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Distribution of Minerals in Quinoa (Chenopodium quinoa Willd.) Seeds

Yotaro KONISHI^a, Shigeru HIRANO^{ab}, Hideki TSUBOI^c & Masao WADA^c

- ^a Graduate School of Human Life Science, Osaka City University
- ^b Dai-Nippon Meiji Sugar Co., Ltd.

^c Application Technology Department, Naka Customer Center, Hitachi Science Systems Ltd.

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Distribution of Minerals in Quinoa (Chenopodium quinoa Willd.) Seeds

Yotaro Konishi,^{1,†} Shigeru Hirano,^{1,2} Hideki Tsuboi,³ and Masao WADA³

¹Graduate School of Human Life Science, Osaka City University,

3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

²Dai-Nippon Meiji Sugar Co., Ltd., 1-5-3 Nihonbashi, Chuo-ku, Tokyo 103-0027, Japan

³Application Technology Department, Naka Customer Center, Hitachi Science Systems Ltd.,

11-1 Ishikawa-cho, Hitachinaka, Ibaraki 312-0057, Japan

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The distribution of minerals in quinoa (Chenopodium quinoa Willd.) seed was examined using energy dispersive X-ray microanalysis (EDX) in combination with scanning electron microscopy (SEM). Phosphorus, K, and Mg coincided in localization in embryonic tissue. Since phytin globoids have been known to localize in protein bodies in embryonic cells of quinoa seed, it is thought that P is attributed to phytic acid and that K and Mg form to phytate. Calcium and K were present in the pericarp, where the cell wall is thickly developed, suggesting that these minerals are associated with pectin. Sulfur occurred in embryonic tissues, which would be derived from sulfur amino acid residues of storage proteins concentrated in the tissues. Abrasion of quinoa seeds resulted particularly in decrease in Ca content.

Key words: *Chenopodium quinoa* Willd; mineral; X-ray microanalysis; element mapping

Quinoa (*Chenopodium quinoa* Willd.) is an underexploited pseudocereal, originating from the Andes region of South America, and has attracted attention to the world food supply, because the seeds contain about 12% protein with a well-balanced amino acid composition.^{1–3)} Quinoa seeds are also rich in mineral nutrients. Koziol⁴⁾ has summarized that the contents of K (927 mg/100 g), Ca (149 mg/100 g), Mg (250 mg/100 g), P (384 mg/100 g), S (150–220 mg/100 g), Fe (13.2 mg/ 100 g), and Zn (4.4 mg/100 g) in quinoa seeds are much higher than those of cereals such as wheat and rice.

Quinoa seed appears like a convex lens of about 2.5 mm diameter, and starchy perisperm is surrounded by the embryo, where most of the protein, lipids, and minerals are concentrated.^{2,3)} Generally, mineral nutrient reserves, such as K, Mg, Fe, Zn, and so on, in mature seeds, are usually present in the form of phytate. In quinoa seeds, it has been observed that phytin globoids are included in protein bodies of embryonic cells and that P, Mg, and K are localized in the globoids with

Table 1. Mineral Contents of Quinoa Seeds

	Whole seed (A)	Dehulled seed (B)	B/A
Ca	86.3 ± 0.6	55.1 ± 0.4	0.63
Р	411.0 ± 4.1	404.9 ± 3.0	0.99
Κ	732.0 ± 5.5	656.0 ± 4.3	0.90
Mg	502.0 ± 2.4	467.9 ± 4.4	0.93
Fe	15.0 ± 0.1	14.2 ± 0.1	0.95
Zn	4.0 ± 0.1	4.0 ± 0.1	1.00

Values (mg/100 g) are mean \pm SD of 3 experiments. Quinoa whole and the dehulled seeds were ashed at 550°C for 24 h, then the samples were dissolved in 0.1 N HCl and filtered. Each of the minerals was measured by a Seiko SAS7500 atomic absorption spectrophotometer.

energy dispersive X-ray (EDX) analysis.^{5,6)} These analyses, however, were done by point analysis which involves analyzing areas of the size of the electron beam. In the aspect of mineral nutrition, we need the information of the overall distribution of mineral nutrients in whole quinoa seeds. Quinoa seeds are usually abraded for food uses to remove the pericarp, which contains saponin with a bitter taste.⁷⁾ Therefore, analysis of the dehulled quinoa seed is needed.

In this study, we examined the overall distribution of some minerals of quinoa whole seeds and the dehulled seeds by EDX analysis, in which an electron beam is two-dimensionally used to scan the surface of specimen (*i.e.* 1 μ m in depth) to collect characteristic X-rays, permitting a record of element mapping.

Mature quinoa seeds (var. *Real*, a product of Bolivia) without perianth were used in this study. Abrasion of quinoa seeds was done with a Toshiba brown rice pearling mill CRM 500 (Tokyo) for 1 min, which had been controlled to yield 93% in weight of native seeds.⁸⁾ Some mineral contents of quinoa whole and the dehulled seeds were measured according to the AOAC method.⁹⁾ As shown in Table 1, it was found that the degree of loss of Ca was higher than those of other minerals by abrasion.

For element mapping, a quinoa seed was cut in cross

[†] To whom correspondence should be addressed. Fax: +81-6-6605-2813; E-mail: konishi@life.osaka-cu.ac.jp



Fig. 1. Refractive Electron Image (REI) and Element Mapping of a Quinoa Seed Fractured in Cross Section. In the REI, the hypocotyl-radicle axis (H) is seen in the upper left, and radicle (R) and cotyledon (C) are in the lower right. Because of limitation of the stage area, a part of the seed is out of sight. In recording element mapping, the K α line of the characteristic X-ray was counted and expressed as counts per sec (cps) with different colors. PC, pericarp; P, perisperm. Scale bar indicates 650 μ m.

section with a cutter knife, and was put on a stage and fixed with a commercial adhesive. EDX analysis was done at a stage temperature of -10° C, at a sample chamber pressure of 50 Pa, and at accelerating voltage of 20 kV with a Horiba EMAX-7000 EDX spectrophotometer in combination with a Hitachi S-2380N variable pressure scanning electron microscope. It should be noted that this type of analysis is qualitative because of variability in X-ray photon collection arisen from the surface roughness of specimen.

As shown in Fig. 1, in quinoa whole seed, it was found that P, K, and Mg were coincidently located in embryonic tissue, except for procumbium, showing a donut-like distribution in the hypocotyl-radicle axis. These observations were similar to that of seeds of *Amaranthus*,¹⁰ taxonomically close to *Chenopodium*. By a point EDX analysis, P, K, and Mg have been detected in carbon-coated embryonic tissues⁵ or the globoid crystals obtained from powdered preparation of embryonic tissues⁶ of quinoa. Prego *et al.*⁶ concluded that P, K, and Mg are component of the phytin globoid crystals within protein bodies and that X-ray intensities of the three elements were not significantly different between cotyledon and hypocotyl-radicle axis. Element mapping analysis in this study supports their observations. Thus, P is suggested to be phytic acid, and K and Mg are conceived to form complexes with phytic acid.

Varriano-Marston and DeFrancisco⁵⁾ have recognized that K is located in the peranth and pericarp (layer beneath the perianth). We also found that K occurred in pericarp and seed coat (Fig. 1), in contrast to *Amaranthus* seeds.¹⁰⁾ Since pericarp and seed coat are composed of cell wall layers, K is suggested to be associated with carboxyl group of pectin molecules in the cell wall.

Calcium was scarcely found in embryonic tissues of quinoa seeds. Similar observations have been previously reported.^{5,6)} In this study, we found that Ca occurred mostly in the pericarp and seed coat as well as in the boundary between perisperm and embryo (Fig. 1). From the data reported here, it is likely that Ca is associated with the carboxyl groups of pectin molecules in cell wall to form Ca-pectin complexes, as in *Amaranthus* seeds.¹⁰

According to De Bruin,¹¹⁾ total sulfur content of quinoa seeds has been shown to be 150–220 mg/100 g. Since the amount of S is similar level to P, K, Mg, or Ca, it was possible to record mapping of the element. As shown in Fig. 1, S was uniformly distributed in hypocotyl-radicle axis of embryonic tissues, which was contrast to the distribution of P, K, and Mg in the same

Mg P RE 255 0 611 cps 0 1092 cps K S Ca 742 cps 0 786 cps 0 480 cps

Fig. 2. Refractive Electron Image (REI) and Element Mapping of the Dehulled Quinoa Seed Fractured in Cross Section. In the REI, pericarp (PC) scarcely remained. Cotyledon (C) was not seen due to preparation of the specimen. Element mapping was done similarly to that described in the legend of Fig. 1. Scale bar indicates $650 \,\mu\text{m}$.

region. A similar observation has been also found in Amaranthus seeds.¹⁰⁾ Brinegar et al.^{12,13)} have found 11S globulin (Chenopodin) and high-cysteine 2S protein as storage proteins of quinoa seeds, which comprise 35% and 37%, respectively, of total protein. The 2S protein has 15.6 mol% of cysteine and 0.6 mol% of methionine. Therefore, the distribution of S in the embryonic tissues suggests to be derived from sulfur amino acid residues of these proteins. Mapping of Fe and Zn could not be displayed in this study, because of the lower contents (see Table 1).

Figure 2 shows mineral mapping of a dehulled quinoa seed. As one would expect, Ca and K in pericarp had mostly disappeared. There were no effects of abrasion on P, K, and Mg localized in the embryo. In the aspect of nutrition, thus, abrasion has the disadvantage of loss of the Ca content, in particular (Table 1).

In conclusion, this study provides not only basic knowledge of the overall distribution of minerals in quinoa seeds, but also new information on the fact that abrasion for food uses of quinoa seeds decreases mineral nutrients.

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