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Research note

Calcium content and speciation in alkaline-cooked corn studied by synchrotron Ca K-edge X-ray absorption spectroscopy

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ABSTRACT

Using Ca K-edge X-ray absorption spectroscopy the calcium uptake and species in alkaline corn have been studied and compared with corn starch and crystalline cellulose as main compounds in corn endosperm and pericarp. XANES data showed that calcium binds preferably to hemicelluloses in the pericarp. The main calcium species found by EXAFS in cellulose and starch is calcium carbonate although some protein-calcium species could be formed within the starch granules. From X-ray diffraction and microscopy techniques, pericarp dissolution, mainly at the amorphous hemicellulose fraction was inferred. The hemicellulose dissolution during steeping increases the apparent pericarp crystallinity, while the relative calcium content determined by XANES absorption edges reduces. XANES and EXAFS spectroscopies showed to be a valuable tool in order to determine the calcium species and to make a semiquantitative determination of calcium in the different nixtamalized corn fractions.

Tortillas and related products such as corn chips and *nachos*, among others, are made from corn dough prepared after an alkaline cooking process known as *nixtamalization* (FAO, 1992, González et al., 2005). During nixtamalization, a significant amount of calcium is incorporated into the corn grain (FAO, 1992). *Tortilla* is known to be a good source of bioavailable calcium, presumably because of the synergetic effect of an increase in calcium concentration together with the increment of the calcium-to-phosphorus ratio from 1:20 in raw corn to 1:1 in *tortilla* (FAO, 1992). The corn grain is basically formed of pericarp, endosperm, germ and the grain tip cap (Watson, 1994) with relative weight fractions of about 5.5% for pericarp, 9.6% for germ and 84.9% for endosperm (Bressani et al., 2004). Calcium binding abilities follow a trend where pericarp ˃ germ ˃ endosperm (González et al., 2005). Pericarp is mainly composed of cellulose and hemicellulose, and is supposed to have the highest calcium affinity (González et al., 2005). Under the typical *nixtamalization* condition reported herein, depicted in Figure S1 (Supplementary Information), evidence of partial hemicellulose dissolution as well as native cellulose framework exposition and swelling upon alkali penetration was observed, in accordance with the early work of Paredes-López and Saharoupolus-Paredes (1983).

Calcium uptake during nixtamalization has been largely studied. Valderrama-Bravo et al. (2010) showed that calcium incorporation not only depends on calcium ion diffusion, but is also related to calcium-salt clustering in the pericarp structures that are structurally affected during the nixtamalization time. Laria et al. (2005) described the initial free diffusion of the alkaline solution through the tip cap towards the fissures between the pericarp and the seed coat and through the pericarp surface. Laria et al. (2007) showed that the thermal profile governs the calcium diffusion kinetics coupled with the loss of material. Agitation and cooking time have been reported as additional factors influencing calcium uptake kinetics (Ruiz-Gutiérrez et al., 2010), as well as steeping time and temperature (Bressani et al., 2004). With respect to calcium species in the corn fractions, González et al. (2005), proposed that calcium in the hull is mainly linked to the carboxylate groups of the hemicellulose uronic acids, and found that hull loses its calcium binding ability because of hemicellulose dissolution. In the endosperm, Robles et al. (1988) found that Ca^{2+} binds mainly to the amylose fraction of the corn starch, preventing extensive gelatinization. They also suggested that Ca-induced interactions would

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occur between starch and the rest of the non-starch polymers. Finally, Reguera et al. (2000) cited by González et al. (2005) indicated that Ca incorporated to the endosperm forms inclusion compounds of Ca salts of fatty acids within the amylose helical structure.

X-ray diffraction (XRD) of nixtamalized pericarp samples show $CaCO_3$ and evidence of a partial dissolution of the amorphous hemicelluloses, but no evidence of calcite in the nixtamalized endosperm (Figure S2, Supplementary Information). XRD in nixtamalized celluloses confirmed that calcium binds only to the paracrystalline regions of cellulose, and that $Ca(OH)_2$ does not disrupt the crystal structure (Figure S3, Supplementary Information).

Synchrotron X-ray absorption near edge spectroscopy (XANES) in the Ca K-edge and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) of the pericarp, endosperm, starch and cellulose samples were obtained at different nixtamalization times and compared with calcium compounds: Ca, CaO, $Ca(OH)_2$, and $CaCO_3$. Synchrotron techniques offer the advantage of atomic scale resolution and sensitivity with minimum or null sample treatment (Sanghamitra et al., 2012). XANES is particularly suitable for chemical speciation of elements even in very diluted samples and in complex matrices (Parsons et al., 2008) and EXAFS is very sensitive to first neighbour distances. The XANES measurements in the calcium compounds (Figure S4 and Table S1, Supplementary Information) demonstrate the feasibility of qualitative identification of the Ca species in the nixtamalized samples.

Fig. 1 presents the normalized fluorescence Ca K-edge XANES spectra of the corn starch (Fig. 1a), endosperm (Fig. 1b), Elcema cellulose (Fig. 1c) and nixtamalized pericarp (Fig. 1d). Raw corn has a reported calcium content of about 70 ppm while processed raw corn starch has 10 ppm (Serna-Saldivar et al., 1990). This content

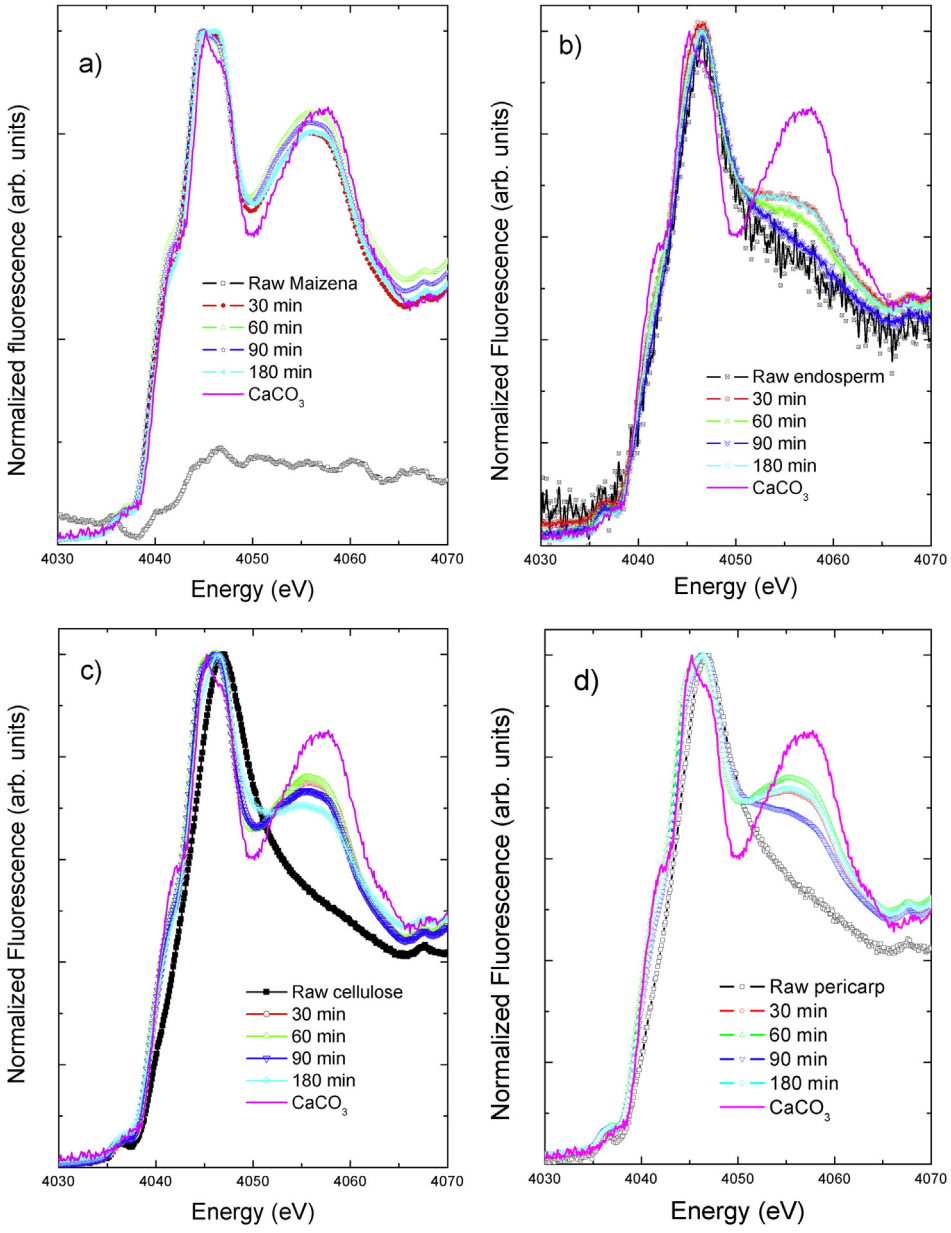

Fig. 1. Ca K-edge XANES spectra of series of raw and nixtamalized products compared with the $CaCO_3$ spectrum; a) Maizena corn starch, b) endosperm, c) Elcema cellulose d) pericarp.