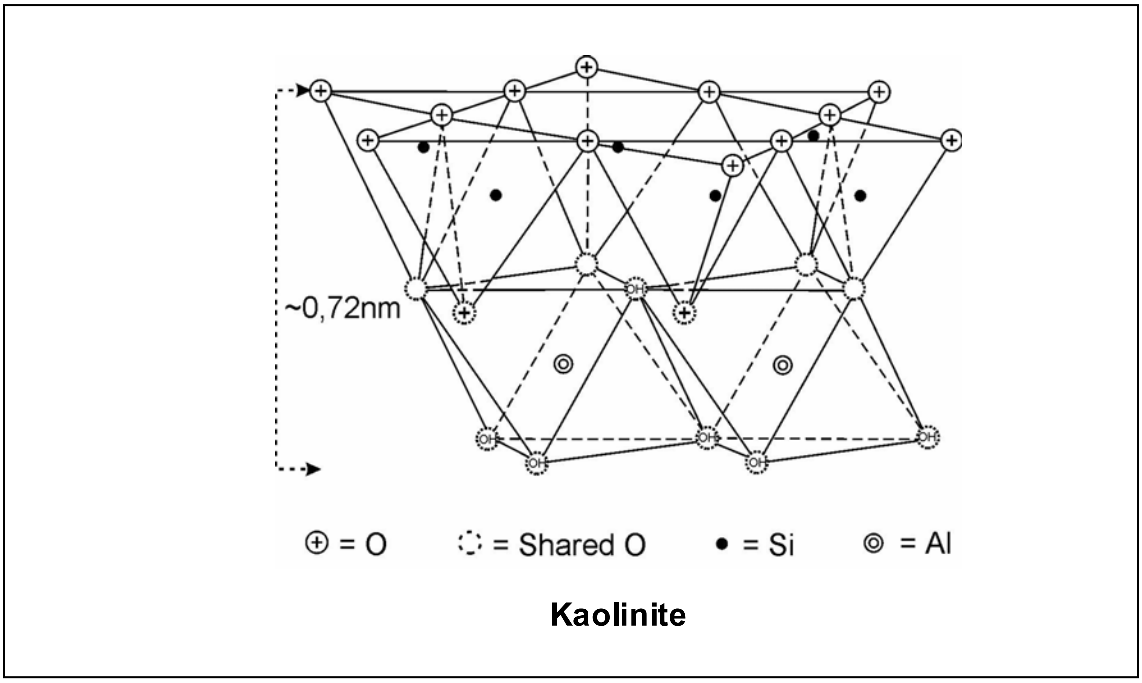
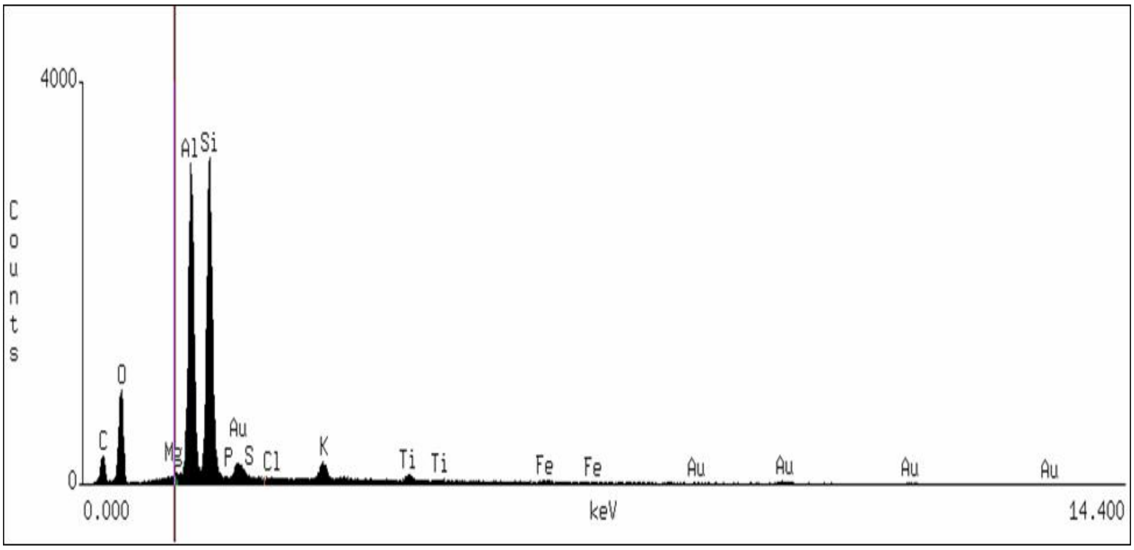


Figure 1



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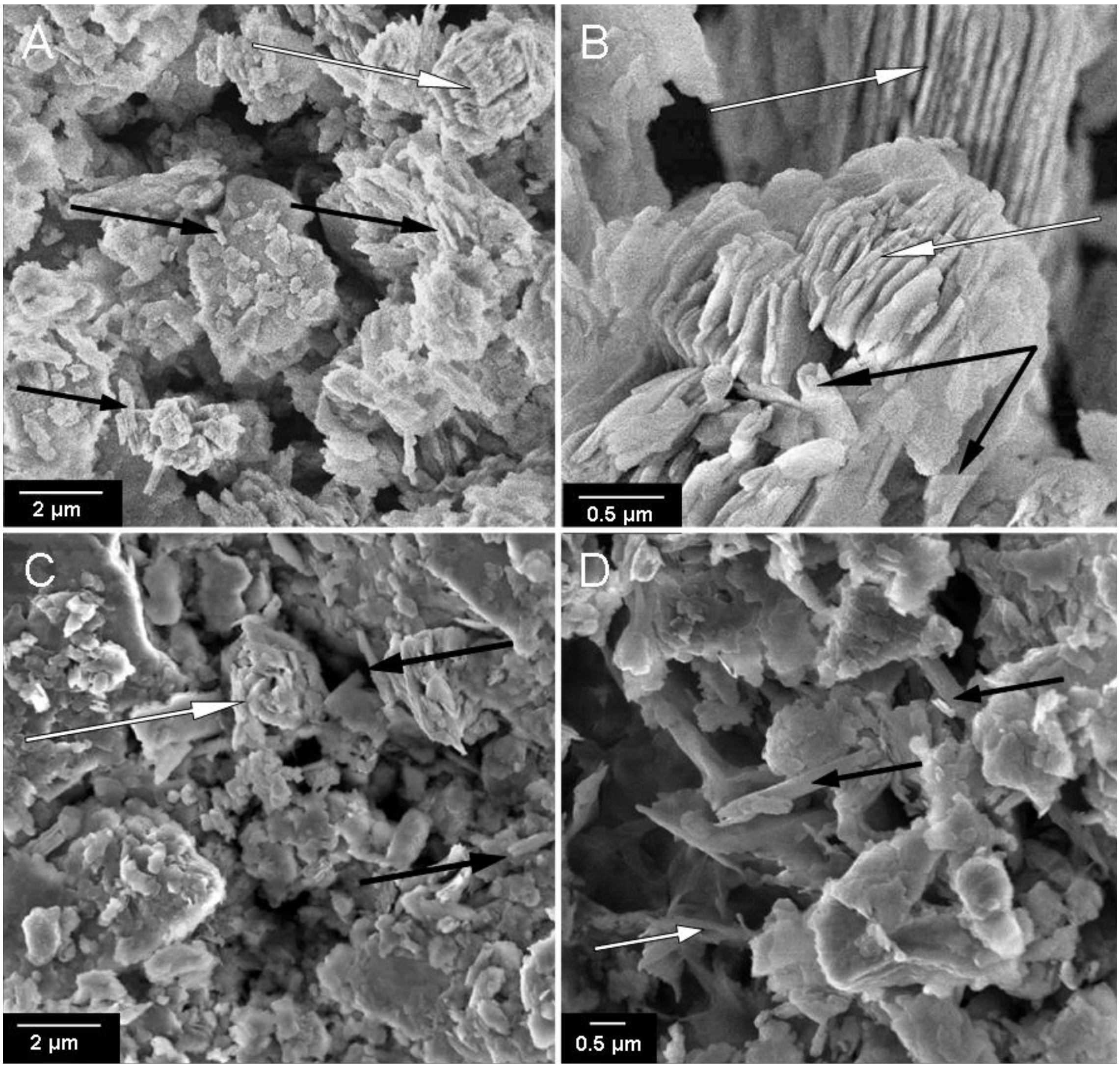

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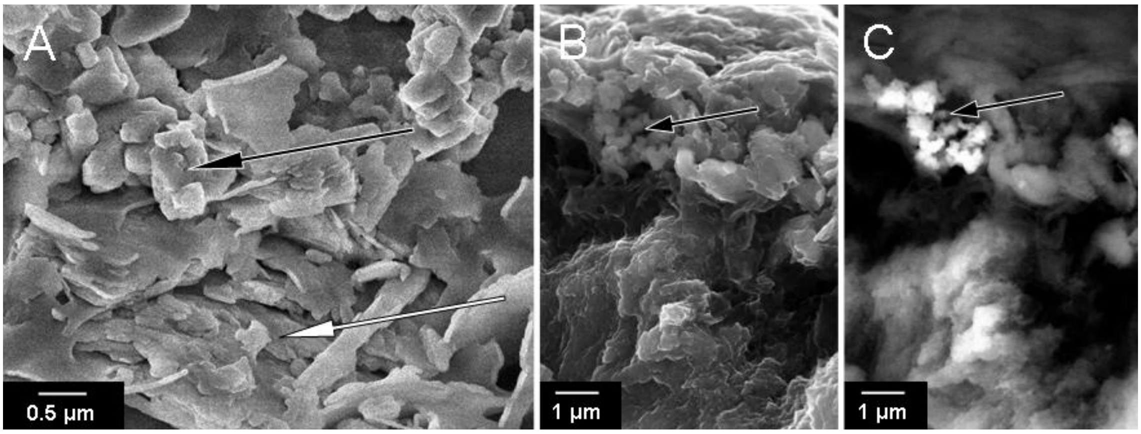
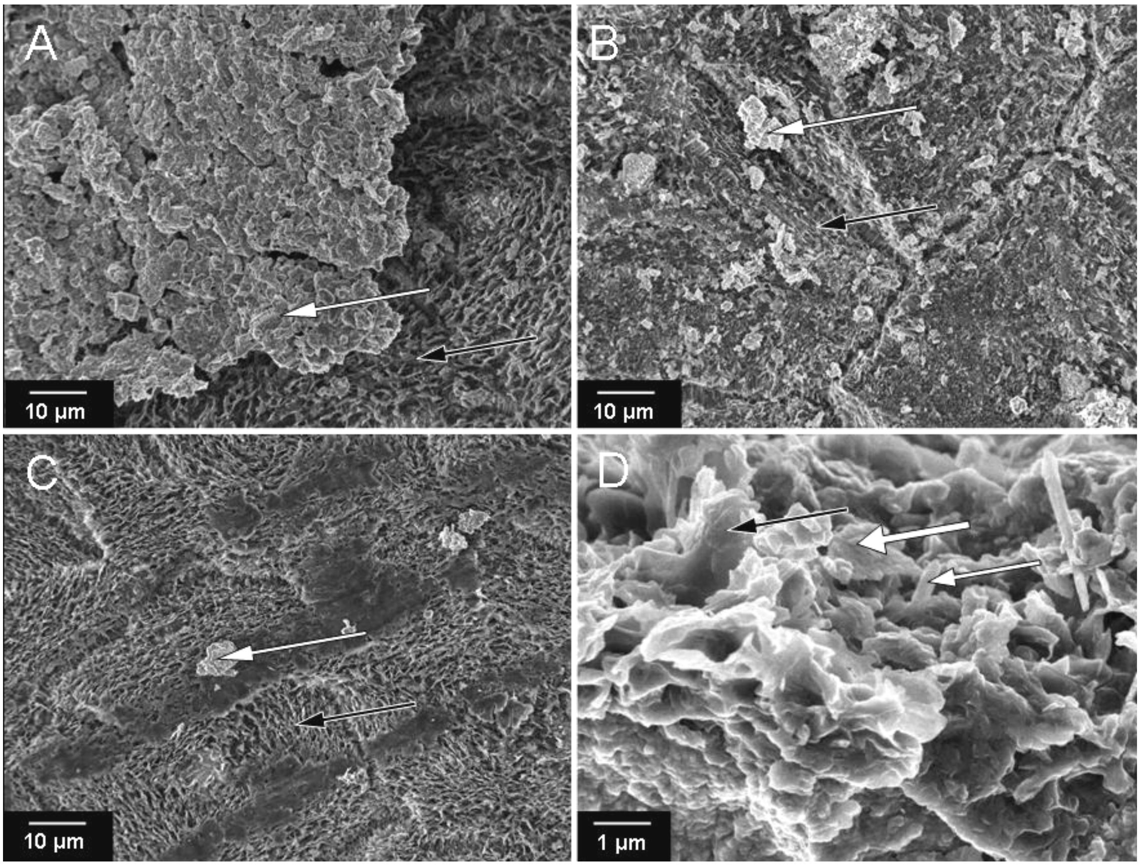


Figure 4

Figure 5



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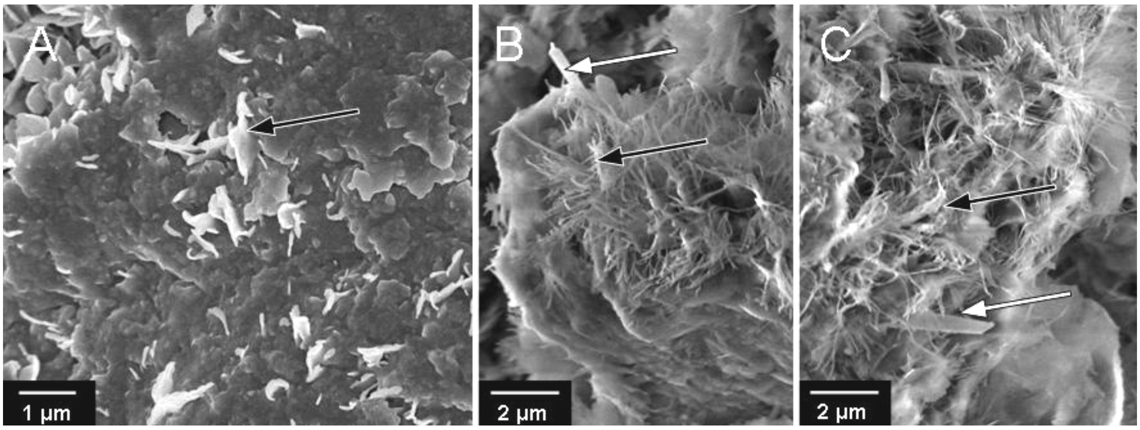

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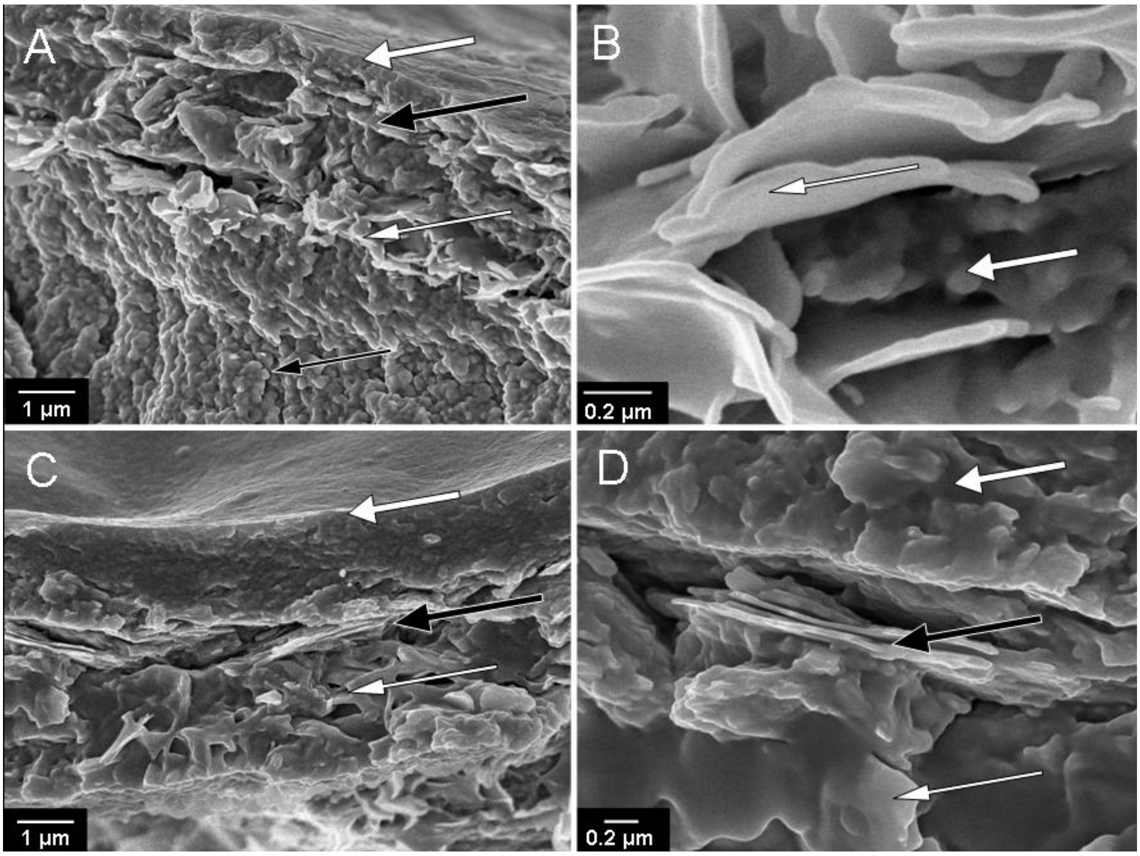

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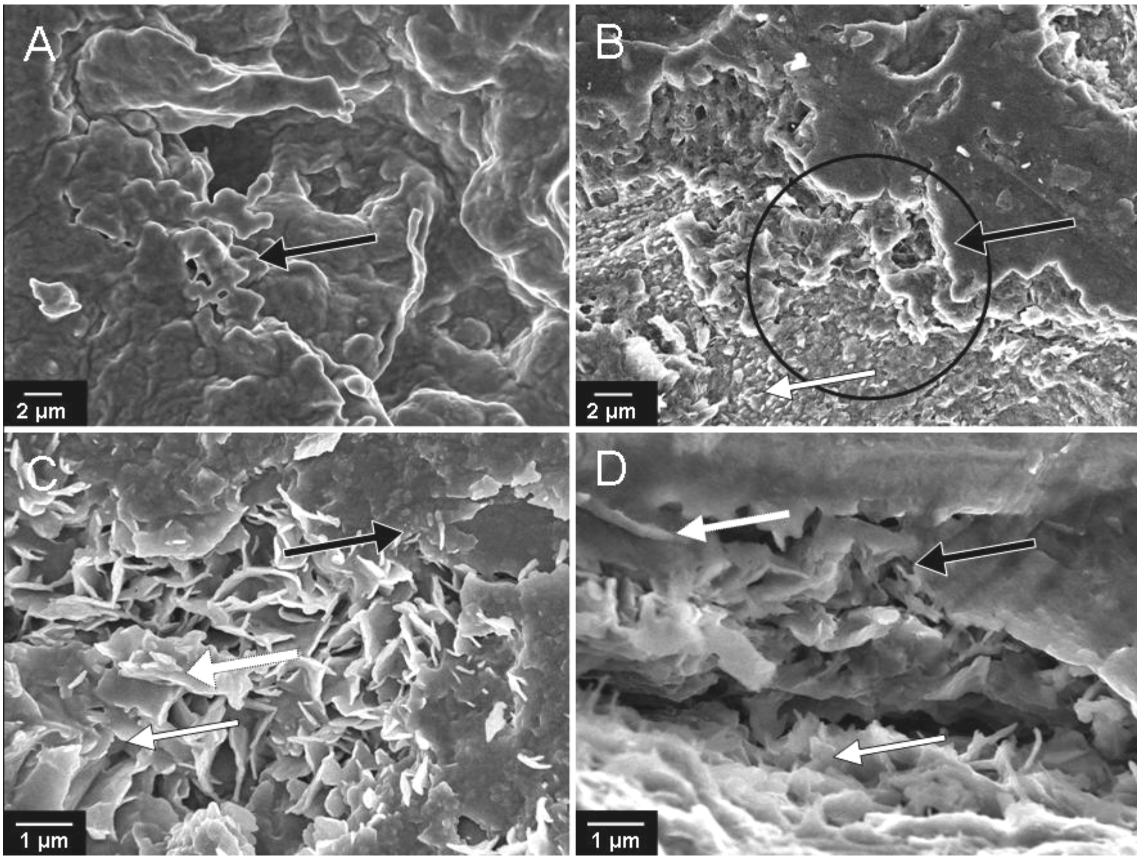

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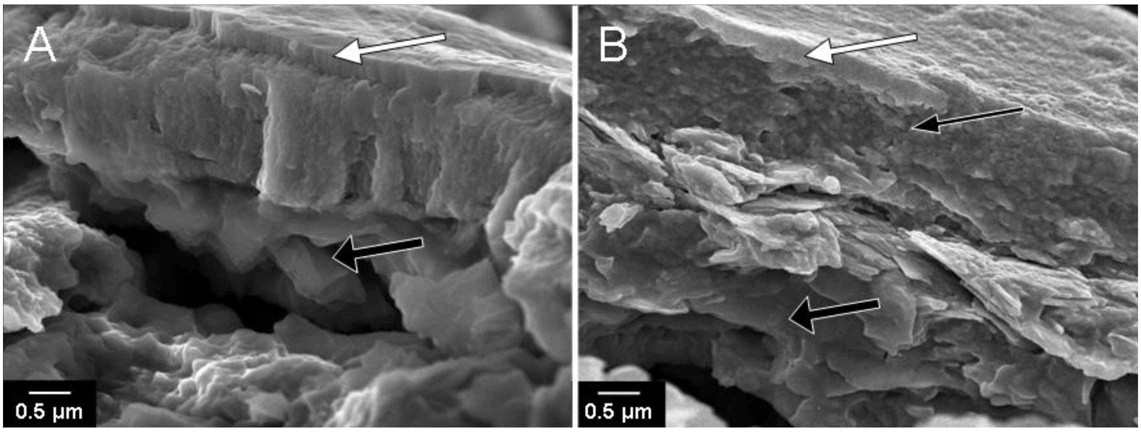

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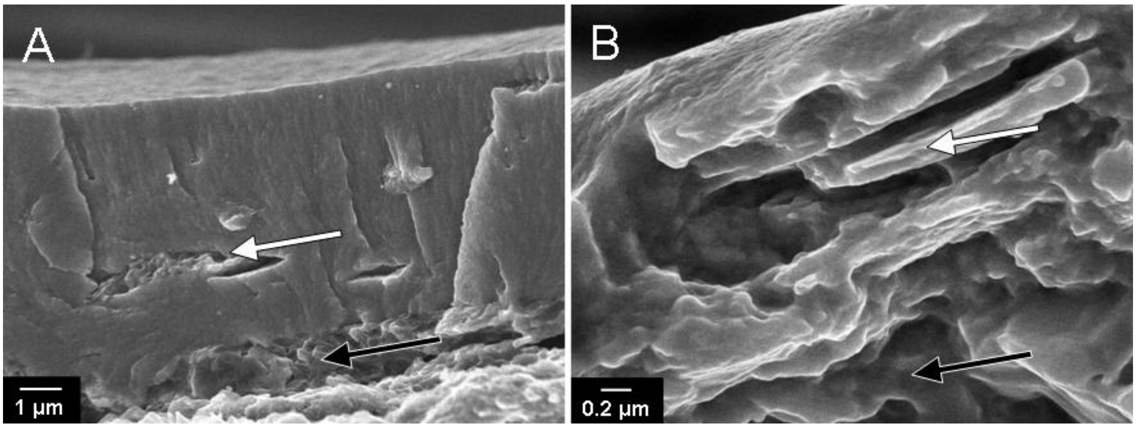

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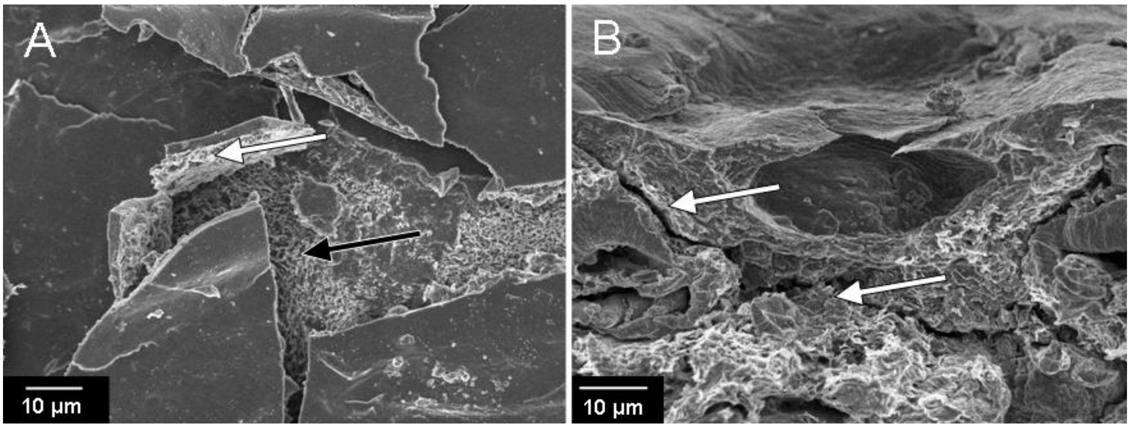

Figure 12