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### ► To cite this version:

Alejandra Ramirez-Martinez, M.A. Salgado-Cervantes, G.C. Rodriguez-Jimenes, M.A. Garcia-Alvarado, Fabien Cherblanc, et al.. Water transport in parchment and endosperm of coffee bean. Journal of Food Engineering, 2013, 114, pp.375-383. 10.1016/j.jfoodeng.2012.08.028 . hal-00754699

**HAL Id: hal-00754699**

**<https://hal.science/hal-00754699>**

Submitted on 20 Nov 2012

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# Water transport in parchment and endosperm of coffee bean

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## Abstract

This paper aims at contributing to identify the eventual regions where fungus *Aspergillus ochraceus* could grow and produce ochratoxin A (OTA) during drying of coffee beans. Internal structure of coffee bean was analyzed by optical microscopy for endosperm and parchment. From the expression of the dissipation in the grain due to the water transport, we show that a relationship formally analogous to an equation of diffusion governs the water transport. Three structures with mass transfer resistance potential are studied: parchment, silver skin and endosperm. An experimental technique to study the water transfer into the parchment was proposed. In the endosperm, for moisture contents above 65%, a constant transport coefficient controls the drying kinetics of the whole bean. Below this moisture content, water transport coefficient (with and without silver skin) were significantly lesser than those for the whole bean. This is firstly due to the reduction of the pore space occupied by water and second to the increasing bonding energy between solid structure and water as moisture content decreases. The contribution of parchment to the protection of the endosperm is highlighted.

*Keywords:* Coffee internal structure, drying, sorption isotherms, water transport coefficient, ochratoxin A.

## NOMENCLATURE

$a$	Thermodynamic activity	
$C$	Volumetric concentration	$\text{kg} \cdot \text{m}^{-3}$
$D$	Dissipation	$\text{J} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$
$h$	Parchment thickness	m

41	$k_c$	Mass transfer coefficient	$m \cdot s^{-1}$
42	$K_{eq}$	Average water distribution constant between phases	
43	$K \left( \frac{m}{kg} \right)$	Water transport coefficient in a structure	$kg \cdot s \cdot m^{-3}$
44	$l$	Characteristic length for diffusion	m
45	$m$	Mass	kg
46	$M$	Molecular mass	$kg \cdot kgmol^{-1}$
47	$N$	Mass flux	$kg \cdot m^{-2} \cdot s^{-1}$
48	$r$	Mass transfer resistance	$kg \cdot m^{-2} \cdot s^{-1}$
49	$R$	Gas constant (8314.0)	$J \cdot kgmol^{-1} \cdot K^{-1}$
50	$S$	Entropy	$J \cdot K^{-1}$
51	$t$	time	s
52	$T$	Temperature	K or $^{\circ}C$
53	$U$	Internal energy	J
54	$v$	apparent velocity	$m \cdot s^{-1}$
55	$V$	Volume	$m^3$
56	$X$	Moisture content	$kg \cdot \left( \frac{kg}{dm^3} \right)$
57			
58	<b>Greek symbols</b>		
59			
60	$\mu$	Chemical potential	$J \cdot kg^{-1}$
61	$\rho$	Density	$kg \cdot m^{-3}$
62	$\Delta_w$	Water transport coefficient	$m^2 \cdot s^{-1}$
63			
64	<b>Subscripts</b>		
65			
66	0	At initial or in one side	
67	1	At the other side	
68	$a$	For air	
69	$av$	Averaged	

70	<i>e</i>	At equilibrium
71	<i>en</i>	In endosperm
72	<i>pa</i>	In parchment
73	<i>s</i>	For dry matter
74	<i>w</i>	For water
75	$\alpha$	In a heterogeneous structure

76  
77

## 78 1. INTRODUCTION

79 Coffee is the second most valuable legal commodity in the world (Pendergrast, 1999;  
80 Kouadio *et al.*, 2007). According to FAO (2008), coffee is sold in 78 countries around the world and  
81 20 to 25 million families depend on its trade. Coffee cherries are subjected to two different post-  
82 harvest treatments where the main objectives are to remove the various layers surrounding coffee  
83 beans and to dry them in order to prevent the growth of microorganisms (Paulino De Moraes &  
84 Luchese, 2003; Suárez-Quiroz *et al.*, 2004). The most usual treatment is called “wet”. In this  
85 method, coffee cherries are put in a tank filled with water in order to separate the defective beans  
86 and to remove the pulp and mucilage. Then, “washed” coffee beans are dried. An alternative is to  
87 use the “dry” method in which coffee cherries are directly dried to get grayish beans known as  
88 "coffee coke" or “natural coffee”. After drying, the parchment and the other layers covering the  
89 beans are removed mechanically to get the “green” coffee.

90 Regardless the post-harvest method, drying can be carried out naturally (using sun) and/or  
91 artificially (using dryers). Drying has been identified as a step where fungal contamination can  
92 develop (Frank, 2000; Paulino de Moraes & Luchese, 2003; Taniwaki *et al.*, 2003; Kouadio *et al.*,  
93 2007). Particularly, *Aspergillus ochraceus*, a common host fungus, produces a toxin (Ochratoxin A,  
94 OTA) which have teratogenic, immunotoxic and possibly neurotoxic and carcinogenic properties.  
95 Moreover, this toxin has a high thermal stability up to 250°C (FAO, 2008). Considering the risk for  
96 human health, fungus development should be avoided to prevent OTA production. Among the  
97 factors that govern the fungal development, water activity ( $a_w$ ) has been underlined to be the most  
98 important (Suárez-Quiroz *et al.*, 2004; Kouadio *et al.*, 2007). Actually, temperature influences the  
99 production rate while not being a limiting factor (Suárez-Quiroz *et al.*, 2004). The optimal conditions  
100 for the growing of *A. ochraceus* are given by a water activity of 0.95 and a temperature of 35°C  
101 while its development is inhibited with a water activity lower than 0.80 and a temperature less than  
102 10°C (Suárez-Quiroz *et al.*, 2004). From this research, it results that 0.8 is a critical value for the  
103 prevention of OTA production. However, it represents an average value over the whole coffee bean  
104 that does not account for the water distribution resulting from moisture diffusion during the drying  
105 process. Moreover, *A. ochraceus* develops at the coffee bean surface while fungal spores penetrate

106 about a few micrometers inside. Then, the development of *Aspergillus ochraceus* in coffee bean  
107 may be seen as a competition between its capacity of water supply and a decrease on the water  
108 activity in the internal parts of the grain consecutive to drying. When coffee bean has not been  
109 damaged (cracks, separation of the parchment) this competition takes place on the surface of the  
110 grain, and it is the combination between the water activity and the water transport properties in the  
111 parchment and the surface layer of the endosperm. As consequence, it seems essential to analyze  
112 precisely the water distribution rather than its average content (Frank, 2000).

113 During the drying process, water transport coefficient is one of the most important  
114 parameters because it governs water distribution in the grain (Geankoplis, 1998). Usually, water  
115 transport is evaluated from the fitting of an adequate Fick's law equation to experimental drying  
116 kinetic (Mulet, 1994; Maroulis *et al.*, 1995; Wang & Brennan, 1995; Bialobrzewski & Markowski,  
117 2004; Efremov & Kudra, 2004; Hernández *et al.*, 2008). Sfredo *et al.* (2005) and Correa *et al.*  
118 (2006) have determined the water transport coefficient in coffee cherries. Both rely on a Crank's  
119 solution of Fick's law valid for sphere (Crank, 1975) since it is a fair approximation of the coffee  
120 cherry geometry. The water diffusivity values measured obtained by Sfredo *et al.* (2005) lie in the  
121 range  $[0.1-1 \times 10^{-10}] \text{ m}^2 \cdot \text{s}^{-1}$  at 45°C and  $[0.3 - 3 \times 10^{-10}] \text{ m}^2 \cdot \text{s}^{-1}$  at 60°C, while those found by  
122 Correa are  $2.91 \times 10^{-10}$ ;  $3.57 \times 10^{-10}$  and  $4.96 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$  at 40, 50 and 60°C respectively. To  
123 improve the geometrical description of coffee cherries, Hernández *et al.* (2008) developed a Fick's  
124 law solution considering a non-conventional geometry: prolate spheroid geometry.

125 In many products with a complex micro-structure such as wood and pasta (Mrani & Bénet,  
126 2005), Agar gel (Mrani *et al.*, 1995) and latex (Auria *et al.*, 1991), water transfer is controlled by  
127 physicochemical and mechanical interactions occurring at the interfaces between phases:  
128 capillarity, osmotic effects, surface adsorption, liquid-gas phase change (Bénet *et al.*, 2009), water  
129 transfer between cells and walls. Therefore, transfer coefficients represent a superposition of  
130 different phenomena and depend on moisture content. In particular water transfer coefficients  
131 cancel as the moisture content tends towards zero. In this case, the use of diffusion and of Crank's  
132 solutions to describe mass transfer may be questionable for media presenting a complex  
133 microstructure.

134 Finally, the objective of this study is to contribute, through microscopic analysis and local  
135 mass transfer measurements, the potential regions where fungus could develop and produce OTA  
136 during drying processes. Therefore, this paper deals with the four following aspects: 1) Analysis by  
137 a thermodynamic approach of the law for water transport in a complex media 2) Microscopic  
138 observation of coffee bean in order to identify the different structures of coffee beans and their  
139 heterogeneity; 3) Characterization of the relationship between water activity and moisture content  
140 and 4) Study of the dependence of transport properties on moisture content.

141 These physical characteristics will be useful to improve the numerical modeling of the  
 142 drying process. By simulating various drying scenarios, it should lead to propose different strategies  
 143 to avoid the development of fungus.

144  
 145  
 146 **2. Thermodynamic approach to water transport in complex media**

147  
 148 Complex media such as food, gel and biological tissues are characterized as having several  
 149 structures ( $\alpha$  at Equation 1) which can be solid, liquid or gas phases, superficial layers, film layers,  
 150 membranes, cells, and cell walls. In such complex media the use *a priori* of a law similar to Fick's  
 151 law seems not appropriate. However many experimental results of media as complex as coffee  
 152 endosperm (wood, gels, food) seem to show that this law is sufficient to describe water transfer at  
 153 the macroscopic level as it will be demonstrated in the following discussion.

154 The thermodynamic state of water in a structure  $\alpha$  is characterized by the mass chemical  
 155 potential, given by (Callen, 1985):

156  
 157 
$$\mu_{w\alpha} = \left( \frac{\partial U \alpha}{\partial m_{w\alpha}} \right)_{S\alpha, V\alpha, m_{\alpha j}, j \neq w} \quad (1)$$

158  
 159 Where  $\mu_{w\alpha}$  is the water chemical potential at structure  $\alpha$  and is defined as the partial derivative  
 160 of the internal energy contained in a Representative Elementary Volume (REV), with respect to  
 161 water mass, taking entropy, volume of  $\alpha$  in the REV and the mass of the other constituents as  
 162 constants. The chemical potential characterizes the action of the other media constituents upon the  
 163 water from the structure  $\alpha$ , regardless of the form of the water: liquid, gas, adsorbed by the liquid  
 164 phases, in films or in superficial layers.

165 Water transport phenomena in the structure obey the second principle of thermodynamics.  
 166 Assuming uniform and constant temperature, in the absence of chemical reactions and neglecting  
 167 the effect of gravity, the dissipation in structure  $\alpha$  due to water transport phenomena in all forms  
 168 can be written as (Müller, 2001; Kuiken, 1994):

169  
 170 
$$D_{w\alpha} = -\rho_{w\alpha} v_{w\alpha} \nabla \mu_{w\alpha} \geq 0, \quad \forall \alpha \quad (2)$$

171  
 172 Where  $D_{w\alpha}$  is the dissipation in structure  $\alpha$ . Considering the Gibbs Duhem relationship (Callen,  
 173 1985) applied to each phase, Eq. 2 is retained when water transport is handled by the mechanisms  
 174 of filtration of the phases and their surface layers (Prigogine & Mazur, 1951; Bénet & Jouanna

175 1982). The positivity of the dissipation term is ensured if the mass flow of water in structure  $\alpha$  is of  
 176 the following form:

177

$$178 \quad \rho_{\alpha w} v_{w\alpha} = -K_{\alpha} X_{\alpha} \nabla \mu_{w\alpha}, \quad \forall \alpha \quad (3)$$

179

180 Where  $X_{\alpha}$  is the moisture content of the structure  $\alpha$ . Eq. 3 is the expression of the  
 181 second principle of thermodynamics. It highlights the fundamental property of the chemical potential  
 182 (Callen, 1985) i.e. regardless the form in which a constituent is present (water in this case), it moves  
 183 from high chemical potential values to low chemical potential values. The function  $K_{\alpha} X_{\alpha}$  is  
 184 positive and represents the water transport coefficient within  $\alpha$ . This function depends on the  
 185 moisture content of  $\alpha$ . In agricultural products such as coffee, cocoa and wheat the characteristic  
 186 dimensions of the structures  $\alpha$  are very small if compared with those of the grain. For coffee, as  
 187 will be shown later, the relationship between cell size and the grain is on the order of  $10^{-3}$ ; the ratio  
 188 for the cell wall is about  $10^{-4}$ . We will assume that the equilibration time between two grain  
 189 structures  $\alpha$ , for example, between the cell and the cell wall is very fast compared to the drying  
 190 time which can be of the order of one day. We adopt the assumption of local equilibrium at  $\alpha$ : the  
 191 thermodynamic equilibrium of water between the different structures is performed. This hypothesis  
 192 implies that the chemical potential of water is the same in all structures  $\alpha$  and its chemical  
 193 potential is symbolized by  $\mu_w = \mu_{w\alpha} \quad \forall \alpha$ .

194

195 Then, the global flux of water is obtained by,

196

$$197 \quad \rho_w v_w = \sum_{\alpha} \rho_{\alpha w} v_{\alpha w} = - \left( \sum_{\alpha} K_{\alpha} X_{\alpha} \right) \nabla \mu_w \quad (4)$$

198

199 Each structure is characterized by a desorption isotherm, which represents the monotonic  
 200 variation of moisture content  $X_{\alpha}$  as a function of water activity ( $a_{w\alpha}$ ) in the structure  $\alpha$ . We will  
 201 use the inverse function  $a_{w\alpha} = a_{w\alpha}(X_{\alpha})$ . The chemical potential of water mass in the structure  
 202 is given by the relationship (Callen, 1985):

203

$$204 \quad \mu_{w\alpha} = \mu_w = \frac{RT}{M_w} \ln a_{w\alpha}(X_{\alpha}), \quad \forall \alpha \quad (5)$$

205

206 As  $\mu_w$  value has being fixed, the moisture contents of each structure  $X_\alpha$  adapt to meet the  
 207 equality of chemical potentials (Eq. 5). The average moisture content of the medium in a REV is  
 208 defined by,

209

$$210 \quad X = \frac{m_w}{m_s} = \sum_{\alpha} \frac{X_{\alpha} m_{s\alpha}}{m_s} \quad (6)$$

211

212 Where  $m_w$  is the total mass of water in the REV,  $m_s = \sum_{\alpha} m_{s\alpha}$  is the total mass of solid in the

213 REV and  $m_{s\alpha}$  is the mass of solid in the structure  $\alpha$  in the REV. In the absence of dissolution or

214 chemical reactions, the relationships  $m_{s\alpha}/m_s$  are constant, knowledge of moisture content in the

215 different structures  $X_\alpha$  give the value of  $X$  by (Eq.6) and  $\mu_w$  by (Eq.5). So there is a relationship

216 between  $X$  and water activity denoted by  $a_w$   $X$  :

217

$$218 \quad \mu_w = \frac{RT}{M_w} \ln a_w X \quad (7)$$

219

220 Conversely according to Eq.7, knowledge of  $X$  lets us know the value of  $\mu_w$ . With this

221 value, Eq. 6 gives the moisture contents in each structure. There is a relationship of the form

222  $X_\alpha = X_\alpha X$ ,  $\forall \alpha$  and therefore the coefficients  $K_\alpha X_\alpha$  in Eq. (4) can be expressed as a

223 function of  $X$ . The global transport coefficient can also be expressed as:

224

$$225 \quad K X = \sum_{\alpha} K_\alpha X_\alpha X \quad (8)$$

226

227 Given this relationship, the overall (global) flux of water is expressed by:

228

$$229 \quad \rho_w v_w = -K X \nabla \mu_w \quad (9)$$

230

231 From Eq. (7), Eq. (9) can be written as:

232

$$233 \quad \rho_w v_w = -K X \frac{RT}{M_w a_w} \frac{\partial a_w}{\partial X} \nabla X \quad (10)$$



234

235

236 Defining,

237

238

$$\Delta_w X \cong K X \frac{RT}{M_w a_w} \frac{\partial a_s}{\partial X} \quad (11)$$

239

240 Eq. (10) becomes,

241

242

$$\rho_w v_w = -\Delta_w X \bar{V} \frac{\partial X}{\partial t} \quad (12)$$

243

244 Formally Eq. (12) is presented in a similar form to Fick's law. This is valid only to describe  
 245 the diffusion of a constituent in a unique phase: solid, liquid or gas. The transport coefficient  
 246 depends on moisture content. With the assumption of local equilibrium, Eq. (12) allows us to  
 247 describe the water transport in a complex media, formed of juxtaposed structures, in which various  
 248 mass transport mechanisms are present. This relationship involves the assumption of a  
 249 thermodynamic equilibrium localized between the different forms of water. The formal similarity  
 250 between Eq. (12) and Fick's law authorizes the use of all the mathematical developments  
 251 concerning this law. In particular the use of mathematical solutions developed by Crank for  
 252 particular geometries remains applicable. However, it is improper to call  $\Delta_w X$  as water  
 253 diffusivity in media because it combines several transport phenomena; it will be called the water  
 254 transport coefficient later in this document.

255

256

### 257 3. MATERIALS AND METHODS

258

259 Fermented washed coffee beans (Arabica variety) from crops 2008 and 2009 were used in  
 260 this study. Both samples were obtained from "Beneficio La Cuchilla" located in Huatusco, Veracruz,  
 261 Mexico. Moisture content was determined by the method from AOAC (1990) No. 22.013, in which  
 262 samples are introduced into a vacuum oven and subjected to an absolute pressure of 13.3 kPa and  
 263 a temperature of 60°C until two consecutive weights differ from less than 10<sup>-4</sup> g.

264

#### 265 3.1 Coffee bean general structure characterization

266

267 For the characterization of the general structure, measures of the three principal axes of  
 268 fermented washed coffee beans were made using an electronic Vernier. Also a computer  
 representation was generated from a real coffee bean. Three cameras where set up surrounding

269 one coffee bean and shoot at the same time. The obtained pictures served to generate a  
270 geometrical model using the software ImageWorks © (2008).

271

### 272 **3.2 Preparation of samples for microscopic observation of coffee bean**

273 The cellular distribution of coffee bean was studied from coffee bean slices. The resulting  
274 slices were stained by immersion in safranin for 30 min, followed by washings with ethanol of  
275 different concentrations, and left in contact with fast green for 10 min, finally they were washed in  
276 pure ethanol and observed in an optical microscope Leica DM 500. Pictures of the slices were  
277 taken using a camera coupled to the microscope. Also the cell diameter and cellular wall thickness  
278 was measured using the software Image J © (2008). To analyze the internal heterogeneity and  
279 transport properties, subsamples of coffee beans were prepared. Using a special cylindrical cutting  
280 tool (Fig.1.a), coffee beans were separated in 6 different parts (Fig. 1.b). In the following discussion  
281 these parts are denominated: parchment (a), silver skin (b), endosperm part 1 (c), endosperm part 2  
282 (d), extremities (e, f). The 2 parts of the endosperm (c, d) are separated by the natural discontinuity  
283 observed in Fig. 1.

284

### 285 **3.3 Distribution of water activity**

286 In order to check if water content heterogeneities can be observed throughout a coffee  
287 bean, sorption isotherms of the different parts were determined. With the subsamples prepared  
288 (Fig. 1.b), 5 different sorption isotherms have been determined by considering the whole coffee  
289 bean and the 4 internal parts: parchment (a), endosperm part 1 (c), endosperm part 2 (d) and  
290 extremities (e, f). The silver skin (b) is too thin and light to get some accurate sorption  
291 measurements.

292 Sorption isotherm points for water activities less than 0.92 were obtained by the standard  
293 method using saturated salt solutions at 35°C (AOAC, 1990), while water activities between 0.92  
294 and 0.99 were measured by means of a mechanical method (Ouoba *et al.*, 2010). This new method  
295 allows to measure high water activity values in a shorter time (about one day) avoiding the risk of  
296 fungal development.

297

298

### 299 **3.4 Mass transfer in coffee bean**

300 To identify eventual heterogeneities in water transport, water transport coefficients were  
301 evaluated with 4 different samples: the whole bean, the endosperm with silver skin, the endosperm  
302 without silver skin and the parchment.

303

#### 304 **3.4.1 Determination of the water transport coefficient in the endosperm**

305 Analytical solutions of the Fick's equation were established for various configurations  
306 (Crank, 1975). In the case of an infinite slab, the asymptotic solution is given by,

307

308 
$$\frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \exp \left( - \frac{\pi^2 \Delta_{wen} t}{4l^2} \right) \quad (13)$$

309

310 This asymptotic solution is valid only for  $x - x_e / x_0 - x_e < 0.7$  (Crank, 1975). To develop this  
311 solution, we made the following hypothesis (i) initial moisture content is uniform, (ii) interfacial mass  
312 transfer negligible and (iii) a constant transport coefficient over time which implies to consider short  
313 times. To approach these conditions, we adopted an incremental method which consists in two  
314 stages: (i) equilibrium of a coffee sample with a saturated salt solution to obtain uniform initial  
315 moisture content; (ii) change in the saturated salt solution to start the drying process. Ten samples  
316 of endosperm, previously separated from coffee beans with and without silver skin, were glued on  
317 an aluminum plate. The aluminum plate was disposed in the device described in Fig. 2 in which the  
318 samples were equilibrated at 35°C with a saturated salt solution. The equilibrium of the samples  
319 was checked by the weight stability over time. The initial salt solution was then replaced by a  
320 potassium acetate solution fixing water activity at 0.21. From that point, the plate weight was  
321 recorded continuously. At the end of the experiment, the moisture content was determined by  
322 standard methods (AOAC, 1990). The water transport coefficient in endosperm ( $\Delta_{wen}$ ) was  
323 calculated by fitting Eq. (13) to the weight loss kinetics at times that satisfy  $x - x_e / x_0 - x_e$   
324  $< 0.7$ . Like in this case the sample was dehydrated by one side, the characteristic length for diffusion  
325 ( $l$ ) is the complete thickness of the sample. This procedure was repeated with different initial salt  
326 solutions in order to impose water activities of 0.43, 0.50, 0.62, 0.75 and 0.84.

327 The experimental device described in above paragraph is such that the endosperm sample  
328 were dehydrated by one side under natural convection, therefore in order to verify assumption (ii),  
329 the mass Biot number defined by (Córdova *et al.*, 1996) and described in Eq. (14) was estimated.  
330

331 
$$Bi_m = \frac{k_c l}{\Delta_{wen}} \frac{K_{eq} \rho_{sa}}{C_{sen}} \quad (14)$$

332

333 Where the mass transfer coefficients ( $k_c$ ) must be calculated for natural convection. The empirical  
334 correlations reported by Geankoplis (1998) were used.

335

### 336 **3.4.2 Determination of water transport coefficient on a whole grain with high moisture** 337 **content**

338 At coffee bean fresh state, it can be admitted that the porous space is saturated with water.  
339 Water transport may be characterized by an averaged water transport coefficient ( $\Delta_{wav}$ ) which

340 corresponds at the moisture content of green coffee bean supposed uniform on all the grain. In  
 341 order to take account of the shape of the grain, Hernandez *et al.*, (2008) show that prolate spheroid  
 342 geometry fairly approximates the shape of a coffee bean, and the asymptotic solution Fick's second  
 343 law in this case is,

344

$$345 \quad \frac{X - X_e}{X_0 - X_e} = 0.78 \exp \left( - \frac{12.3 \Delta_{wav} t}{l^2} \right) \quad (15)$$

346

347 In this case, the characteristic length for diffusion ( $l$ ) is the focal distance of prolate spheroid. In  
 348 order to measure the averaged water transport coefficient in the whole coffee bean, tests were  
 349 conducted in a pilot plant composed of a fixed bed dryer and an imposed transversal air flow with a  
 350  $0.0024 \text{ m}^2$  section. The air flow can be regulated up to  $2 \text{ m s}^{-1}$  and  $80^\circ\text{C}$ . Tests were carried at two  
 351 temperatures:  $35^\circ\text{C}$  and  $45^\circ\text{C}$  and the air velocity was imposed at  $1.5 \text{ m} \cdot \text{s}^{-1}$ . These conditions are  
 352 similar to those encountered in solar drying where the risk of OTA development is high (Mburu,  
 353 1999). In each test, the drying kinetics is evaluated by recording the weight loss as function of time  
 354 and moisture content is calculated at the end. Averaged water transport coefficient was calculated  
 355 by fitting Eq. (15) to the experimental results that satisfied  $(X - X_e) / (X_0 - X_e) < 0.7$  with semi-log  
 356 regression. Statistical validation was performed through the 95% confidence interval of the  
 357 parameter fitted.

358

### 359 **3.4.3 Determination of the transfer coefficient in the parchment**

360 Parchment samples look like 6mm diameter and 0.1mm thickness confetti (a in Fig. 1). The  
 361 thickness of parchment is negligible with respect to endosperm and the methodology described in  
 362 previous section is not appropriate. Moreover, since the thickness is not uniform, discrepancies are  
 363 introduced in the estimation of diffusivity. Therefore, we adopt an averaging point of view by relying  
 364 on a global water transfer resistance. The water flux ( $N_w$ ) is assumed to be proportional to the  
 365 water activity difference  $(a_{w1} - a_{w0})$  imposed on both sides of the parchment,

366

$$367 \quad N_w = r (a_{w1} - a_{w0}) \quad (16)$$

368

369 Thus, an experimental method has been developed to determine the water transfer resistance ( $r$ )  
 370 of the parchment. The parchment sample was disposed between two deformable polypropylene  
 371 tubes (T1, T2) (Fig. 3) and compressed. Then, the compression effort was maintained by needless  
 372 (E) ensuring perfect airtightness. Each tube is connected to saturated salt solutions imposing 2

373 different values of water activity,  $a_{w0}$  on bottom surface and  $a_{w1}$  on top. The entire device was  
 374 placed in a closed thermo-regulated chamber at 35°C, and the weight of bottom salt solution is  
 375 recorded continuously. The water activity difference activates a water flux  $N_w$  through the  
 376 parchment sample evaluated by the weight loss or gain of the bottom salt solution. The flux was  
 377 calculated from the slope obtained by linear regression in the linear zone of weigh vs. time plot. To  
 378 increase the water vapor flux and therefore decrease measurement discrepancies, five systems  
 379 (Fig. 3) were set together. Tests have been carried out with 3 and 5 devices and compared to  
 380 validate the method. The moisture content of the parchment is evaluated from the average of  
 381 moisture content imposed on both sides by water activities  $a_{w0}$  and  $a_{w1}$  using the sorption  
 382 isotherm determined as is described in section 3.3. Experimental conditions are summarized in  
 383 Table 1. Statistical validation was performed through 95% interval confidence of the slope obtained  
 384 by linear regression. A comparison between endosperm and parchment water transport coefficients,  
 385 may be obtained from the Eq. (16) expressed in terms of parchment water transport coefficient ( $\Delta_{wpa}$ ) as follows,

$$N_w = \frac{\Delta_{wpa} C_{spa}}{h} (X_1 - X_0) \quad (17)$$

387

388

389

390 where  $X_0$  and  $X_1$  are the parchment moisture content at water activities  $a_{w0}$  and  $a_{w1}$   
 391 respectively.

392

393

## 394 4. RESULTS AND DISCUSSION

395

### 396 4.1. Characterization of the structure

#### 397 4.1.1 Characteristic dimensions

398 Characteristic dimensions of coffee bean were determined as exposed in section 3.1. The  
 399 obtained values were for the major axis: 11.6 mm, small axis: 8.1 mm, thickness: 4.6 mm, surface:  
 400  $1.293 \times 10^{-4} \text{ m}^2$ , volume:  $1.99 \times 10^{-7} \text{ m}^3$ , and the focal distance calculated considering a prolate  
 401 spheroid geometry (Eq. 15) was  $4 \times 10^{-3} \text{ m}$ .

402

#### 403 4.1.2. Internal structure

404 Cross-sections perpendicular to the coffee major axis were sliced from fermented washed  
 405 coffee beans. All slices were prepared as described in section 3.2 and images were taken by optical  
 406 microscopy. The objective is to identify some heterogeneities in the internal structure has already  
 407 reported (Eira *et al.*, 2006; De Castro & Marraccini, 2006).

408 Observations reveal a rupture of the tissue in the upper part of the endosperm (Fig. 4).  
409 Since it does not have a specific anatomical name, it will be called “natural discontinuity”. Mucilage  
410 left-over was found in the natural discontinuity as shown by Sutherland *et al.* (2004).

411 Heterogeneities in physical properties can result from variations in the cell arrangement and  
412 distribution. When focusing at the cell shape, two different geometries are encountered:  
413 “rectangular” and “polyhedral” depending on the number of cell edges. On cross-section images, it  
414 is generally observed that the natural discontinuity is surrounded by “rectangular” cells while the  
415 rest of endosperm is made up of “polyhedral” cells. Therefore, the cells pattern and distribution  
416 seems to be oriented by the natural discontinuity. However, even though some differences in the  
417 cells arrangement are observed, internal structure dimensions are almost uniform over the whole  
418 bean. On a zooming image (Fig. 5), cells dimensions are indicated. Cell diameters were between 30  
419 to 60 $\mu\text{m}$  while the wall thickness ranges from 9 to 11 $\mu\text{m}$ .

420 The microstructure of parchment is shown in Fig. 6. One can notice the fibers with a high  
421 level of cross-linking in agreement with the description made by Kasser & Kasser (1969). Regarding  
422 to the chemical composition, the main compound of endosperm is a polymannan while parchment is  
423 principally composed of lignin and pentose. Thus, coffee parchment has a structure that strongly  
424 differs from the endosperm and this aspect should result in differences in physical properties.

425

## 426 **4.2 Sorption isotherms**

427 Five sorption isotherms were obtained: parchment, internal and external endosperm,  
428 extremities and whole bean. The experimental points are plotted in Fig. 7. The continuous lines  
429 represent the best fit with GAB model except at high water activities ( $a_w > 0.84$ ) where the Ferro-  
430 Fontan model is used (Ferro-Fontan *et al.*, 1982). No significant differences between the sorption  
431 isotherms of the endosperm, extremities and the whole bean were observed. However, the  
432 behavior of parchment was found to be different at high water activities ( $a_w > 0.8$ ). It indicates a  
433 lower hygroscopic nature in the parchment which may be attributed to its lignocellulosic  
434 composition. This aspect is of particular importance since *Aspergillus ochraceus* develops  
435 principally in this region. The sorption behavior difference shown in Fig. 7 implies a moisture content  
436 discontinuity at the endosperm/parchment interface, i.e., at equilibrium the moisture of parchment is  
437 lower.

438

## 439 **4.3. Water transport coefficients**

### 440 **4.3.1. Water transport coefficient in the endosperm**

441 The transport coefficient ( $\Delta_{wen}$ ) of endosperm (c in Fig. 1.b) with and without silver skin (b  
442 in Fig. 1.b) was evaluated by the method described in section 3.4.1. The average thickness of  
443 samples was 0.9 mm, and the water transport coefficients obtained at different moistures are

444 plotted in Fig. 8. The moistures associated with water transport were calculated as the mean  
 445 between the initial and final moisture which are considered for the slope of Eq. (13) log  
 446 transformation. This figure shows that the water transport coefficient depends on moisture content  
 447 at moistures  $< 0.65$ . This effect confirm the fact that at high moisture contents ( $>0.65$ ),  
 448 corresponding to high activity values ( $a_w > 0.95$ ), the water is practically “free”, i.e., its mobility is  
 449 maximal, and therefore it leads a constant value for the water transport coefficient. As the moisture  
 450 content decreases, two phenomena participate to reduce the water diffusivity which tends to zero.  
 451 First, the reduction of water volume fraction inside the pore space decreases water flow; second,  
 452 the increase of water bonding with solid structure since hygroscopic effects become predominant.  
 453 Moreover, it has already been observed that, during the drying process, the entrance in the  
 454 hygroscopic domain corresponds to the transition from a water saturated system to a non-saturated  
 455 system, i.e., a gas phase appears and its volume fraction increases. Therefore, the combination of  
 456 these two effects account for the decreasing transport coefficient observed experimentally as the  
 457 moisture content tends to zero. Regarding to the silver skin, Fig. 8 results show that it leads to 10%  
 458 decrease of the effective diffusivity.

459 The Biot mass number were calculated with Eq. (14) using the  $\Delta_{wen}$  values of Fig. 8, with  
 460 the following values:  $l = 0.009$  m (average endosperm thickness),  $k_c = 0.007$  m  $\cdot$  s $^{-1}$  (Geankoplis  
 461 1998 correlation for natural convection),  $\rho_{sa} = 1.1$  kg  $\cdot$  m $^{-3}$ ,  $C_{sen} = 800$  kg  $\cdot$  m $^{-3}$  and  $K_{eq} = 0.63$   
 462 . This last value was calculated as indicate Cordova et al., (1996), and represents the average  
 463 distribution constant between air and product moistures at low contents in product. The mass Bi  
 464 number obtained were from 30 to 120. These values confirm the negligible interfacial resistance  
 465 assumption required in Eq. (13).

466

#### 467 **4.3.2. Averaged water transport coefficient in the whole grain with a high moisture content**

468 The averaged water transport coefficient at high moisture content can be evaluated from  
 469 the drying kinetic of the whole bean (Fig. 9) by means of linear regression onto Eq.(15). It can be  
 470 noticed in Fig. 9 that the curves show a linear behavior between 1 h and 4 h for the test at 45 °C  
 471 and between 1 h and 8 h for the test at 35 °C. It is in these intervals that are determined the  
 472 transport coefficients. Average initial moisture of coffee beans ( $x_0$ ) was 1.054, and the equilibrium  
 473 moisture ( $x_e$ ), calculated with sorption isotherms was 0.069. Values obtained at 35°C and 45°C  
 474 were respectively  $(2.84 \pm 0.125) \times 10^{-11}$  and  $(9.41 \pm 0.494) \times 10^{-11}$  m $^2$ .s $^{-1}$ . The error estimation  
 475 represents the 95% confidence interval. The averaged transport coefficient at 45°C agrees with the  
 476 water diffusivity reported by Sfredo *et al.* (2005) which ranges between  $1.0 \times 10^{-11}$  to  $10 \times 10^{-11}$   
 477 . The lower and upper limits of averaged water transport coefficient were included in the Fig.  
 478 8. One can note that this value agrees with the endosperm one for moisture contents higher than

479 0.65. Regarding to the whole coffee bean at high moisture content, these results confirm the water  
480 transport coefficients obtained for endosperm at high moisture contents. Additionally, the mass Bi  
481 number evaluated in the past section was for natural convection, and the averaged water transport  
482 coefficient evaluated in this section was under forced convection. Like the interfacial mass transfer  
483 is promoted by forced convection, it is evident that the use of Eq. (15), which implies a negligible  
484 interfacial mass transfer, is justified.

485

#### 486 **4.3.3. Water mass transfer resistance in parchment**

487 Fig. 10 shows the weight variation over time of the bottom salt solution for various  
488 experiments. After a transitional period required to equilibrate samples with both salt solutions,  
489 weight gain varies linearly allowing to identify the water resistance coefficient,  $r$ , by means of Eq.  
490 (16). Results are summarized in Table 1. The errors listed in Table 1 are the result of 95%  
491 confidence interval obtained from linear regression of the slope in linear zone of data in Fig. 10. The  
492 water transport coefficient in parchment ( $\Delta_{wpa}$ ) can be determined by using Eq. (17). The  
493 parchment average thickness was approximated 0.1 mm, and the volumetric concentration of the  
494 dry solid was taken  $800 \text{ kg}\cdot\text{m}^{-3}$ . The values obtained are plotted in Fig. 8. Regarding water mass  
495 transfer coefficient a unique value of  $5 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$  has been reported by Nilnont *et al.* (2012).  
496 They estimated the water mass transfer in parchment using the water diffusivity which was  
497 calculated by fitting the Fick second law solution (Eq. 13) on their drying kinetics results. Water  
498 diffusivity is a common name for the water transport coefficient deduced in section 2. Moreover, the  
499 reported value is two magnitude order lower than the calculated in this work. However Nilnont *et al.*  
500 (2012) values were obtained from drying kinetics performed with 50 g of parchment in a tray drier  
501 and they state that parchment is extremely thin but did not report this thickness. The water transport  
502 coefficient obtained from Eq. (13) is highly dependent on characteristic length of diffusion. Then, the  
503 values of resistance listed in Table 1, and the water transport coefficient in parchment plotted in Fig.  
504 8 have more confidence.

505

506

## 507 **5. CONCLUSIONS**

508 Coffee bean is a system extremely heterogeneous in a macroscopic level (parchment,  
509 endosperm, furrow) as well as in a cellular level. Parchment and endosperm present significant  
510 differences in their structures. Parchment structure is fibrous, very close to the wood, while that of  
511 the endosperm revealed cells of form and orientation fairly uniform. This difference in structure is  
512 reflected by the difference of their isotherms for water activities ranging between 0.8 and 1. This  
513 difference is particularly important because it is in this interval of water activity that fungus develops.  
514 It has been shown that by adopting the water chemical potential as the gradient for transport and  
515 the assumption of a local equilibrium inside media, water transport can be described by a law which



516 combine the different transport mechanisms. The averaged coefficient  $\Delta_w X$  depends, for an  
517 isothermal case and an undeformable solid phase, on the moisture content of media. Silver skin  
518 weakly reduces the water transfer from the endosperm to the parchment. Furthermore, in a fresh  
519 state, the silver skin is hydrated and fills the furrow. As drying goes forward, the silver skin gets  
520 thinner and a gas phase appears. This could lead to fungal development in the furrow and will be  
521 the focus of further investigations. The water transfer resistance of parchment associated with its  
522 weak hygroscopic nature can lead to a moisture content discontinuity between external gas phase  
523 and the gas phase located at the parchment/endosperm interface. This activity difference can be  
524 evaluated through Eq. 17. For instance, with a mass flux corresponding to the drying kinetics at  
525 35°C (Fig. 9), the water activity difference between both sides of parchment is about 0.49.  
526 Therefore, parchment reduces the risk of *Aspergillus ochraceus* contamination in the endosperm if  
527 compared to a case where it has been destroyed. Finally, the experimental techniques presented  
528 should allow a fine analysis of the drying process inside a coffee bean, but description of water  
529 transfer at the microscopic scale can only be carried out by numerical simulation. These models will  
530 allow the estimation of drying conditions that prevent the fungal development.

531

### 532 **Acknowledgments**

533 The authors wish to thank Mexican CONACyT and University Montpellier 2 for the financial support  
534 given for the stages and missions of A. Ramirez-Martinez in Montpellier and the missions of the  
535 Professors both in Veracruz and Montpellier through the project "PCP Optimización del secado de  
536 café".

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