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# *Calcium*
## *Chemistry, Analysis, Function and Effects*

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CHAPTER 16

# Calcium – Function and Effects: Rice Calcium and Phytic Acid Levels

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## 16.1 Introduction

Rice is the seed of the monocot plant *Oryza sativa* or *Oryza glaberrima*. Basically, rice is a starchy crop, which acts as the primary food source for more than half of the world population. According to data of 2010, rice is the second-highest produced grain worldwide, after maize. In Asia, it serves as the major source of energy, protein, thiamine, riboflavin, niacin, iron and calcium in the diet (Juliano, 1997). Rice is also the most important staple food in China. In 2012, the national production was estimated at 20.6 million tons (FAO, 2014). Previous reports indicated a rice consumption in China of 251 g per capita per day, accounting for 30.4% of the supply of dietary energy, 19.5% of dietary protein, and 2.5% of dietary fat (Kennedy *et al.*, 2002).

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Rice does not fulfill all nutritional requirements. It does not supply minerals adequately because of its low content of minerals, and moreover a loss of minerals takes place during processing. In addition, rice contains phytic acid. Phytic acid is the most important antinutritional factor (ANF) impeding the availability of divalent minerals. It forms complexes with mineral ions, such as Fe, Zn and Ca, thereby reducing their bioavailability.

The concentrations of minerals and mineral inhibitors vary due to genetic diversity, soil and climate of cultivation, and agricultural practices (such as irrigation and fertilization), postharvest conditions and processing prior to consumption (Phuong *et al.*, 1999; Liang *et al.*, 2007). Genetic factors determine the seed morphology and to some extent the levels of minerals, which mostly occur as phytic acid chelates. Cultivation practice affects the uptake of minerals from soil and their distribution throughout the plant (Slingerland *et al.*, 2009).

Rice has the highest food yield and food energy yield among all the important cereals, and contrary to maize that is predominantly used for feed or industrial purposes, 95% of rice is for food use, so even a small change in its nutritive value is highly significant. Total mineral content (ash content) of brown rice and white rice (milled rice, polished rice) is about 1–1.5% and 0.5–0.8%, respectively. Calcium, iron, zinc and cadmium are the most relevant mineral elements in rice. Rice also contains phytic acid, approximately 1% in brown (cargo) rice, and much less in white (polished) rice. Phytic acid is of interest because of its antinutritional effect, although at low concentrations it also has positive effects on human health. In this chapter we focus on calcium, in relation to the antinutritional effect of phytic acid.

## 16.2 Calcium in Rice

Calcium plays an important role in human health since it participates in building stronger, denser bones early in life and keeps bones strong and healthy later. Approximately 99% of the body's calcium is stored in the bones and teeth. In addition to the obvious structural role of the skeleton, it also functions in muscle and nerve activity, coagulation of blood, and other physiological phenomena. Notably, calcium deficiencies constitute predisposing conditions for some common chronic diseases. They increase the risk of cancer, particularly of breast, colon, and prostate gland, as well as of metabolic disorders, *e.g.* metabolic syndrome, and hypertension (Peterlik and Cross, 2005).

It is vital, therefore, that adequate dietary calcium is consumed at all stages of life. Dairy products are excellent sources of calcium, both qualitatively and quantitatively. Both the amount in diet, and the absorption of dietary calcium in foods are critical factors. Food made of diverse ingredients will contain different levels of calcium, whereas it may contain antinutritional factors such as oxalic acid and phytic acid, which bind calcium and reduce its absorption. Green leafy vegetables, seeds and legumes are good sources of calcium. Some vegetables such as kale, celery, collard, pak-chee-lao, Chinese cabbage and soybean sprouts, containing low levels of dietary fiber, phytic acid and oxalate, have a higher calcium dialyzability (20–39%) than Indian mulberry and sesbania leaves (11–18%); and even 1.3–1.6 times that of milk powder. In contrast, amaranth, wild betal and white and black sesame seeds that contain high levels of oxalate (680–2620 mg/100 g) had the lowest dialyzable calcium (Achiraya *et al.*, 2004).

### 16.2.1 Calcium Contents in Rice Products

Calcium contents of rice products reported in different studies are summarized in Table 16.1.

Rice and rice products are poor sources of calcium, and only a few studies have been published. Calcium contents in brown rice depend on variety and cultivation location. Generally, white polished rice contains lower levels of calcium than the original brown cargo rice, and this loss is mainly caused by polishing (Doesthale *et al.*, 1979). Levels of calcium in other rice products are mainly due to processing and/or added ingredients. For example, higher levels of calcium in infant foods result from ingredients formulation and fortification (Liang *et al.*, 2010).

From Table 16.1, we can also see significant differences in calcium contents published by different researchers. This may stem from both the rice products sampled as well as the methods of analysis used. Atomic absorbance spectrophotometry (AAS), energy-dispersion X-ray, and inductively coupled plasma (ICP)-AAS or ICP-OES (optical emission spectrophotometry)

**Table 16.1** Calcium contents of rice products (mg/100 g, dry basis). Calcium contents of rice products published by different researchers are summarized. There are not many studies on calcium nutrition of rice products. The data showed a big variation of different products, and indicated the effects of processing and materials used.

| Products | Average | Lowest value | Highest value | Number of samples | References |
|---|---|---|---|---|---|
| **Brown rice** | | | | | |
| Worldwide | 12.1 | 3.7 | 26.4 | 1259 | Gregorio *et al.* (2009) |
| Bangladesh | 22.2 | 17 | 32 | 10 | Tamanna *et al.* (2013) |
| China | 28.6 | 24.0 | 33.0 | 3 | Liang *et al.* (2010) |
| Germinated rice | 38.7 | — | — | 1 | Liang *et al.* (2010) |
| Parboiled rice | 1.9 | 1.3 | 2.3 | 9 | Tamanna *et al.* (2013) |
| Milled rice | 3.4 | 2.52 | 4.74 | 4 | Ma *et al.* (2005) |
| Milled rice | 6.8 | 5.0 | 11.0 | 8 | Liang *et al.* (2010) |
| Cooked rice (polished) | 8.23 | 7.08 | 9.07 | 4 | Ma *et al.* (2005) |
| Rice noodle | 14.01 | — | — | 1 | Ma *et al.* (2005) |
| Rice noodle | 27.8 | 3.0 | 75 | 7 | Liang *et al.* (2010) |
| Rice cracker | 26.7 | 6 | 59 | 7 | Liang *et al.* (2010) |
| Infant food | 455.0 | 408 | 532 | 4 | Liang *et al.* (2010) |

are presently the main methods for mineral analysis. Procedures for pretreatment of samples, their digestion and detection limits of equipment also affect the absolute levels of minerals reported in rice (Liang *et al.*, 2007).

### 16.2.2 Availability of Calcium from Rice Products

Low bioavailability of dietary calcium is one of the main reasons for deficiencies. Factors such as the physical state of calcium (soluble or insoluble) in food, the presence of inhibitors of mineral uptake (*e.g.* oxalic acid, phytic acid), the individual calcium status of the consumer, will influence the absorption of calcium by the human body. It was reported that the *in vitro* solubility of calcium ranged between 0 and 87%, with lowest average (12%) in brown rice and highest average (50%) in infant foods (Liang *et al.*, 2010). Mineral solubility could be improved by various strategies. For calcium in rice products, phytic acid is the main factor that inhibits its availability, since only traces of oxalic acid are present. Enzymatic pretreatment of white rice with phytase was shown to significantly improve mineral solubility (Liang *et al.*, 2009).

## 16.3 Phytic Acid in Rice

### 16.3.1 Phytic Acid and its Chemical Determination

#### *16.3.1.1 Phytic Acid*

Phytic acid, or myo-inositol 1,2,3,4,5,6 hexakis dihydrogen phosphate (also known as inositol hexaphosphoric acid or myo-inositol hexakisphosphate-IP6), has the molecular formula $C_6H_{18}O_{24}P_6$ and molecular weight 660.04. Phytic acid is a saturated cyclic acid and a natural plant compound found in most cereal grains, legumes, roots, tubers, nuts and oilseeds. Phytic acid has a unique structure that explains its characteristic properties. Phytic acid has 12 replaceable protons and at physiological pH, the phosphate groups of phytic acid are negatively charged, allowing them to form complexes (chelates) with multivalent cations, positively charged proteins, and starch (either directly or indirectly) (Figure 16.1).

Phytic acid is the principal storage form of phosphorus in many plant tissues, especially in bran and seed. Phytate occurs in cereals as a mixed potassium, magnesium, and calcium salt of phytic acid (De Stefano *et al.*, 2002). Phytate is heat resistant and cannot be digested by humans or nonruminant animals. Phytate can be degraded by phytase, either as endogenous enzyme in seeds and accumulated during germination, or by exogenous microbial enzymes, to myo-inositol or lower inositol phosphates (IP1–IP5), while releasing phosphorus and minerals at the same time.

Endogenous phytase, which is mainly located in the outer layer of cereals kernels, is activated and accumulated during seed germination, and acts on phytic acid to release inorganic phosphate, which is then utilized for plant

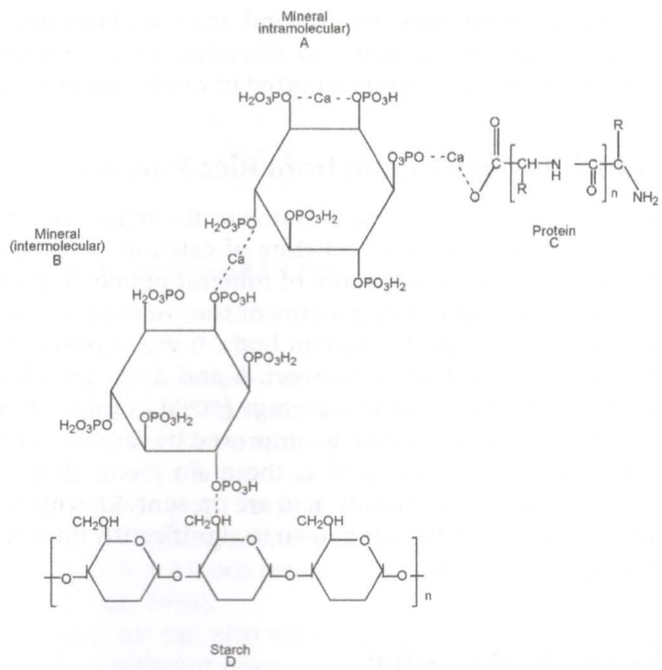


**Figure 16.1** Chelates of phytic acid with different compounds in food. Chelates of phytic acid with minerals, protein and starch are illustrated. Calcium is used as model mineral. (A) Mineral chelated in one molecular of phytic acid; (B) mineral chelated in two molecules of phytic acid; (C) chelate with protein; (D) chelate with starch. The figure is adapted and modified from Oatway *et al.* (2001).

growth, and serves as a natural buffer in grains as well. With degradation and the release of phosphate by phytase, lower inositol phosphate esters, such as pentakis-, tetrakis-, tris-, bis- and monophosphate, and even inositol are generated (Lönnerdal *et al.*, 1989). Steeping in demineralized water with 0.5 mM calcium chloride and 0.1 M hydrogen peroxide at 20 °C for 24 h led to the lowest phytase activity in brown rice, which was only 1/4 that of raw rice. Phytase activity increased with prolonged sprouting time and gradually reached stable levels in the sprouting stage. After 5 d sprouting, the phytase activity in brown rice reached 320–340 U $kg^{-1}$(unless stated otherwise, all are expressed on dry matter basis), which was about 1.5 times higher than in the raw material. Compared to extreme conditions (either strong acidic or alkaline), steeping in demineralized water at neutral pH (6.8) provided the optimum pretreatment prior to sprouting at 25 °C, to activate maximum levels of phytase (Ou *et al.*, 2011).

It was reported that application of microbial phytase in rice fractions led to a decrease of phytic acid content and an increase of free phosphate. In white rice, in kernel as well as ground flour, phytic acid contents decreased to levels below the detection limit after treatment with 500 U $kg^{-1}$ dry matter phytase, at 55 °C, pH 2.5–4 for 30 min. An increase of soluble phosphorous indicated stronger effects on flour. Under the same conditions, added phytase had no significant effect on phytic acid content in brown-rice kernels, which suggested that testa and aleurone layers acted as a barrier to influx of, *e.g.*, phytase and diffusive loss of matter.

#### *16.3.1.2 Chemical Determination of Phytic Acid*

Among the different techniques proposed to determine phytic acid, the most widely accepted are the AOAC anion-exchange method, and the high-performance liquid chromatography (HPLC) method. The anion-exchange method was adopted as the China National Standard Analysis Method. The method consists of subsequent extraction, separation on an anion-exchange resin, and spectrophotometric detection of the reaction product with ferric chloride ($FeCl_3$) and sulfosalicylic acid. Phytic acid in samples is extracted by a solution of sodium sulfate (100 g $L^{-1}$)–hydrogen chloride (1.2%) at room temperature for 2 h. The extract is then filtered or centrifuged for clarification. The clarified extract is mixed with sodium hydroxide (30 g $L^{-1}$) and distilled water followed by separation on an anion resin column (resin, AG1-X4, 100–200 mesh). The column is then washed with sodium hydroxide (0.05 mol $L^{-1}$). Phytic acid is eluted with sodium chloride (0.7 mol $L^{-1}$). Next, the absorbance of a mixture of eluate and $FeCl_3$ (0.03%) and sulfosalicylic acid (0.3%) is measured at 500 nm using a spectrophotometer (Ma *et al.*, 2005). The limitation of this method is that it cannot distinguish IP6 from other inositol phosphates (IP1–IP5), so the detected result is higher than the real value of IP6.

The HPLC method can identify different forms of inositol phosphates. This method is sensitive and suitable for detection of low concentrations.

Phytic acid is normally recognized as an ANF in cereals and legumes. It combines minerals and proteins, and influences their solubility and bioavailability. The intake of much phytic acid might be one important factor causing deficiency of essential nutrients.

In recent years, some beneficial health effects of phytic acid have also been reported. Phytic acid is an effective antioxidant (Cornforth, 2002). It has also been reported that phytic acid can reduce the toxicity of some heavy metals due to its strong chelating capacity (Persson *et al.*, 1998).

### 16.3.2 Phytic Acid Contents of Rice and Rice Products

#### *16.3.2.1 Phytic Acid in Brown Rice*

Rice cultivation is ideally suited to countries and regions with low labor costs and high rainfall; however, rice can be grown practically anywhere, even on a steep hill or mountain area with the use of water-controlling terrace systems. It was reported that rice consumption in sub-Saharan Africa is increasing yearly and will rise by 50% from 2005 to 2015 (Gregorio *et al.*, 2009). Currently, it is estimated that more than fifty thousand varieties of rice exist in China, of which about two hundred and thirty are grown at a commercial scale.

Phytic acid contents can fluctuate because phytates are the main form of storage phosphorous in cereal grains, representing about 70% of total phosphorous in the seed. During the development of the rice seed, phosphorous is deposited in the form of mixed phytates, together with some mineral cations, such as potassium, magnesium, calcium, iron, and zinc. This process is influenced by genetic characteristics, environmental conditions and agricultural practice. Table 16.2 presents published data of phytic acid in brown rice.

Different phytic acid contents were found in brown rice from different sources. The highest phytic acid content was 19.4 mg $g^{-1}$, in commercial brown rice from China, and the lowest was 4.1 mg $g^{-1}$, from Bangladesh. Phytic acid ranged from 4.05–6.35, 6.9–19.4 and 8.6–17.6 mg $g^{-1}$, respectively, in brown rice from Bangladesh, China and Korea. Combined effects of rice

**Table 16.2** Phytic acid content (mg $g^{-1}$) of brown rice from Bangladesh, China and Korea. Phytic acid contents in brown rice from different countries were summarized. Rice from Bangladesh had the smallest variation, while rice from China had the biggest phytic acid contents range. Different sources of samples, either by cultivation practices of sample collections support the effects of genetic characteristics, agricultural practice and cultivation location on phytic acid contents in rice.

| Country | Average | Lowest | Highest | Number of samples | Origin of samples | References |
|---|---|---|---|---|---|---|
| Bangladesh | 5.06 | 4.05 | 6.35 | 10 | Collected from Bangladesh Rice Research Institute | Tamanna *et al.* (2013) |
| | 9.6 | 7.2 | 11.9 | 56 | Collected from regional Academy of Agricultural Science | Liang *et al.* (2007) |
| | 17.5 | 14.9 | 19.4 | 3 | Purchased at supermarkets in Beijing | Liang *et al.* (2010) |
| | 8.73 | 6.9 | 10.3 | 72 | Grown at the experimental farm | Liu *et al.* (2005) |
| | 8.15 | 6.75 | 9.42 | 24 | Grown at four ecologically different locations | Liu *et al.* (2005) |
| China | 8.68 | 6.99 | 10.34 | 29 | Grown at the experimental farm | Wu *et al.* (2007) |
| Korea | 12.6 | 8.6 | 17.6 | 68 | — | Lee *et al.* (1997) |

genotype, environment (*e.g.* soil, temperature, rainfall), and cultivation practice underlie such significant differences. The contribution of genetic characteristics to phytic acid contents was demonstrated by growing different varieties under the same environmental conditions, with the same cultivation practice (Liu *et al.*, 2005; Wu *et al.*, 2007). A comparison of 24 rice varieties, grown in four ecologically different locations of China, *i.e.* Hangzhou, Jiaxing, Changzhou and Xi'an, showed that location represented a greater contribution to phytate levels than cultivars (Liu *et al.*, 2005). The environmental effect appears to be predominant in determining phytic acid.

In addition, sensitivity and accuracy of determination method may also influence results. Tamanna *et al.* (2013) selected ten high-yield rice varieties cultivated in Bangladesh, which differed in their morphology, 5 long-, 3 medium- and 2 short-grain. The lowest contents and the smallest variation of phytic acid contents were found for those genotypes may be the result of low sensitivity of the determination method. They determined phytic acid contents with the following method. Phytic acid reacts with $FeCl_3$ and form ferric phytate. The available ferric ion after reaction is determined by developing a blood-red color with potassium thiocyanate (Tamanna *et al.*, 2013). The AOAC method, which gives higher values, was applied in the other studies.

### 16.3.2.2 Phytic Acid in Rice Products

Variation of phytic acid contents gives the possibility for production of rice with low phytic acid contents in grains. Using suitable cultivars for a given location is an effective approach to achieve high yield and control the phytic acid contents in rice.

The rough rice, or paddy, contains inedible and edible parts. The grains are first "milled" using a huller to remove the outer inedible part, *i.e.* the husk (or hull). The product of "milling" is the edible part, which is called brown rice. Brown rice is not widely consumed because its sensory properties are not appreciated by most consumers, especially in Asia. Brown rice is polished to remove the bran, thereby creating polished rice (also called white rice). White rice is commonly consumed as cooked rice or used as raw material for food. An overview of commercial rice products (Liang *et al.*, 2010) is listed in Table 16.3.

White rice is the most popular rice product all over the world, whereas the other rice products have their more specific consumer markets. For example, parboiled rice is mainly consumed in South Asia, Europe, Africa and the Middle East; germinated rice is appreciated by Japanese. Rice noodle is frequently consumed as breakfast in the South of China.

Phytic acid contents in processed rice products are summarized in Table 16.4.

Germinated rice contained the highest concentration of phytic acid of all processed rice products, followed by parboiled rice, both of them had a similar phytic acid concentration as brown rice (Liang *et al.*, 2007; Tamanna *et al.*, 2013). Rice noodles had the lowest level.

**Table 16.3** Commercial rice products.

| Category | Product | Processing |
|---|---|---|
| Primarily processed products[a] | Brown rice | Hulled only |
| | Germinated rice | Brown rice, germinated until a sprout length of 0.5–1.0 mm is reached |
| | Parboiled rice | Paddy is parboiled, followed by hulling, milling and polishing |
| | White rice | Milling and polishing to remove the outer layer of brown rice and obtain nice appearance and edible quality |
| Intensively processed products[b] | Rice noodle[c] | White rice soaked in water, ground with or without water, steamed, extruded, cooled and dried |
| | Rice noodle[d] | White rice together with other ingredients, such as starch or soy protein soaked or not soaked in water, ground, steamed, extruded, cooled and dried |
| | Rice crackers | Rice mixed with water, pulped, molded, puffed, and baked |
| | Infant foods | White rice ground to powder, roasted, enzyme-treated, drum dried and formulated with other ingredients |

[a]Primarily processed products: still can recognize the shape of rice kernel, include brown, white and germinated rice.
[b]Mainly originate from further processing of white rice, include rice noodles, rice crackers and rice-based infant foods.
[c]Ingredients of rice noodles are white rice and water, no other cereal materials added.
[d]Other cereal materials were used together with rice.

**Table 16.4** Phytic acid contents (mg $g^{-1}$) of rice products. Phytic acid contents of different types of intensively processed rice products published by different researchers are summarized. Germinated rice and rice noodle by Ma *et al.* only had one sample so there were no lowest and highest values for those products. Germinated and parboiled rice had the same levels of phytic acid contents as brown rice. Affected by processing procedures, rice noodle had the lowest level.

| Products | Average | Lowest | Highest | Number of samples | References |
|---|---|---|---|---|---|
| Germinated rice | 13.1 | — | — | 1 | Liang *et al.* (2010) |
| Parboiled rice | 5.34 | 4.25 | 6.65 | 9 | Tamanna *et al.* (2013) |
| Milled rice | 1.15 | 0.55 | 1.83 | 4 | Ma *et al.* (2005) |
| Milled rice | 1.6 | 0.6 | 2.4 | 8 | Liang *et al.* (2010) |
| Cooked rice | 0.31 | 0.14 | 0.38 | 4 | Ma *et al.* (2005) |
| Rice noodle | 0.14 | — | — | 1 | Ma *et al.* (2005) |
| Rice noodle | 1.2 | 0 | 4.1 | 7 | Liang *et al.* (2010) |
| Rice cracker | 1.4 | 0.8 | 2.6 | 7 | Liang *et al.* (2010) |
| Infant food | 2.3 | 0.9 | 5.9 | 4 | Liang *et al.* (2010) |

Phytic acid contents of most rice products are much lower than that of brown rice. High-pressure steaming for parboiled rice production had no significant effect on phytic acid contents, and parboiled rice (without milling and polishing) had even higher phytic acid contents than raw brown rice (Tamanna *et al.*, 2013). Commercial-scale germination duration to produce germinated rice is apparently insufficient to activate and accumulate endogenous phytase, which could have reduced phytic acid and thus lowered phytic acid contents (Liang *et al.*, 2008a). The phytic acid content in milled rice is much lower than in brown rice, due to milling and polishing (Liang *et al.*, 2008b). The combined effects of loss during soaking, degradation by endogenous phytase and micro-organisms in rice-noodle processing brought out the lowest phytic acid content in rice noodles (Liang *et al.*, 2009).

## 16.4 Location of Calcium, Phosphorous and Phytic Acid in Rice Kernel

Brown rice (hulled rice) is composed of surface bran (6–7% by weight), endosperm (~90%) and embryo (2–3%). As in most cereal grains, the kernel does not reveal a homogeneous structure from its outer (surface) to its inner (central) part (Itani *et al.*, 2002). Milling by abrasion is an important mechanical procedure for the production of white rice, which is referred to as milled, polished or whitened rice when 8–10% of the outer layer (mainly bran) of brown rice is removed (Kennedy *et al.*, 2002). As a consequence, information on the location of components will greatly help to improve sensory properties and retain essential nutrients in white rice. Early studies described the effect of milling on levels of minerals and their spatial distribution in relation to approximate milling degrees, such as lightly milled, reasonably milled and well milled, or as fractions I, II and III, respectively (Kennedy and Schelstraete, 1975; Tabekhia and Luh, 1979). A study on the effect of milling on mineral and trace element composition of raw and parboiled rice indicated that milling rates of brown rice of 5% and 10% led to phosphorous decrease from 349 mg/100 g to, respectively, 167 and 101 mg/100 g, while for parboiled rice they were reduced from 350 mg/100 g to 219 and 138 mg/100 g (Doesthale *et al.*, 1979).

Development of precisely controlled milling machines, and X-ray imaging enabled the study of the spatial distribution of compounds and elements in rice kernels. Studies on Indian rice indicated that milling extent significantly influences losses of magnesium and calcium (Bajaj *et al.*, 1989). The distribution of minerals such as magnesium, potassium, phosphorus, calcium and sulfur in quinoa seeds was mapped by X-ray fluorescent microscopy techniques (Emoto *et al.*, 2004).

Using two varieties of short-grain brown rice as samples, precise abrasive milling was used to obtain a range of milling degrees, and X-ray imaging methods were applied to map the distribution of different minerals.

### 16.4.1 Location of Elements with X-Ray Microscope

X-ray images indicated that a high calcium density layer is located in the outer layer of the brown-rice kernel. Most calcium is found in rice bran, in contrast to the location of zinc (Liang *et al.*, 2008b). The distribution of calcium in the kernel differs with variety (Figure 16.2). In Ji 307, a distinct region with a high density of calcium occurs around the kernel. The embryo is the part that contains the highest density of calcium. Very little calcium is located in the inner bran layer and core endosperm. In Nanjing No. 1, a high calcium density in the bran, but not in the embryo is observed. On the other hand, some calcium is located in the endosperm. Thus, considering the human nutrition of calcium, it would be easier to maintain more calcium in white rice of Nanjing No. 1 than in Ji 307.

Images of spatial distribution of phytic acid (as phosphorous) in the whole brown-rice kernel and in the embryo obtained by X-ray fluorescent scanning are shown in Figure 16.3. Phosphorous is distributed unevenly in the whole brown rice kernel. The highest density of phosphorous occurred at the boundary of embryo and endosperm (Figure 16.3a). In contrast with the high density of zinc in embryo, there is not much phosphorous located in the embryo, which is similar to the case of calcium. The whole kernel is practically surrounded by a high-density phosphorous layer that tends to decrease from the surface region inward. When compared with other varieties, we observed that Ji 307 has a similar phosphorous distribution compared with Bijing 37, both being short-grain japonica rice. The distribution of phosphorous in the rice kernels suggested that at least the outer layer should be removed if we want to significantly decrease phytic acid in milled rice, since 70–85% of phosphorous occurs as phytic acid in rice.

### 16.4.2 Location of Phytic Acid by Abrasive Method

From Figure 16.4 we conclude that retention of phytic acid decreases and mass loss increases with prolonged milling. Although it was observed earlier that all minerals (including phosphorus) decrease from the outermost fraction (Itani *et al.*, 2002) it appears here that more than 70% of phytic acid was removed by milling off 8% of the outmost layer, which was accomplished by 60 s milling time. In practice, this 8% of kernel represents mainly the bran. With progressive milling, the rate of loss of phytic acid and mass decreased. This may be caused by the harder structure of the inner parts of the rice kernel. The results also tell us that about 80% of kernel weight only contains less than 5% total phytic acid.

X-ray images showed the location of elements in rice kernels, while abrasive milling approaches enabled a quantification of the distribution of phytic acid. In conclusion, the location of the minerals (phosphorous, calcium and zinc) differs per element and rice variety. From the fact that calcium occurs in the same parts where phosphorous predominates, we could expect that most of the calcium is present in the form of phytate. Consequently, the bioavailability of calcium could be improved when phytic acid is degraded.

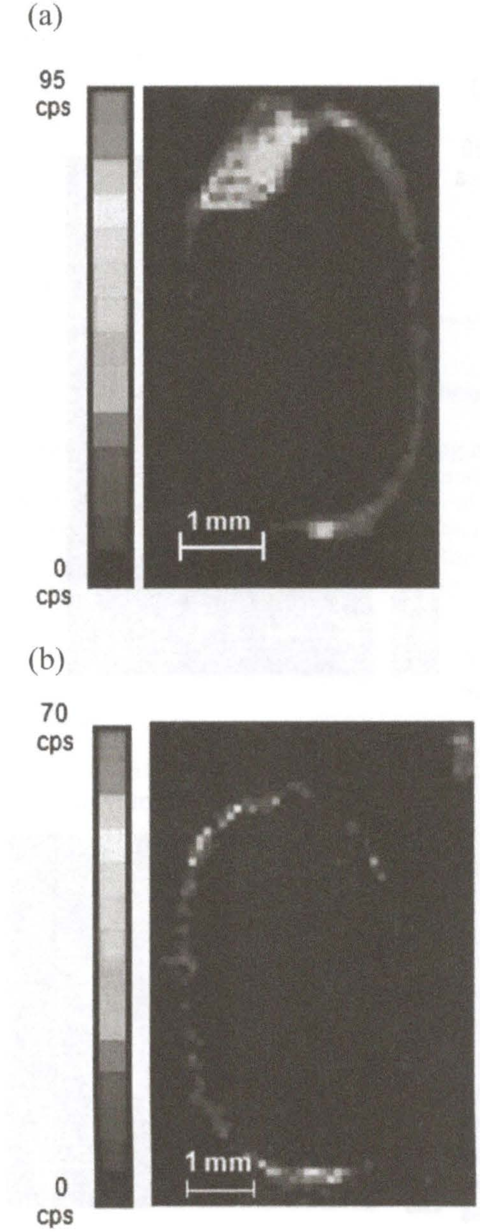


**Figure 16.2** Location of calcium in short-grain rice ((a) variety Ji 307; (b) variety Nanjing No. 1). Both varieties are japonica rice (short grain). The images illustrate the calcium location in brown-rice kernels. Most of the calcium in Ji 307 is located in the outer layer of the kernel and the calcium in the endosperm part is below the detection limits, while a low density of calcium in the endosperm of the kernel of Nanjing No. 1 was measured. The highest density of calcium in Ji 307 is at the embryo part.

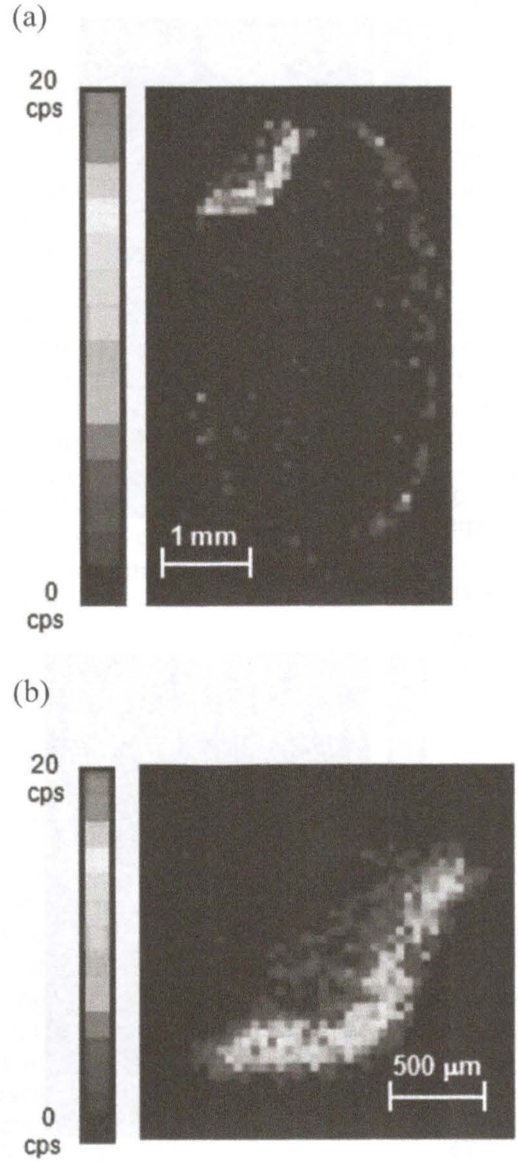


**Figure 16.3** Location of phosphorous in rice Ji 307. (a) Whole kernel; (b) embryo. Images of phosphorous location (as an index of phytic acid) indicate that phosphorous is distributed unevenly in the whole brown rice kernel. The highest density occurred at the boundary of the embryo and endosperm (a and b).

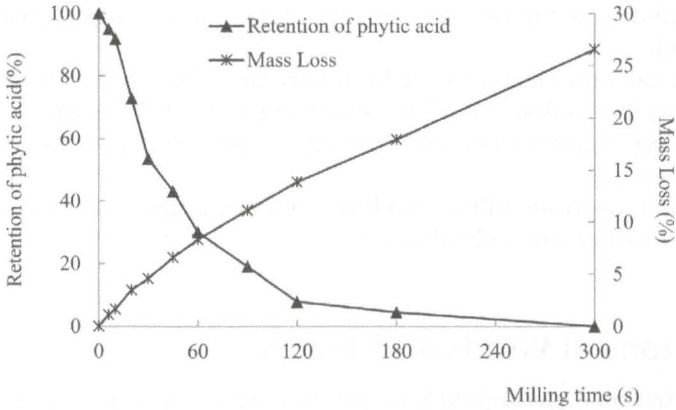


**Figure 16.4** Retention of phytic acid and mass loss during milling (rice variety Ji 307). Retention of phytic acid in milled rice and mass loss caused by milling are shown for comparison. Retention of phytic acid in milled rice is the result of uneven distribution of phytic acid in the kernel, while mass loss is mainly influenced by the hardness of different layers of the kernel. For example, for Ji 307, when we remove 10% of the outer layer of brown rice, about 75% phytic acid would be removed at the same time.

## 16.5 Conclusion

With the new paradigm shift from green revolution to nutritional revolution, one must realize that any small increase of nutritional value of rice could improve the health of the rice-eating population. Promising approaches for enhancing the bioavailability of minerals in rice products include: (i) increase of mineral levels by controlled loss during milling, supplementation or fortification, (ii) increase bioavailability through added enhancers or by removal of inhibitors or (iii) combinations thereof. The genetic variation and significant effect of location provided hope for plant scientist to develop high minerals and low phytic acid contents rice by traditional breeding methods for human health. The uneven distribution of minerals and inhibitors in the rice kernel inspired food scientists to develop and apply new technologies for improved rice nutrition. Fortification with minerals should take into account their interactions, palatability especially for iron compounds, and opportunities for enhancement of bioavailability by enhancing components from food ingredients.

## Summary Points

- The chapter focuses on calcium and phytic acid in rice.
- Rice contains low levels of calcium and relatively high phytic acid.
- Contents of calcium and phytic acid varied with rice genotypes and cultivation locations.

- Calcium and phytic acid are distributed unhomogeneously in rice kernel.
- Most calcium locates in the bran part and more than 70% phytic acid locates in less than 8% of the outermost layer of rice kernel.
- Soaking, germination and treatment with phytase could degrade phytic acid.
- Calcium nutrition of rice products could be improved by supplementation, fortification and enhancers.

## Definitions of Words and Terms

**Antinutritional factor (ANF).** Factor that negatively affects digestion and/or absorption of nutrients, such as protein and minerals. For example, oxalic acid is a ANF for calcium. This is because when oxalic acid present, calcium in food will be formed into an insoluble state and can no longer be absorbed by humans.

**Brown rice.** The name comes from the color, also known as hulled rice. It is the edible part of paddy obtained after removing of husk with a huller. Brown rice is normally milled and polished for white color and nice taste.

**Germinated rice.** Brown rice is soaked for water absorption and then followed with germination under certain conditions till the sprout length is 0.5–1.0 mm.

**Rice milling.** Processing procedure of rice production, the technology is based on an abrasive mechanism. Milling removes the outer layer of brown rice (bran) and a white color product is obtained.

**Rice noodle.** White rice soaked in water or not soaked, ground with or without water, a mixture of rice flour and water steamed, extruded for noodles, heated, cooled to obtain final fresh noodle or dehydrated to dried rice noodle.

**Parboiled rice.** Paddy (rough rice) is subjected to a steaming or parboiling process followed with drying to remove water. The same processing as normal paddy is undertaken. Parboiling causes nutrients from the outer husk, especially thiamine, to move into the grain itself.

**Phytase.** General name of enzymes that can degraded phytic acid (phytate). Phytase can be intrinsic components in seeds and activated by germination, or substances isolated from micro-organisms.

**Phytate.** Salt form of phytic acid. Mineral cations include sodium, potassium, calcium, zinc and so on.

**Phytic acid.** Myo-inositol 1,2,3,4,5,6 hexakis dihydrogen phosphate (also known as inositol hexaphosphoric acid or myo-inositol hexakisphosphate-IP6). The molecular formula is $C_6H_{18}O_{24}P_6$ and molecular weight 660.04.

**White rice.** Also known as milled rice, polished rice, it is the most popular and normal rice product on market.

## List of Abbreviations

| | |
|---|---|
| **AAS** | Atomic absorption spectrophotometry |
| **ICP** | Inductively coupled plasma |
| **OES** | Optical emission spectrophotometry |
| **ANF** | Antinutritional factor |
| **HPLC** | High-performance liquid chromatography |
| **$FeCl_3$** | Ferric chloride |

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