



## Kernel characterization and starch morphology in five varieties of Peruvian Andean maize

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### ABSTRACT

Peruvian Andean maize (PAM) has been commonly used as an ingredient that confers color, flavor, and texture in culinary. Nevertheless, no studies are focusing on agro-industrial interest characteristics to develop new products. This study aimed to evaluate the physicochemical, nutritional, and technological characteristics of kernels and the starch granule morphology of the five main PAM varieties: *Chullpi*, *Piscorunto*, Giant *Cuzco*, *Sacsa*, and Purple. PAM's characterization was performed according to the official methods, and its morphology was observed by scanning electron microscopy (SEM). Physically, the varieties of larger kernels (Giant *Cuzco* and *Sacsa*) presented a higher 1000-kernel weight and a lower hectoliter weight than those of smaller size (*Piscorunto*, Purple, and *Chullpi*). Nutritionally, PAM had higher ether extract (5%) and ash (2%) contents than other pigmented maizes. Likewise, they presented more significant amounts of essential amino acids, as leucine (10 mg/g protein) and tryptophan (up to 2 mg/g protein); unsaturated fatty acids, oleic (30%) and linoleic (53%); and minerals, as magnesium (104 mg/100 g). SEM showed that endosperm structure and starch morphology vary according to maize types and their grain location. Starch granules of floury PAM varieties were small and polyhedral in the sub-aleurone endosperm, whereas those of the central area were bigger and spherical. In *Chullpi*, it was observed a portion of vitreous endosperm with a compact structure. The low protein content (8.3%) and the endosperm structure of floury varieties of PAM influenced their pasting properties. Their pasting temperature was <69 to 71 °C>, peak viscosity <3200 to 4400 cP>, and setback <1250 to 1706 cP>; therefore, they do not retrograde easily. The results suggest that PAM has characteristics that would help elaborate regional products with added value, such as soups, willows, beverages, and porridges.

### 1. Introduction

Growing consumer interest in more differentiated food products, such as traditional products associated with a specific place of origin, has been observed in recent years (Balogh et al., 2016; ONUDI, 2011; Stolzenbach et al., 2013). Moreover, nowadays, it is known that the pandemic caused by Covid-19 has brought significant changes to the food system. In particular, the restrictions on movements (within and between countries) have posed severe problems for the production and the entire food supply chain affecting its availability (FAO, 2020; Hobbs,

2020; Hoover, 2020). Therefore, it is necessary to look for foods that guarantee food self-sufficiency; thus, local crops should be promoted to diversify the population's diet. This is an excellent opportunity for small producers that would not have to compete for prices with generic and standardized products. Instead, it rewards them for using traditional methods to cultivate deep-rooted regional products with unique properties.

Peru is considered the country with the greatest phenotypic diversity of maize worldwide. According to the latest report from the *Universidad Nacional Agraria de la Molina* and the Ministry of Agriculture, 55

**Abbreviations:** PAM, Peruvian Andean maizes; SEM, Scanning Electron Microscope; SS, Sub-aleurone endosperm; CS, Central endosperm; RVA, Rapid Visco Analyzer; PT, Pasting Temperature; PV, Peak Viscosity; BD, Breakdown Viscosity; SB, Setback viscosity; FV, Finale Viscosity.

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varieties of maize present active cultivation in the country (UNALM/MINAGRI, 2014). The Peruvian Andean maize (PAM) constitutes a nutritional and economic wealth for rural farmers, who market and use them as an ingredient to add color, flavor, and texture to traditional dishes (Salhuana, 2004). Although for several years, prejudice and the lack of cultural identity meant that its cultivation was left aside, being consumed by low-income inhabitants. Today, due to the trend of reevaluation of native foods, PAM is used in many sophisticated restaurants where it is consumed in different ways: fried (*cancha*), boiled (*mote*, *choclo*), in beverages (*chicha morada*), desserts (*mazamorra morada*), among others.

PAM's valorization has led to an increase in their production for both the national and international markets. According to the data supported by MINAGRI (2018), between 2008 and 2018, the production, yield, and price of PAM increased 22%, 23%, and 75%, respectively (see supplementary material, Table S-1). In 2018, PAM was considered one of the fastest-growing Peruvian emerging crops due to the 170% increase in its exports compared to the previous year (AGAP, September 4, 2018). In 2019, its sales generated USD 104 million (Mendieta, 2020). The most commercialized varieties are Giant *Cuzco* and Purple (local and foreign market), followed by *Chullpi*, *Sacsá*, and *Piscorunto* (local market). Among the most common marketing formats, these maizes are commonly sold as dry grain, whole flour, or fried snack.

In a previous review carried out by our team, Salvador-Reyes and Clerici (2020), the history, general characteristics, scientific studies, and the importance of PAM in the Peruvian population's diet were detailed. Nevertheless, it was observed that much of the information available is focused on the agronomic aspects of PAM, and little is known about its characteristics of industrial interest.

The knowledge of cereal grains properties represents the first step to select them and suggest their possible industrial uses (Anderson & Almeida, 2018; Serna-Saldivar & Carrillo, 2018). Physical characteristics and structure of kernels help to determine their processing properties related to handling and yield production; as their chemical, nutritional, and technological properties, besides starch morphology, play a significant role in the texture, stability, appearance, and nutritional value of food products contributing to define its proper utilization to develop high-quality and nutritious foods.

In this sense, the present study aimed to characterize the kernel properties, nutritional composition, and the starch morphology of the five main varieties of PAM (*Chullpi*, *Piscorunto*, Giant *Cuzco*, *Sacsá*, and Purple) to determine their possible industrial use. Thus, we hope to open a way to a more in-depth study that increased their valuation since traditional foods can enrich and improve our diet while perpetuating essential elements of local knowledge and cultural heritage.

## 2. Material and methods

Kernels of five PAM varieties (*Chullpi*, *Piscorunto*, Giant *Cuzco*, *Sacsá*, and Purple) were purchased from local Peruvian markets. According to the producer's specifications, they were cultivated in the *Qolqanpata* Andean Botanical Garden and the *Retiro* Experimental Ecological Center located in the region of Cuzco (13°31'06"S, 71°58'41"W).

The kernels were used for physical and morphological analyzes, and whole flours (obtained by grinding in a hammer mill) were used for chemical, nutritional, and viscosity analyzes.

### 2.1. Physico-chemical characterization

Physical properties of kernels were performed by measuring their dimensions (length, width, and thickness) with a digital caliper. Quality parameters, hectoliter and 1000-kernel weight, were determined using a hectoliter scale and analytical balance, respectively. Instrumental color was determined in kernels, whole flours, and retrograde flours (obtained from the 2.3 analysis). Color parameters ( $L^*$ ,  $a^*$ , and  $b^*$ ) were measured in the CIELab system using the CR-400 Chroma Meter (Konica Minolta,

Japan).

The water activity ( $a_w$ ) was determined using the Aqualab-CX3 hygrometer (Decagon device, Washington, USA). The pH-value and titratable acidity were carried out following the methodology described by Mutlu et al. (2018), and results were expressed as a sulfuric acid percentage (Bhat et al., 2011).

### 2.2. Nutrients characterization

#### 2.2.1. Chemical composition

It was determined by the AACCI methods (2010) for moisture (44–01.01), protein (46–13.01, factor = 5.97), ether extract (30–25.01), dietary fiber (32–05.01), and ash content (08–01.01). Digestible carbohydrate content was calculated by difference, subtracting protein, ether extract, dietary fiber, and ash contents from the sample's initial dry weight.

#### 2.2.2. Amino acid profile

A total of 18 amino acids were determined, including 9 essential (phenylalanine, histidine, leucine, isoleucine, lysine, methionine, threonine, valine, and tryptophan) and 9 non-essential (aspartic acid, glutamic acid, alanine, arginine, cysteine, glycine, proline, serine, and tyrosine).

The quantification of amino acids was performed using high-performance liquid chromatography (Hagen et al., 1989; White et al., 1986), except for tryptophan, determined by the enzymatic method (Lucas & Sotelo, 1980).

#### 2.2.3. Fatty acid profile

The identification and quantification of fatty acids were performed by the AOCS (2014), method Ce-1a-13, using gas chromatography (brand Agilent Technologies, model 7890A).

#### 2.2.4. Minerals

It was determined using a flame atomic absorption spectrometer (model AAnalyst 200, Perkin Elmer) following the procedure described by Rebellato et al. (2015). During the determination of calcium and magnesium, a solution of lanthanum dioxide was added until obtaining a final concentration of 0.5% to reduce possible interferences.

### 2.3. Morphological characterization

#### 2.3.1. Kernels

The microstructure of kernels was observed with a field emission Scanning Electron Microscope (SEM) (Zeiss, model SIGMAVP). Previously, PAM kernels were cut transversely and left in a desiccator (with silica) for 7 days. Later, the cuts were mounted on aluminum specimen stubs with double-sided adhesive tape and covered by a layer of 15 nm gold. The SEM operating conditions were: electron beam current = 80  $\mu$ A, constant acceleration voltage = 10 kV, and working distance = 8.5 mm. The images were taken in four kernel areas: pericarp, sub-aleurone endosperm (SS), central endosperm (CS), and germen at 1000, 2000, and 6500x of magnification.

#### 2.3.2. Starch granules

They were observed using the same methodology and samples from the kernel analysis (2.3.1). In this case, the images were focusing on SS and CS areas at 6500x of magnification. The starch granules dimensions (length, diameter, area, and perimeter) were analyzed using the digital image processing software Image J (National Institutes of Health, ver. 1.50i).

The starch granules morphology was also observed using a polarized light microscope (Olympus, model BX51/BX52) with a 100x objective and a digital camera (Canon PowerShot A620/ 7.1 megapixels). The samples were sprinkled on a slide, then a drop of immersion oil was added and mixed with a spatula.

## 2.4. Pasting properties

Pasting properties of PAM whole flours (<250  $\mu\text{m}$ ) were determined by the AACCI (2010) method 76–21.01, in a 23 min-test using a Rapid Visco Analyzer (RVA) (Peter, Sweden, model RVA-4500). The parameters recorded were: pasting temperature (PT), peak viscosity (PV), breakdown viscosity (BD), setback viscosity (SB), and final viscosity (FV).

## 2.5. Texture profile

Immediately after the measurements in the RVA, samples were poured into plastic tubes (inner diameter = 25 mm, height = 30 mm) and cooled at 4 °C for 18 h. Then, they were allowed to thaw for 1 h before analyzing their texture profile at room temperature. The textural parameters, firmness and elasticity, were recorded in a texture analyzer (TA-XT2, Stable Micro Systems Ltd., Godalming, UK) using an aluminum probe of 3.5 mm diameter (P45). The deformation level was 25% of the sample's original height at a speed of 1 mm/s with a 5 g force transducer.

## 2.6. Statistical analysis

This study was carried out with 25, 10, and 3 replicates for physical analyses of dimensions, weight, and instrumental color, respectively. The chemical composition, pasting profile in RVA, and texture analyses were performed with 3 replicates. The results were reported as mean  $\pm$  standard deviation. The collected data was evaluated by analysis of variance (ANOVA) at a significance level of 5%. The difference between means was evaluated by the Scott-Knott test of multiple comparisons (p

< 0.05) using the statistical program SISVAR, version 5.6 (UFLA, Lavras MG-Brazil).

## 3. Results and discussion

### 3.1. Physico-chemical properties of PAM

Fig. 1 shows the visual aspects and color parameters of kernels, whole flours, and retrograde flours of PAM, and Table 1 reveals their physicochemical properties. The results are discussed below.

#### 3.1.1. Instrumental color

PAM kernels (Fig. 1A) had different colorations: yellow (*Chullpi*), black with white spots (*Piscorunto*), pale yellow (*Giant Cuzco*), red–orange with white stripes (*Sacsa*), and an intense and homogeneous purple (*Purple*). After milling, the whole flours obtained (Fig. 1B) presented a higher luminosity ( $L^* > 70$ ), preserving the color hue of the kernel, being: pale yellow (*Chullpi*), light gray (*Piscorunto*), white (*Giant Cuzco*), pale red (*Sacsa*), and light purple (*Purple*). Afterward, the retrograde flours (Fig. 1C) presented colors as the whole flours, except for *Purple* maize, which increased its color intensity.

Serratos (2012) explained that the variety of colorations of PAM is the result of its adaptation to adverse growing climates, which over the years produced genetic mutations in the plant as a measure of resistance. In 2004, Smith observed that high altitudes and low growing temperatures promote natural pigments such as anthocyanins (responsible for blue, purple, and black colorations). In contrast, warm climates increase the concentration of carotenoids (responsible for red, yellow, and orange colorations). This information would explain our results as *Piscorunto* and *Purple* maizes are cultivated in the central region of Peru,



Fig. 1. Samples of (A) kernels, (B) whole flour, and (C) gels of five varieties of Peruvian Andean maize (PAM), and their color coordinates in CIELab space.

**Table 1**  
Physico-chemical properties of five varieties of Peruvian Andean maize (PAM).<sup>1</sup>

Properties	PAM				
	<i>Chullpi</i>	<i>Piscorunto</i>	Giant <i>Cuzco</i>	<i>Sacsa</i>	Purple
<b>Kernel</b>					
Dimension <sup>2</sup>					
Length (mm)	18.47 ± 1.14 <sup>b</sup>	18.28 ± 1.28 <sup>b</sup>	20.36 ± 1.13 <sup>a</sup>	18.23 ± 0.64 <sup>b</sup>	12.62 ± 1.13 <sup>c</sup>
Width (mm)	7.93 ± 0.95 <sup>c</sup>	9.54 ± 0.68 <sup>d</sup>	17.34 ± 1.05 <sup>a</sup>	15.37 ± 0.98 <sup>b</sup>	11.37 ± 1.09 <sup>c</sup>
Thickness (mm)	5.17 ± 0.50 <sup>c</sup>	5.74 ± 0.53 <sup>b</sup>	6.13 ± 0.56 <sup>a</sup>	6.07 ± 0.52 <sup>a</sup>	5.18 ± 0.60 <sup>c</sup>
Quality parameters <sup>3</sup>					
Hectoliter weight (kg/100L)	58.79 ± 0.66 <sup>b</sup>	57.34 ± 0.49 <sup>b</sup>	51.42 ± 0.37 <sup>c</sup>	50.06 ± 0.37 <sup>c</sup>	61.56 ± 0.76 <sup>a</sup>
1000-kernel weight (g)	324.28 ± 1.02 <sup>a</sup>	427.89 ± 1.93 <sup>c</sup>	1340.63 ± 2.82 <sup>a</sup>	1197.58 ± 3.30 <sup>b</sup>	386.89 ± 1.03 <sup>d</sup>
<b>Whole flour</b>					
Water activity <sup>3</sup> (a <sub>w</sub> )	0.34 ± 0.02 <sup>ns</sup>	0.34 ± 0.03 <sup>ns</sup>	0.33 ± 0.02 <sup>ns</sup>	0.36 ± 0.01 <sup>ns</sup>	0.30 ± 0.03 <sup>ns</sup>
pH <sup>4</sup>	6.34 ± 0.03 <sup>a</sup>	6.30 ± 0.00 <sup>a</sup>	6.36 ± 0.03 <sup>a</sup>	6.35 ± 0.02 <sup>a</sup>	6.15 ± 0.03 <sup>b</sup>
Titration acidity (%) <sup>4,5</sup>	0.18 ± 0.00 <sup>c</sup>	0.13 ± 0.00 <sup>d</sup>	0.23 ± 0.01 <sup>b</sup>	0.23 ± 0.00 <sup>b</sup>	0.30 ± 0.01 <sup>a</sup>

<sup>1</sup> Results are presented as mean ± standard deviation. Means followed by different letters on the same line differ significantly from each other for the Scott-Knott test of multiple comparisons ( $p < 0.05$ ); ns = not significant.

<sup>2</sup> n = 25 replicates.

<sup>3</sup> n = 10 replicates.

<sup>4</sup> n = 3 replicates.

<sup>5</sup> Results are expressed in % of sulfuric acid (factor = 0.049) according to Mutlu et al. (2018).

which is about 2800 m of altitude where temperatures reach 4 °C. In contrast, *Sacsa* and *Chullpi* are grown in warmer climates, about 14 °C.

The differences observed in the luminosity and hue of the color between the kernels, whole flour, and retrograde flours of PAM may be due to the accumulation of pigments, which are usually located in the pericarp and the aleurone layers while the endosperm remains white (Espinosa et al., 2009). Thus, once kernels are milled, the whole flour obtained has a greater luminosity as pigments remain encapsulated, and the retrograde flours have a greater intensity of color due to the release of the soluble pigments in water. Our observations would indicate that PAM can be used to color food products as soups, sauces, and creams.

### 3.1.2. Kernel shape and size

Significant differences ( $p < 0.05$ ) were observed in the shape and size of PAM kernels among the studied varieties (Table 1). *Chullpi* and *Piscorunto* kernels presented an elongated shape and low thickness. Meanwhile, Giant *Cuzco*, *Sacsa*, and Purple had circle shapes and different sizes.

These characteristics may be linked to evolutionary factors. Based on the study of Paliwal et al. (2000), evolved races present larger grains and homogeneous shapes than the primitive ones. Considering the classification of PAM races (UNALM/MINAGRI, 2014): *Chullpi* and *Piscorunto* belong to derivate races, which are characterized by having small kernels with irregular shapes, whereas Giant *Cuzco*, *Sacsa*, and Purple belong to *Cuzco*, a second derivation race whose grains resulted from the hybridization of derivate races to improve their crop yield (Giant *Cuzco* and *Sacsa*) or increased its pigment concentration (Purple).

### 3.1.3. Quality parameters

PAM varieties with smaller kernels (Purple, *Chullpi*, and *Piscorunto*) had a higher hectoliter weight and a lower 1000-kernel weight than those of larger size (Giant *Cuzco* and *Sacsa*) (Table 1). In general, PAM's

hectoliter weight was in the range of 50.06–61.56 kg/100L. These values are behind those informed for commercial corn (69 to 75 kg/100L) (UNALM/MINAGRI, 2014) and the Mexican blue maize (61–84 kg/100L) (Escalante-Aburto et al., 2013; Mutlu et al., 2018).

According to Balbi et al. (2006), the low density of PAM kernels would be related to environmental factors of Peruvian highlands as temperature variation and water stress conditions. These circumstances shorten the period of filling the grain, decreasing its final weight and the number of cells destined to accumulate starch and proteins. Therefore, the PAM's low hectoliter weight already indicates a lower protein content, as shown in Section 3.2.

### 3.1.4. Chemical properties

No significant differences in water activity were observed between the samples (Table 1). Purple maize presented a lower pH-value and higher titration acidity than the other maizes. However, it was behind the limit of 0.5% established by the CODEX STAN 154-1985 (FAO/OMS, 2007).

Wadleigh and Shive (1939) observed that the increase in soil pH levels decreases maize's organic acids and minerals. Therefore, the low pH and high acidity of Purple maize may be related to its growing soil conditions, since the appropriate soil pH level for its development is between 6.0 and 6.5 (slightly acidic) (MINAGRI/INIA, 2016), whereas for the other maizes it is between 7 and 7.6 (neutral to slightly alkaline) (Jara, 2016; Quevedo, 2013).

## 3.2. Nutritional composition of PAM

Table 2 shows the nutritional composition of PAM, which results are presented and discussed below.

### 3.2.1. Chemical composition

In general, significant differences ( $p < 0.05$ ) were observed in the chemical composition among PAM varieties: *Chullpi* presented a higher content of proteins, Purple higher contents of ethereal extract and ash, whereas *Piscorunto*, Giant *Cuzco*, and *Sacsa* had a higher concentration of dietary fiber.

The chemical composition differences can be related to genetic factors, type of maize, and environmental growing conditions. *Piscorunto*, Giant *Cuzco*, *Sacsa*, and Purple varieties are classified as floury maizes since their endosperm is composed exclusively of soft starch. Meanwhile, *Chullpi* is considered a sweet type of maize since it presents a part of its endosperm in a vitreous state (Paliwal et al., 2000).

The higher protein content of *Chullpi* can be linked with the greater amount of protein matrices that vitreous endosperm has comparing to the floury one (Larkins, 2018; Rausch & Eckhoff, 2016). Our results were similar to those obtained by Taylor and Allen (2005), Gayral et al. (2015), Xu et al. (2019), and Zhang and Xu (2019), who determined that the protein content in sweet maizes (ranging from 8.7 to 13.2%) was significantly higher than in the floury ones (ranging from 4.7 to 9.1%).

The high ether extract and ash contents of Purple maize can be associated with the soil conditions. As mentioned above (Section 3.1.3), it grows in slightly acid soils and areas with little rainfall, which generated stress in the plant, increasing the absorption of nutrients from the soil (Agama-Acevedo et al., 2011). On the other hand, the high dietary fiber content of Giant *Cuzco*, *Piscorunto*, and *Sacsa* varieties can be related to the greater thickness and number of their pericarp layers compared to Purple and *Chullpi* maizes (Section 3.3; Fig. 2).

Compared to other native pigmented maizes, PAM had a higher content of ethereal extract and ash, but a lower protein content, than some varieties of Mexican pigmented maizes (Agama-Acevedo et al., 2005; Mutlu et al., 2018; Rodriguez, 2019; Urias-Lugo et al., 2015), and Argentina native maizes (Heck et al., 2019). On the other hand, the dietary fiber values of PAM were higher than those observed in the Mexican blue maize (Bello-Pérez et al., 2015; Camelo-Méndez et al., 2017), Italian pigmented maizes (Rocchetti et al., 2018), and other

**Table 2**  
Nutrients composition of five varieties of Peruvian Andean maize (PAM) whole flour.

Nutrients (on dry basis <sup>1</sup> )	PAM				
	<i>Chullpi</i>	<i>Piscorunto</i>	<i>Giant Cuzco</i>	<i>Sacsá</i>	Purple
<b>Chemical composition<sup>2</sup>(%)</b>					
Protein	9.64 ± 0.06 <sup>a</sup>	7.28 ± 0.11 <sup>c</sup>	8.94 ± 0.19 <sup>b</sup>	8.49 ± 0.21 <sup>b</sup>	8.66 ± 0.08 <sup>b</sup>
Ether extract	5.27 ± 0.10 <sup>b</sup>	4.76 ± 0.10 <sup>c</sup>	4.33 ± 0.16 <sup>d</sup>	4.43 ± 0.09 <sup>d</sup>	5.73 ± 0.10 <sup>a</sup>
Ash	1.90 ± 0.05 <sup>b</sup>	1.67 ± 0.07 <sup>c</sup>	1.96 ± 0.05 <sup>a</sup>	1.86 ± 0.02 <sup>b</sup>	2.01 ± 0.07 <sup>a</sup>
Dietary fiber	14.82 ± 1.45 <sup>b</sup>	17.35 ± 0.81 <sup>a</sup>	20.06 ± 1.22 <sup>a</sup>	20.29 ± 0.28 <sup>a</sup>	13.65 ± 0.49 <sup>b</sup>
Digestible carbohydrates <sup>3</sup>	68.37	68.94	64.71	64.94	69.95
<b>Amino acids<sup>4</sup></b>					
Essentials					
Histidine	0.24 (2.39)	0.20 (2.61)	0.16 (1.79)	0.21 (2.36)	0.24 (2.66)
Isoleucine	0.30 (3.01)	0.24 (3.16)	0.20 (2.24)	0.26 (2.94)	0.33 (3.70)
Leucine	0.97 (9.75)	0.76 (10.16)	0.64 (7.05)	0.92 (10.48)	1.20 (13.39)
Lysine	0.29 (2.90)	0.25 (3.30)	0.19 (2.13)	0.25 (2.83)	0.30 (3.35)
Methionine	0.12 (1.24)	0.15 (2.06)	0.12 (1.34)	0.17 (1.88)	0.16 (1.85)
Phenylalanine	0.39 (3.94)	0.32 (4.26)	0.27 (2.91)	0.36 (4.12)	0.48 (5.43)
Threonine	0.37 (3.73)	0.24 (3.16)	0.20 (2.24)	0.27 (3.06)	0.31 (3.46)
Tryptophan	0.10 (1.04)	0.08 (1.10)	0.06 (0.67)	0.07 (0.82)	0.19 (2.08)
Valine	0.38 (3.84)	0.32 (4.26)	0.27 (2.91)	0.35 (4.00)	0.43 (4.85)
Non-essentials					
Aspartic acid	0.63 (6.33)	0.55 (7.28)	0.43 (4.70)	0.58 (6.60)	0.72 (8.08)
Glutamic acid	1.44 (14.52)	1.25 (16.62)	1.06 (11.63)	1.48 (16.84)	1.89 (21.13)
Alanine	0.60 (6.02)	0.47 (6.32)	0.40 (4.36)	0.55 (6.24)	0.69 (7.74)
Arginine	0.44 (4.46)	0.40 (5.36)	0.34 (3.69)	0.46 (5.18)	0.54 (6.00)
Cystine	0.05 (0.52)	0.09 (1.24)	0.05 (0.56)	0.08 (0.94)	0.09 (1.04)
Glycine	0.34 (3.42)	0.27 (3.57)	0.22 (2.46)	0.28 (3.18)	0.34 (3.81)
Proline	0.73 (7.37)	0.57 (7.55)	0.49 (5.37)	0.67 (7.66)	0.79 (8.89)
Serine	0.40 (4.05)	0.33 (4.40)	0.27 (2.91)	0.39 (4.48)	0.45 (5.08)
Tyrosine	0.30 (3.01)	0.26 (3.43)	0.22 (2.46)	0.30 (3.42)	0.38 (4.27)
<b>Fatty acids<sup>5</sup></b>					
Palmitic	0.59 (12.29)	0.42 (11.83)	0.42 (12.50)	0.44 (12.68)	0.51 (13.35)
Stearic	0.11 (2.29)	0.06 (1.69)	0.06 (1.79)	0.07 (2.02)	0.08 (2.09)
Oleic	1.46 (30.42)	1.01 (28.45)	0.98 (29.17)	1.06 (30.55)	1.27 (33.25)
Linoleic	2.52 (52.50)	1.99 (56.06)	1.83 (54.46)	1.83 (52.74)	1.88 (49.21)
Arachidic	0.02 (0.42)	0.01 (0.28)	0.01 (0.30)	0.01 (0.29)	0.02 (0.52)
α-linolenic	0.07 (1.46)	0.04 (1.13)	0.04 (1.19)	0.04 (1.15)	0.04 (1.05)
Cis-11-eicosenoic	0.01 (0.21)	0.01 (0.28)	0.01 (0.30)	0.01 (0.29)	0.01 (0.26)
Behenic	0.01 (0.21)	0.00 (0)	0.00 (0)	0.00 (0)	0.00 (0)
Lignoceric	0.01 (0.21)	0.01 (0.28)	0.01 (0.30)	0.01 (0.29)	0.01 (0.26)
Total saturated (%)	15.42	14.65	15.18	15.56	16.49
Total monounsaturated (%)	30.63	28.73	29.46	30.84	33.51
Total polyunsaturated (%)	53.96	57.18	55.36	53.89	50.00
Omega-3 (%)	1.46	1.13	1.19	1.15	1.05
Omega-6 (%)	52.50	56.06	54.46	52.74	49.21
Trans(%)	0.00	0.00	0.00	0.00	0.00
<b>Minerals<sup>2</sup> (mg/100 g)</b>					
Magnesium	93.73 ± 1.66 <sup>b</sup>	74.47 ± 3.48 <sup>c</sup>	118.15 ± 9.83 <sup>a</sup>	99.22 ± 7.99 <sup>b</sup>	134.07 ± 3.17 <sup>a</sup>
Calcium	1.03 ± 0.03 <sup>b</sup>	2.69 ± 0.18 <sup>a</sup>	0.82 ± 0.04 <sup>c</sup>	1.39 ± 0.16 <sup>b</sup>	2.32 ± 0.18 <sup>a</sup>
Zinc	1.64 ± 0.10 <sup>b</sup>	1.46 ± 0.03 <sup>b</sup>	1.69 ± 0.08 <sup>b</sup>	1.70 ± 0.18 <sup>b</sup>	2.67 ± 0.04 <sup>a</sup>
Iron	1.92 ± 0.13 <sup>b</sup>	1.38 ± 0.07 <sup>b</sup>	1.72 ± 0.05 <sup>b</sup>	1.75 ± 0.24 <sup>b</sup>	2.23 ± 0.14 <sup>a</sup>
Copper	0.13 ± 0.02 <sup>a</sup>	0.08 ± 0.01 <sup>b</sup>	0.08 ± 0.01 <sup>b</sup>	0.09 ± 0.01 <sup>b</sup>	0.18 ± 0.02 <sup>a</sup>

<sup>1</sup> Samples with moisture (%): *Chullpi* (11.58 ± 0.14), *Piscorunto* (11.36 ± 0.09), *Giant Cuzco* (11.29 ± 0.13), *Sacsá* (11.26 ± 0.24), and Purple (10.79 ± 0.12).

<sup>2</sup> Results are presented as mean ± standard derivation. Means followed by different letters on the same line differ significantly from each other for the Scott-Knott test of multiple comparisons (p < 0.05).

<sup>3</sup> Calculated by difference subtracting protein (factor = 5.97), ether extract, non-digestible carbohydrates, and ash contents from the initial dry weight of the sample.

<sup>4</sup> Values are expressed g/100 g of dry matter. Numbers in parentheses are expressed as mg/g protein from each PAM variety.

<sup>5</sup> Values are expressed g/100gof dry matter. Numbers in parentheses are expressed as % of the total fatty acids from each PAM variety.

floury maizes (Rohlfing et al., 2010; Taylor & Allen, 2005), which were in a range of 8–11%.

The differences in chemical composition between PAM and other pigmented maizes may be related to the cultivation system and environmental conditions of each region. The low protein content of PAM may be linked to the use of a greater amount of organic fertilizers than chemicals during its cultivation (Agama-Acevedo et al., 2011; Fiedor & Burda, 2014). Meanwhile, its high content of ethereal extract and ash can be associated with the stress produced in the plant by temperature fluctuation, which affects lipid biosynthesis (Kaplan et al., 2017; Schlueter et al., 2007) and increases the absorption of minerals from the soil (Ogunyemi et al., 2018). On the other hand, the high content of dietary fiber may be linked to the pericarp development of South

American native maizes, which had a greater pericarp thickness than those from North America and Europe. (Brewbaker et al., 1996; Serna-Saldivar, 2016).

### 3.2.2. Amino acid profile

All essential amino acids in PAM were detected, being leucine the most abundant with a concentration above 13 mg/g of protein (Table 2). When performing the amino acid score calculations (see supplementary material, Table S-2), it was determined that the limiting amino acid in PAM was lysine. However, *Giant Cuzco* and *Sacsá* maizes also had valine and isoleucine as limiting amino acids. In general, PAM presented significant amounts of tryptophan, particularly in *Chullpi* and Purple maizes. Considering the results (Table S-2), a 100 g portion of PAM

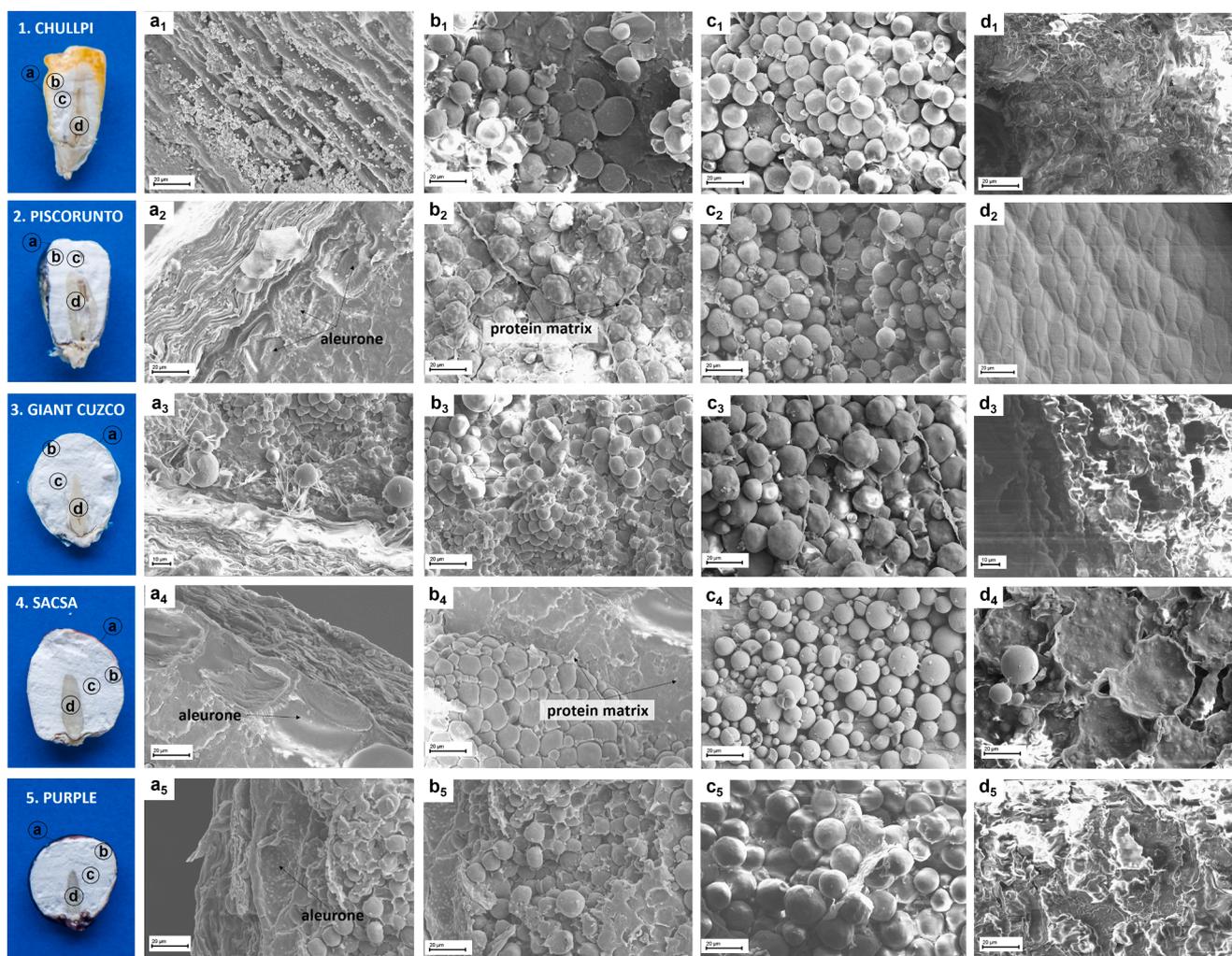


Fig. 2. Scanning electron micrographs (SEM) of (a) pericarp, (b) sub-aleurone endosperm, (c) central endosperm, and (d) germ of five varieties of Peruvian Andean.

whole kernels complies with the tryptophan requirements for adults (WHO/FAO/UNU, 2007).

Although tryptophan is considered as one of the limiting amino acids of maize (Badui, 2006), its high concentration in PAM could be related to the *flo-2* gene present in floury maizes. According to Nelson et al. (1965), this gene increases the glutenin content in the endosperm, increasing the concentration of tryptophan and methionine in the kernel. Moro et al. (1996), Jia et al. (2013), and Nankar et al. (2016) have proven this theory by comparing the amino acid profile of floury maizes with some hard and hybrid varieties. On the other hand, the high concentration of tryptophan in Purple and *Chullpi* maizes can be associated with their high ethereal extract content (Table 2) since the germ proteins are of better quality than those of the endosperm (Ramírez, 2001).

Compared with other native maizes, the lysine and tryptophan concentrations of PAM were as those reported by Vera-Guzmán et al. (2012) in creole varieties of yellow corn (tryptophan 0.57 mg/g protein, lysine 3.36 mg/g protein) and blue maize (tryptophan 0.54 mg/g protein, lysine 2.92 mg/g protein), and high than those observed by Panda et al. (2014) for high-quality protein corn (lysine 1.81 mg/g protein).

The non-essential amino acid profile of PAM (Table 2) was composed by aspartic acid, glutamic acid, arginine, alanine, cysteine, glycine, proline, serine, and tyrosine. The acidic amino acids (aspartic and glutamic) represent 15 to 30% of the total amino acids. Similar results have been observed by Mbuya et al. (2011) in native African maizes (25%). The cysteine content ranged from 0.52 to 1.24 mg/g protein, which was

below the values informed by Panda et al. (2014) for commercial maize (2.13 mg/g protein) and high-protein maize (2.77 mg/g protein).

Differences in the amino acid profile between PAM and maizes from other regions may be related to genetic factors that control the amino acid synthesis (Armstrong et al., 2000). Although the protein content of PAM was lower than commercial corns, it has a better quality. Purple maize presented the best amino acid profile among the studied samples since it had a higher content of essential amino acids, especially tryptophan. A 100 g serving complies with the daily essential amino acid requirements, except for lysine. However, that deficit could be supplied by mixing with other plant sources such as legumes, whose lysine concentrations are higher (Rezende et al., 2018; Venn, 2017).

### 3.2.3. Fatty acid profile

The fatty acid profile of PAM (Table 2) was composed on average of 15% of saturated fatty acids (mainly palmitic acid), 30% of mono-unsaturated (oleic acid), and 55% of polyunsaturated, including the essential fatty acids linoleic (53%) and  $\alpha$ -linolenic (1.2%). Besides, *Chullpi* presented traces of behenic acid (<1%), not detected in the other four varieties of PAM.

According to the literature, the fatty acid composition of maize is influenced by its genotype and degree of evolution (Wang & White, 2018). Less evolved varieties usually present high amounts of saturated fatty acids (Duvick et al., 1999). Then, traces of behenic acid in *Chullpi* may be related to its condition as a primitive maize variety. Although the consumption of foods with behenic acid has been associated with

increased cholesterol levels in the blood (Cater & Denke, 2001), the traces observed in *Chullpi* pose no risk.

Considering the concentration of polyunsaturated fatty acids in PAM, a 100 g portion of whole maize complies with the recommendation of linoleic essential fatty acid for adults (FAO, 2010). Compared with other pigmented maizes, the fatty acid profile of PAM was similar to the Mexican blue maize (14% palmitic, 30% oleic, 48% linoleic, 2.4% linolenic) (Urias-Lugo et al., 2015), and some Argentina creole maizes (14% palmitic, 35% oleic, 53% linoleic, 0.75% linolenic) (Heck et al., 2019).

### 3.2.4. Minerals

Significant differences ( $p < 0.5$ ) in mineral content were observed between PAM varieties. Purple maize presented the highest concentrations of the quantified minerals, a fact that may be related to its ash content (2.01%).

In general, the magnesium concentration in PAM was in a range of 74–134 mg/100 g. A 100 g portion contains approximately 50% of the daily recommended intake for adults (FAO/WHO, 2002); therefore, it can be considered a food rich in this mineral. Similar results have been reported for other pigmented maizes such as the blue (107 mg/100 g), purple (136 mg/100 g), red (138 mg/100 g), and white (118 mg/100 g) maizes from Mexico (Dickerson, 2008; Rodriguez, 2019).

The calcium content of PAM was in a range of 0.8–2.7 mg/100 g, presenting a higher in the pigmented varieties *Piscorunto* and Purple. Compared with the literature, the calcium content of PAM was lower than some varieties of Mexican pigmented maizes (24–32 mg/100 g) (Rodriguez, 2019), and the commercial yellow corn (7 mg/100 g) (USDA, 2016).

Other minerals such as zinc, iron, and copper were presented at an average of 1.8, 1.8, and 0.1 mg/100 g, respectively, in PAM. Compared with other studies, PAM had a lower zinc content than some Mexican pigmented maizes (2.8–4.5 mg/100 g) (Rodriguez, 2019) and the commercial yellow corn (2.21 mg/100 g) (USDA, 2016); however, the iron concentration in PAM is up to six times greater than those of others.

## 3.3. Kernel and starch granule morphology of PAM

The maize kernel is composed of three main parts: the outer covering (pericarp), a storage tissue (endosperm), and the embryo (germ). SEM allowed us to observe the details of these structures in PAM. The micrographs obtained at 2000x of magnification are presented in Fig. 2, which is complemented by magnifications of 1000x and 6500x included in the supplementary material (Figure S-1, S-2, and S-3). The observations are discussed below.

### 3.3.1. Pericarp

Differences in the pericarp structure were observed between PAM varieties. *Chullpi* ( $a_1$ ) had a greater thickness, 96.81  $\mu\text{m}$ , than the floury varieties *Piscorunto* ( $a_2$ ), *Giant Cuzco* ( $a_3$ ), *Sacsa* ( $a_4$ ), and Purple ( $a_5$ ), whose measurements were 45.25  $\mu\text{m}$ , 37.17  $\mu\text{m}$ , 36.75  $\mu\text{m}$ , and 31.02  $\mu\text{m}$ , respectively. However, the pericarp of these last presented greater compaction and several layers than *Chullpi*. On the other hand, the aleurone layer of pigmented PAM varieties (*Piscorunto*, *Sacsa*, and Purple) was more visible than the non-pigmented ones.

Singh et al. (2013) mentioned that the thickness of pericarp depends on the maize variety. For example, Espinosa et al. (2009) determined the thickness of the Mexican *criollo* maize (red, blue, and white) in a range of 74–109  $\mu\text{m}$ . Our results were similar to those reported by Brewbaker et al. (1996), who observed that the average pericarp thickness of indigenous maize from South America varies from 25 to 124  $\mu\text{m}$ , and presents a lower thickness compared to the North American improved maizes.

The visibility of the aleurone layer in pigmented PAM varieties may be related to the accumulation of pigments that, depending on the cultivar, can be contained in the pericarp or aleurone (Li et al., 2017).

Paulsmeyer et al. (2017) observed that anthocyanins in purple maize were stored in the pericarp. In contrast, Li et al. (2017) found that they were located inside the aleurone layer in blue maize. According to Salinas-Moreno et al. (1999) and Salinas-Moreno (2009), the accumulation of pigments in *Piscorunto*, *Sacsa*, and Purple maizes suggest that these could be useful for the nixtamalization and elaboration of products with blue or purple colorations.

### 3.3.2. Endosperm

Differences were observed in the endosperm structure and the starch granules morphology between PAM varieties and their location (SS or CS).

- Sub-aleurone endosperm (SS) and central endosperm (CS)

CS presented spherical starch granules and surrounded by some protein matrices, whereas those from SS were smaller, polygonal, and within a compact structure surrounded by a higher number of protein matrices (Figs. 2 and 3).

The difference in the endosperm morphology can be related to the evolutionary factors of maize. Tang et al. (2000) point out that maizes in the evolution process present small starch granules next to the pericarp and big granules in the center. On the other hand, Paes (2006) explained that the high number of protein matrices in SS is linked to the genetic factors that control the biosynthesis of starch, which makes the granules next to the pericarp have a greater number of protein matrices as part of the energy reserve of the kernel.

- Starch morphology

Differences were observed in the shape, size, distribution, and surface of the starch granules between PAM varieties (Fig. 3, Table 3).

Starch granules of the CS of *Chullpi* ( $CS_1$ ), *Sacsa* ( $CS_4$ ), and Purple ( $CS_5$ ) were spherical, whereas those of *Piscorunto* ( $CS_2$ ) and *Giant Cuzco* ( $CS_3$ ) were irregular and polyhedral. In several studies, maize starch granules are described as polyhedral with many faces (Aghazadeh et al., 2017; Ali et al., 2016; Izidoro et al., 2007; Mishra & Rai, 2006). However, granules with spherical shapes, like those of our study, have been observed in hybrid varieties of waxy-corn (Kethaisong et al., 2015) and American tropical maizes (Cui et al., 2014; Lin et al., 2011, 2015; Liu et al., 2018).

According to Valamoti et al. (2008), the shape of the starch granule is linked to the improvement process of the grain. Then, the presence of both spherical and polyhedral starch granules in PAM may be related to its natural evolution process. For example, in wheat grain, einkorn ancestral variety had spherical starch granules (Hidalgo & Brandolini, 2014), while commercial wheat granules are compacted and present angular forms (Gibbon et al., 2003). Torrence and Barton (2016) explained this is due to the compaction that the grain undergoes as part of its genetic improvement to increase its yield.

Concerning the size and distribution of starch granules (Fig. 3, Table 3), *Sacsa* ( $SS_4$  and  $CS_4$ ) had a bimodal distribution presenting large granules Type-A ( $>10 \mu\text{m}$ ) and small granules Type-B ( $<10 \mu\text{m}$ ), whereas in the other PAM varieties only Type-A granules were observed. Starch granules of *Giant Cuzco* ( $SS_4$  and  $CS_4$ ), Purple ( $SS_5$  and  $CS_5$ ), and *Chullpi* ( $SS_1$  and  $CS_1$ ) were bigger than those of *Piscorunto* ( $SS_2$  and  $CS_2$ ).

Several authors attribute the presence of large granules, small granules, or the proportion of both to growing environmental factors (Agama-Acevedo et al., 2013; Kaur et al., 2007). Tester (1997) explained that the stress produced by high temperatures of growing contributes to reducing Type-A starch granules, increasing Type-B starch granules in cereals. Therefore, the size and distribution of the starch granules of PAM could be related to their extreme growing conditions since *Chullpi*, *Piscorunto*, *Giant Cuzco*, and Purple, which presented a monomodal distribution of Type-A granules, grown in areas with cold climate and high altitudes, whereas *Sacsa* is cultivated in areas with climatic

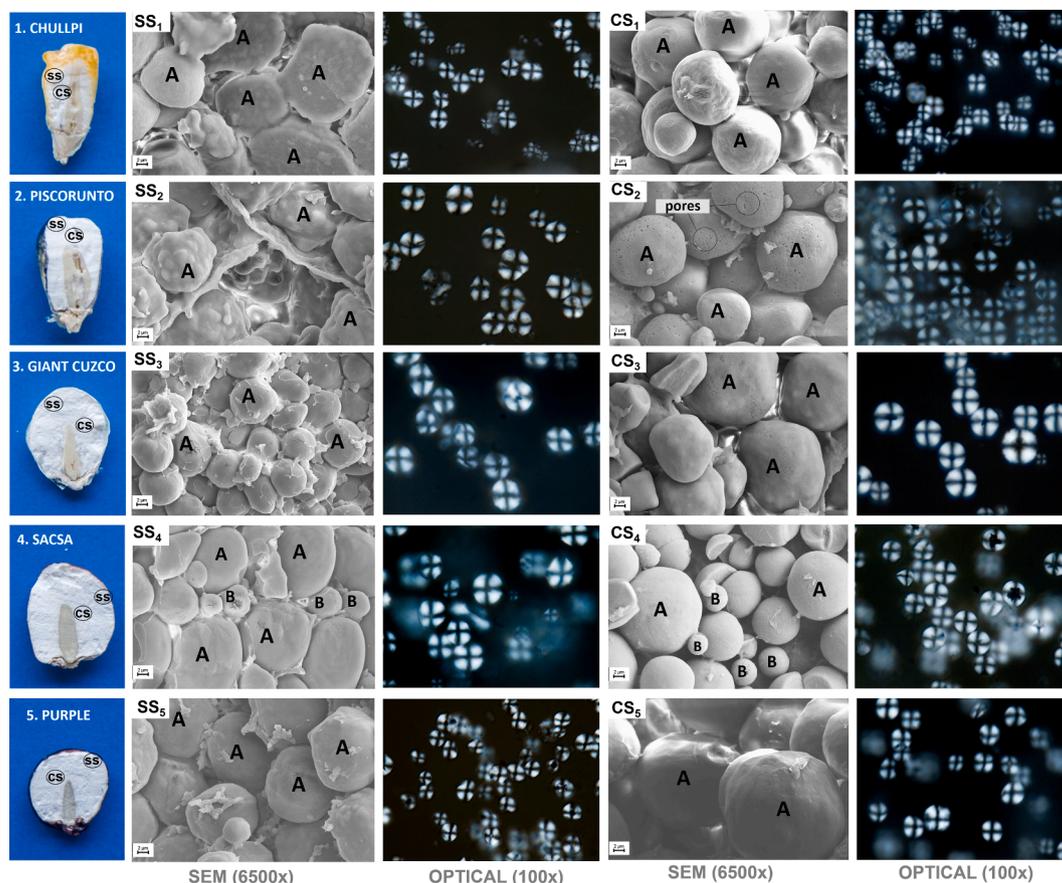


Fig. 3. Comparison of the starch granule morphology from the (SS) sub-aleurone endosperm and (CS) central endosperm, in five varieties of Peruvian Andean maize.

Table 3  
Starch granule morphology of five varieties of Peruvian Andean maize (PAM).

Starch area/ description	PAM				
	<i>Chullpi</i>	<i>Piscorunto</i>	<i>Giant Cuzco</i>	<i>Sacsa</i>	<i>Purple</i>
<b>Sub-aleurone endosperm</b>					
Shape	Polyhedral	Polyhedral	Irregular sphere	Polyhedral	Polyhedral
Surface <sup>1</sup>	Protuberances	Protuberances	Smooth	Smooth	Porous
Distribution	Monomodal	Monomodal	Monomodal	Bimodal	Monomodal
Size <sup>2,3</sup>	Type-A	Type-A	Type-A	Type-A	Type-B
Diameter (µm)	<11.06 to 17.61 > m = 14.00	<10.07 to 15.53 > m = 12.95	<11.70 to 19.58 > m = 15.75	<10.20 to 16.02 > m = 13.80	<2.30 to 7.95 > m = 4.33
Perimeter (µm)	<37.95 to 57.42 > m = 45.70	<34.24 to 50.48 > m = 42.35	<37.32 to 64.58 > m = 50.76	<38.44 to 48.39 > m = 41.04	<10.23 to 26.34 > m = 16.09
Area (µm <sup>2</sup> )	<91.58 to 218.50 > m = 138.59	<80.94 to 180.30 > m = 128.69	<101.20 to 292.80 > m = 186.94	<119.73 to 210.11 > m = 132.91	<15.23 to 59.35 > m = 51.02
<b>Central endosperm</b>					
Shape	Sphere	Irregular sphere	Polyhedral	Sphere	Sphere
Surface <sup>1</sup>	Smooth	Porous	Smooth	Smooth	Porous
Distribution	Monomodal	Monomodal	Monomodal	Bimodal	Monomodal
Size <sup>2,3</sup>	Type-A	Type-A	Type-A	Type-A	Type-B
Diameter (µm)	<12.26 to 15.22 > m = 11.48	<11.18 to 13.75 > m = 12.52	<10.80 to 12.38 > m = 11.06	<12.71 to 17.27 > m = 13.17	<3.26 to 9.73 > m = 5.76
Perimeter (µm)	<41.45 to 53.34 > m = 46.79	<35.59 to 43.68 > m = 40.34	<31.00 to 38.62 > m = 34.46	<42.10 to 56.10 > m = 42.94	<15.85 to 29.80 > m = 18.66
Area (µm <sup>2</sup> )	<106.90 to 179.40 > m = 146.67	<90.11 to 137.80 > m = 115.02	<58.58 to 104.60 > m = 83.10	<130.10 to 231.50 > m = 144.59	<18.40 to 65.62 > m = 24.79

<sup>1</sup> The most prominent appearance.

<sup>2</sup> Differentiation of sizes according to diameter measure Type-A > 10 µm, and Type-B < 10 µm.

<sup>3</sup> Data presented interval <minimum to maximum>, followed by the mean "m".

variations of temperature, so it presents a portion of Type-B starch.

Starch granules with smooth surfaces were observed in the endosperm of *Chullpi* (SS<sub>1</sub> and CS<sub>1</sub>), *Giant Cuzco* (SS<sub>3</sub> and CS<sub>3</sub>), and *Purple* (SS<sub>5</sub> and CS<sub>5</sub>). Some granules of *Piscorunto* (CS<sub>3</sub>) presented pores, with an approximate diameter of 0.3 μm. Meanwhile, starch granules of *Sacsa* (SS<sub>4</sub> and CS<sub>4</sub>) presented both types of surfaces, smooth in large granules and porous in small ones (Fig. 4).

The structure of pores observed in the starch granules of *Sacsa* (Fig. 4a) and *Piscorunto* (Fig. 4b) were similar to those reported by Huber and BeMiller (1997, 2000). The pores on the surface were connected with the granule's center through tunnel-type channels, varying their depth and number depending on maize.

Although it is still unknown how the formation of pores occurs, it has been proven to be related to the botanical source of the starch (Fannon et al., 1992). For example, it is more common to observe pores in the spherical granules of the floursy endosperm than the polyhedral or irregular ones (Dombrink-Kurtzman & Knutson, 1997). Moreover, the formation of pores is directly linked to the α-amylase activity of the grain, occurring first and faster in smaller granules than in larger ones (Blazek & Gilbert, 2010; Lindeboom et al., 2004). This information would explain the presence of pores in Type-B granules and absence in Type-A granules of *Sacsa* maize.

Pores with tunnel-type channels can also be observed in modified starches, where forced hydrolysis (Wu et al., 2011) and ultrasound (Qian et al., 2011) are used to perforate the starch granules. Nevertheless, the diameter of the pores achieved by these methods is on average 1 μm, which is lower than those naturally presented in *Sacsa* and *Piscorunto* maizes.

Porosity in the starch granules of some varieties of PAM can be of great importance. For example, Sujka and Jamroz (2007, 2010) observed that porous starches influence the mechanical and texture properties of food products. Huber and BeMiller (2000) and Weirong and Huiyuan (2002) determined that due to their large contact surface area, they have a higher chemical reaction rate and adsorption, respectively. Meanwhile, Han et al. (2005) and Glenn et al. (2010) showed that pore channels of starch granules serve as protein reserves and act as protectors of antioxidant compounds, respectively.

- Vitreous endosperm

Next to the pericarp (Fig. 5a), the vitreous endosperm of *Chullpi* presented polygonal, elongated, and compact structures with smooth surfaces, whereas close to the floursy endosperm (Fig. 5b), structures were irregular and presented some pores and protuberances.

Tapia et al. (1979) and Paliwal et al. (2000) explained that the compact matrices of the vitreous endosperm of sweet maizes, as *Chullpi*, result from the crystallization process of their sugars. According to Carrera et al. (2005), the differences observed in the two areas of the vitreous endosperm of *Chullpi* may be associated with the stage of the crystallization process. Order structures indicated a complete process,

while the irregular shapes next to the floursy endosperm would be associated with a transition phase.

The presence of vitreous endosperm in *Chullpi* may be linked to differences in its chemical composition (Section 3.2.1, Table 2), as well as its pasting properties and texture profile (Section 3.4, Table 4).

### 3.3.3. Germ

Differences were observed in the germ morphology between the PAM varieties (Fig. 2). Germen cells of *Chullpi* (d<sub>1</sub>), *Giant Cuzco* (d<sub>3</sub>), *Sacsa* (d<sub>4</sub>), and *Purple* (d<sub>5</sub>) presented irregular shapes, whereas those of *Piscorunto* (d<sub>2</sub>) were hexagonal, ordered, and flat. Similar structures have been observed by Rojas et al. (2017) in hybrid maizes where the embryo presented compact tissues and irregular cells.

There were difficulties during the SEM analysis of the germ of *Chullpi*, *Giant Cuzco*, *Sacsa*, and *Purple* kernels. They presented much reflection of light and brightness. Based on Pathan et al. (2010) study, it would be related to the chemical composition of samples since moisture and lipids tend to increase the refraction making difficult the SEM lens approach.

### 3.4. Pasting properties and texture profile of PAM

Table 4 shows the pasting properties and texture profile of PAM whole flours.

#### 3.4.1. Pasting properties

Floursy PAM varieties presented lower PT (69.48–73.82 °C) and higher PV (above 3200 cP), BD (2000–3600 cP), SB (1200–1700 cP), and FV (1900–2900 cP) than *Chullpi*. Though, *Chullpi* presented FV > PV while floursy PAM varieties had FV < PV (Table 4, Figure S-4).

The recorded pasting parameters indicate that the starch granules of floursy PAM have a greater facility to swell during hydration and can be easily broken during shearing at high temperatures; however, once disintegrated (gelatinization), they do not integrate (retrogradation) at the same level and speed during cooling. Whereas in *Chullpi*, the increase in viscosity during heating requires a higher temperature and time, and retrogradation occurs more easily.

According to the literature, this is due to the compaction degree of the endosperm. It is more difficult to break the protein matrix in the vitreous endosperm than in the floursy one since it is harder, more complex, and has numerous protein bodies. Then, it represents a physical barrier for the migration of water to the starch granules delaying its PV and BD (Zhang & Xu, 2019). Narváez-González et al. (2006) observed that maizes with a high proportion of floursy endosperm had lower PT (68–75 °C) and higher PV (3000–3500 cp) than those of hard and vitreous endosperm. Similar results were obtained by Zhang and Xu (2019) when comparing the pasting properties of vitreous and floursy maizes.

Therefore, our results can be related to the differences in the chemical composition and endosperm structure between PAM samples.

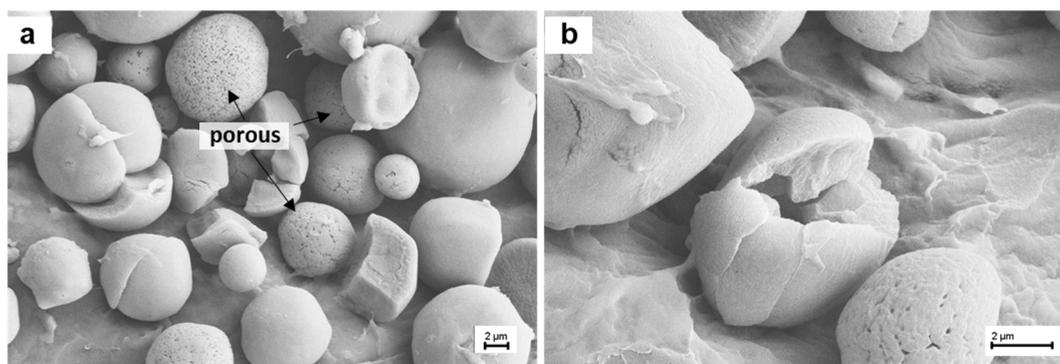


Fig. 4. Scanning electron micrographs (SEM) of (a) porosity and (b) internal pore structure of starch granules of *Sacsa* maize located in the central endosperm.

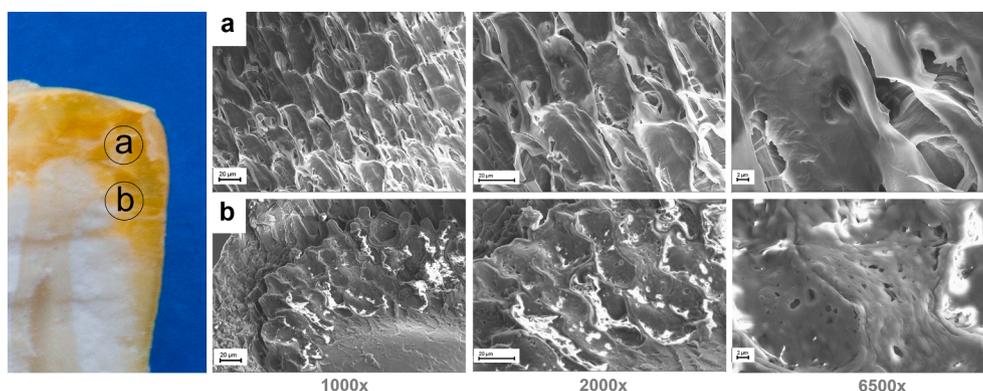


Fig. 5. Scanning electron micrographs (SEM) of the vitreous starchy endosperm of Chullpi maize in two zones: (a) next to pericarp and (b) next to floury endosperm.

**Table 4**  
Technological properties of five varieties of Peruvian Andean maize (PAM) whole flour.

Properties <sup>1</sup>	PAM				
	<i>Chullpi</i>	<i>Piscorunto</i>	<i>Giant Cuzco</i>	<i>Sacsá</i>	Purple
<b>Pasting</b>					
Pasting temperature (°C)	78.47 ± 0.25 <sup>a</sup>	70.78 ± 0.28 <sup>c</sup>	69.48 ± 0.03 <sup>c</sup>	70.53 ± 0.25 <sup>c</sup>	73.82 ± 0.23 <sup>b</sup>
Peak time (min)	7.89 ± 0.04 <sup>a</sup>	6.11 ± 0.04 <sup>b</sup>	5.89 ± 0.04 <sup>c</sup>	6.42 ± 0.04 <sup>b</sup>	6.49 ± 0.14 <sup>b</sup>
Peak viscosity (cP)	1553.33 ± 19.01 <sup>d</sup>	3641.67 ± 85.16 <sup>b</sup>	4419.33 ± 31.53 <sup>a</sup>	3884.67 ± 142.66 <sup>b</sup>	3290.67 ± 153.39 <sup>c</sup>
Breakdown (cP)	695.67 ± 28.43 <sup>d</sup>	2924.00 ± 59.92 <sup>b</sup>	3598.67 ± 47.43 <sup>a</sup>	2772.00 ± 103.70 <sup>b</sup>	2122.33 ± 79.51 <sup>c</sup>
Holding strength (s)	857.67 ± 10.79 <sup>b</sup>	717.25.89 ± 25.89 <sup>b</sup>	820.67 ± 51.33 <sup>b</sup>	1112.67 ± 40.25 <sup>a</sup>	1168.33 ± 87.84 <sup>a</sup>
Setback from trough (cP)	1128.67 ± 44.05 <sup>c</sup>	1251.67 ± 36.91 <sup>c</sup>	1534.33 ± 8.14 <sup>b</sup>	1562.33 ± 29.14 <sup>b</sup>	1706.33 ± 108.62 <sup>a</sup>
Final viscosity (cP)	1986.33 ± 34.15 <sup>c</sup>	1969.33 ± 62.78 <sup>c</sup>	2355.00 ± 43.86 <sup>b</sup>	2675.00 ± 66.20 <sup>a</sup>	2874.67 ± 194.54 <sup>a</sup>
<b>Texture</b>					
Firmness (N)	0.15 ± 0.00 <sup>c</sup>	0.79 ± 0.03 <sup>b</sup>	1.03 ± 0.07 <sup>a</sup>	0.84 ± 0.03 <sup>a</sup>	0.93 ± 0.03 <sup>a</sup>
Elasticity (mm)	3.42 ± 0.19 <sup>c</sup>	5.44 ± 0.37 <sup>a</sup>	5.00 ± 0.25 <sup>a</sup>	4.57 ± 0.29 <sup>b</sup>	4.56 ± 0.22 <sup>b</sup>

<sup>1</sup> Results are presented as mean ± standard deviation. Means followed by different letters on the same line differ significantly from each other for the Scott-Knott test of multiple comparisons ( $p < 0.05$ ).

As previously shown, *Chullpi* had a higher protein content (Table 2) and a portion of more compact vitreous endosperm (Figs. 2, 3, and 5) compared to floury PAM varieties.

Pasting parameters help determine the possible use of maize. Considering our results, from an economic point of view, low PT reduces energy consumption during food processing (Méndez-Montealvo et al., 2005). Then, floury PAM varieties would be ideal for use in the production of *tortillas* through the traditional nixtamalization process since it would save energy, whereas *Chullpi* would be better to produce flours. SB and FV values indicate the ability of the food to form a viscous paste or gels, affecting the final texture of a product and its stability during storage. Minor SB and FV values are ideal for products such as soups, sauces, food mixes, or ice creams where it is required to maintain the texture and avoid syneresis. Therefore, floury PAM varieties would be an excellent option to improve the texture of this kind of product as it increases its viscosity and does not retrograde easily.

### 3.4.2. Texture profile

Retrograde flours from floury PAM varieties had greater firmness and elasticity compared to *Chullpi* (Table 4). After refrigeration, the segregation of water (syneresis) was observed in the retrograde flour of *Chullpi*.

The hardness and elasticity observed in floury PAM varieties may be related to its higher ratio of starch: protein present their endosperm (11:1) compared to the vitreous one (6:1) (Wang & Wang, 2019), leading to a more significant association among starch molecules in the sample. Meanwhile, the syneresis observed in *Chullpi* sample could be associated with the greater association between starch and protein as the flour shows higher protein content (Table 2).

## 4. Conclusion

This study reveals some of the physicochemical, nutritional, morphological, and technological properties of the five main varieties of Andean maize currently cultivated in Peru. Physically, PAM kernels present a variety of sizes, shapes, and colors that allow us to obtain colored retrograde flours. Nutritionally, PAM has a higher concentration of dietary fiber and better quality proteins than other maize, presenting significant amounts of essential amino acids such as leucine and tryptophan. Moreover, PAM is rich in magnesium and unsaturated fatty acids oleic and linoleic. The endosperm of floury PAM varieties presented starch granules with different shapes, sizes, and surfaces; likewise, they have fewer protein matrices that facilitate their gelatinization, obtaining viscosity pastes that do not retrograde easily. Therefore, Peruvian Andean maize can help develop products as soups, willows, beverages, and porridge as a thickener with good nutritional value that also adds color to the product. It is suggested to continue with a study of the functional properties of its isolate starch, which is an ingredient of greater importance in the food industry.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodres.2020.110044>.

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