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Milling characteristics and distribution of phytic acid and zinc in long-, medium- and short-grain rice

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Abstract

Milling and polishing are important operations during the production of white rice. The degree of milling and polishing has a significant effect on the nutritional aspects of white rice, especially on minerals, due to a non-uniform distribution of nutrients in the kernel. Information on the distribution of nutrients in rice will greatly help to understand the effect of milling and aid in designing procedures that improve technological and sensory properties of rice while retaining its essential nutrients as much as possible. In this study, three kernel shapes (short-, medium- and long-grain) of rice were selected for the study of milling characteristics and distribution of zinc (Zn) and phytic acid using abrasive milling and X-ray fluorescent microscope imaging approaches.

Milling characteristics differed with kernel shapes and cultivars. Mass loss (y, %) correlated well with milling duration (x, s) and was fitted using a polynomial equation of $y = ax^2+bx+c$ ($R^2=0.99$). Different kernel shapes of rice resulted in different patterns. Breakage in milling increased with longer duration of milling. The relation between breakage (y, %) and milling duration (x, s) fitted the exponential equation $y = ae^{bx}$. Levels of phytic acid, as well as Zn decreased with prolonged milling. Phytic acid decreased at a higher rate than Zn. The analysis of different milling runs showed that the concentration of phytic acid decreased from the surface region inward, whereas X-ray fluorescent images indicated that the highest concentration of phosphorus was at the interface of embryo and perisperm.

Our results help to understand the milling characteristics of different rice cultivars. Understanding these characteristics offers opportunities to optimize milling procedures for maximum phytate removal, at minimum mineral losses and yield loss.

Key words: mass loss, breakage, rice kernel, distribution, abrasive methods, X-ray fluorescent microscope imaging

Running title: distribution of Zn and phytic acid in rice kernels

Abbreviations:

B37: Bijing 37
G30: Ganwanxian 30
KSA: kernel surface area
PA: phytic acid
PC: protein content
RLW: ratio of length to width
TKW: thousand kernel weight
YBR: yield of brown rice
Z752: Zhongyou 752
Zn : zinc

Introduction

Rice is one of the important cereals in the world. It is commonly used as milled (white) rice produced by removing the hull and bran layer of the rough rice kernel (paddy) (Perdon et al., 2001). Brown rice (hulled rice) is composed of surface bran (6-7% by weight), endosperm (≈ 90%) and embryo (2-3%) (Chen et al., 1998). White rice is referred to as milled, polished or whitened rice when 8-10% of mass (mainly bran) has been removed from brown rice (Kennedy et al., 2002). During milling, brown rice is subjected to abrasive or friction pressure to remove bran layers resulting in high, medium or low degrees of milling depending on the amount of bran removed (Chen, Siebenmorgen, 1997; Chen et al., 1998). Milling brings about considerable losses of nutrients and affects the edible properties of milled rice (Chen et al., 1998; Doesthale et al., 1979). As most cereals, rice does not show a homogeneous structure from its outer (surface) to inner (central) portions (Itani et al., 2002). As a consequence, information on the distribution of nutrients will greatly help to understand the effect of milling and aid in improving sensory properties of rice while retaining its essential nutrients as much as possible.

Depending on the extent of milling, changes of some nutrients, such as surface lipids (Chen et al., 1998; Perdon et al., 2001), protein (Chen et al., 1998; Heinemann et al., 2005), physical properties such as rice paste viscosity (Perdon et al., 2001), and sensory quality of milled rice, including taste (Park et al., 2001; Tran et al., 2004), have been reported. Effect of milling on some macro- and micro-elements, e.g. iron, magnesium, phosphorus, phytic acid, have also been studied (Bryant et al., 2005). Early studies described the effect of milling on minerals or distribution of minerals according to approximate milling degrees, such as lightly milled, reasonably milled and well milled, or as fractions I, II and III, respectively (Kennedy, Schelstraete, 1975; Song et al., 1988; Tabekhia, Luh, 1979). These authors did not provide detailed information about the distribution of these nutrients in rice kernels. Itani et al. (2002) reported the distribution of some nutrients in more detail, although phytic acid and trace minerals were not included. Studies on Indian rice indicated that the extent of milling had a significant effect on losses of magnesium and calcium, but not on phosphorus and trace minerals ($p<0.05$) (Bajaj et al., 1989). Recently, X-ray fluorescent microscopy techniques were developed and applied to map the distribution of minerals such as magnesium, potassium, phosphorus, calcium and sulphur in quinoa seeds (Emoto et al., 2004; Konishi et al., 2004).

Considering world wide deficiencies of iron and Zn, our ultimate aim is to improve the bioavailability of these minerals by reducing insoluble mineral-phytate complexes, and fortification if desired. As the Zn-phytate complex is very stable (Vasca et al., 2002), we focussed on Zn as a target mineral. Our previous study indicated that Zn and phytate contents in Chinese rice cultivars cover a broad range (Liang et al., 2007). The purpose of the present study was to compare the milling characteristics and the distribution of Zn and phytic acid in long-, medium- and short-grain kernels of rice from China, with a view to optimize for maximum phytate removal at minimum losses of Zn. Precision abrasive milling was used to obtain a range of milling degrees, and X-ray imaging methods to map the distribution of different minerals. The degree of milling for specific rice cultivars could be optimized for maximum removal of phytic acid, maximum retention of Zn, and appropriate whiteness to satisfy consumer expectations for white rice.

Materials and methods

Paddy rice and characteristics

Based on our survey of the variation of phytic acid and minerals in rice cultivars cultivated in China (Liang et al., 2007), three cultivars namely Ganwanxian 30 (G30), Zhongyou 752 (Z752) and Bijing 37 (B37) having different levels of phytic acid and minerals were selected. According to the industrial standard of China, the three cultivars were classified as long-grain, medium-grain and short-grain, respectively (CHISA, 2002). G30 and Z752 were obtained from the Jiangxi Seeds Company, and B37 from the Academy of Agricultural Science of Guizhou. All paddies were harvested during the autumn of 2003 and were stored dry and cool (~15°C) less than 90 days before processing and analysis. General characteristics, including crude protein content (PC), yield of brown rice (YBR), breakage from hulling, shape i.e. ratio of length to width (RLW), kernel surface area (KSA), and thousand-kernel weight (TKW), are presented in table 1.

Hulling and Milling

Paddy was dehusked with a lab-scale hulling machine (THU-35C, Satake, Japan). Each cultivar was assessed in triplicates for thousand-kernel weight (TKW), yield of brown rice (YBR) and breakage from hulling.

Only intact brown rice kernels were used for subsequent milling experiments. About 30 (± 1) g of brown rice were milled for the duration of 6, 10, 20, 30, 45, 60, 90, 180 and 300 s, respectively, with a lab-scale milling machine (TM 05C, Satake, Japan) to obtain rice milled to different degrees. Each milling treatment (duration) was performed in triplicates. Yields of white rice and breakage from milling were measured. After milling, whole milled rice kernels (head rice) were separated, and then ground with grinder (HY-04B, Beijing Xinhuanya, China) to pass a 1 mm sieve, and dried at 100°C till constant weight. Dried rice flour was kept in sealed plastic bags at 4°C until chemical analysis.

Zinc (Zn)

Samples of 0.5 g (accuracy 0.1 mg) dried rice flour were digested using a microwave laboratory system (Milestone, Italy) with nitric acid (HNO_3, reagent grade) and hydrogen peroxide (H_2O_2, analytical reagent, Beijing Chemical Works, China) as described by D'Ilio et al. (2002). Contents of Zn in solutions were measured with a Vario 6 Atomic Absorption System (Analytik Jena, Germany). Each sample was digested and measured in triplicates.

Phytic acid

Phytic acid levels in brown rice and milled rice were determined after extraction in 100g L^{-1} Na_2SO_4-HCl (1.2 %), concentration on an anion exchange column, and were analysed spectrophotometrically at 500 nm after reacting with a 0.03% $FeCl_3$ solution containing 0.3% sulfosalicylic acid, according to Ma et al. (2005). All materials were analysed in triplicates.

Sample preparation for SEM

Rice kernels were longitudinally mounted in a brass cylindrical sample holder with carbon conductive glue (Leit- C, Neubauer Chemicalien, Germany). The samples were placed in a sample holder in a ultra microtome (Reichert Ultracut E/FC4D) and cut. These samples were first planed with a glass knife, after which the surface was planed with a diamond knife **(**Histo no trough, 8 mm 45°C, Drukker International, The Netherlands). This method is based on (Nijsse, Van Aelst, 1999).

X-ray fluorescent imaging

X-ray elemental maps were obtained with a micro-X-ray fluorescence instrument developed at Osaka City University (Emoto et al., 2004). The X-ray tube (MCBM 50-0.6B, rtw, Germany) with Mo target was operated at 50 kV and 0.45 mA. The tube was installed into an X-ray tube shield holder equipped with an X-Y-Z positional device, where the polycapillary X-ray lens was attached. The polycapillary lens was designed and manufactured at Beijing Normal University. The length, input focal distance, and output focal distance were designed to be 50 mm, 34 mm, and 16 mm, respectively. A spot size of about 40 mm was obtained at a focal point. A silicon drift X-ray detector (SDD, X-Flash Detector, Type 1201, Rontec, Germany; sensitive area: 10 mm^2, energy resolution: <150 eV at 5.9 keV) was suspended using a down-looking geometry. The sample stage was placed on the X-Y-Z stage [YA05A-R1 (X-Y stage) and ZA07AR3S (Z stage); Kohzu precision, Japan], which was controlled by stepping motors driven by a computer. To control the sample stage, motor drivers and a motor controller (NT2400, Laboratory Equipment Co., Japan) were applied. An SDD signal was analysed by a multi-channel analyser (NT2400/MCA, Laboratory Equipment Co., Japan). To confirm the position of the sample, a visible CCD camera was also installed.

Statistical analysis

Where appropriate, data were presented as means with standard deviation, or by error bars. Significance of differences was tested by two-tailed t-tests.

Results and discussion

Milling characteristics

For the miller, the main quality characteristic of rice is related to the amount of material that needs to be removed to obtain white rice. During the abrasion of rice, not only the outer layers of the kernels are removed, but also kernels are broken. These are also considered a loss. We therefore defined milling characteristics as the mass loss due to bran removal, and breakage during milling. The milling characteristics for the rice cultivars used in this study are shown in figure 1a and 1b.

Figures 1a and 1b show the loss of mass, and breakage, with increasing milling time. For the three cultivars tested, mass losses (figure 1a) were similar: with increasing milling duration more of the outer layers is removed. Loss rates become less at longer milling times. The relation of mass loss (y, %) vs duration of milling (x, s) fitted a polynomial equation of $y = ax^2+bx+c$ (R^2=0.99), as was observed in other studies (Perdon et al., 2001; Singh Gujral et al., 2002). Different kernel shape of rice resulted in different patterns. Z752 had a higher mass loss (figure 1a) at each milling time. To achieve a mass loss of 2%, it took less than 10 s for Z752, and about 20 s for B37 and G30, respectively. Generally, in order to obtain white rice, about 10-15% of mass is removed from the outer layers. In this study, Z752 required the shortest duration of milling to obtain white rice, followed by B37 and G30. The differences among mass loss patterns of the three cultivars might be related to the removal of the embryo. Visual inspection to check the removal of the embryo from brown rice during milling revealed a large variation between the different rice cultivars. Under our experimental milling conditions, one third of the kernels of Z752 and B37 had lost their embryo after 30-45 s milling, corresponding to a mass loss of 3.5-4.5%, whereas more than 90% of the kernels had lost their embryo after 90 s milling, at mass loss of 8.5-9.5%. For G30, about 30% of kernels had lost their embryo at 2% mass loss (20 s milling), whereas after 45 s milling, most kernels had lost their embryo at a mass loss of 5%.

Rice breakage was quantified as the weight of broken rice expressed as a percentage of the total weight of milled rice (Chen et al., 1998). Breakage of the three cultivars was similar (figure 1b), increasing with longer duration of milling. The relation between breakage (y, %) and milling duration (x, s) fitted the exponential equation $y = ae^{bx}$. The different cultivars had different a and b values with a R^2 ranging from 0.76 to 0.95. Of the three cultivars, Z752 had the highest breakage values, and B37 had the lowest at each time interval. After 90 s milling, breakage of Z752 had reached 30%, while breakage of B37 was still low (about 5%). The amount of broken kernels of long-grain in the present study was of a similar magnitude as of long-grain rice reported elsewhere (Chen et al., 1998).

Phytic acid and Zn levels

Phytic acid and Zn levels in rice after increasing degrees of milling are presented in table 2.

Levels of phytic acid and Zn decreased with prolonged milling. Although it has been observed earlier (Itani et al., 2002) that all minerals (including phosphorus) decrease from the outermost fraction, it appears here that phytic acid levels decrease at a higher rate than those of Zn.

Phytic acid levels in brown rice of B37, Z752 and G30 were 8.9, 7.8 and 11.1 g kg^{-1}, respectively. These values differ from our previous results (Liang et al., 2007) probably due to differences of cultivating environments and agricultural practice (Liu et al., 2005a). G30 had the highest phytic acid content in raw brown rice and this decreased quickly during milling. After 30 s milling, phytic acid levels in milled rice of B37 and Z752 were at the same level (7 g kg^{-1}) although they started at different initial values, and it was 8 g kg^{-1} in G30 after the same milling time. After 120 s milling (duration considered to be optimum in commercial milling of white rice), phytic acid in G30 and Z752 were still at the level of 3.2 g kg^{-1}, higher than in B37 (2.0 g kg^{-1}). After 300 s milling, phytic acid in all cultivars were at the level of 0.2 g kg^{-1}. Phytic acid levels in brown rice decreased at a similar rate as reported elsewhere (Doesthale et al., 1979) for phosphorus.

The Zn levels in the brown rice cultivars studies did not decrease significantly (22.1, 22.8 and 19.3 mg kg^{-1}, respectively), and even after 30 s milling (corresponding to a mass loss of about 5%), the Zn levels in all cultivars of milled rice were still at the same level of brown rice. The biggest lost of Zn in Z752 occurred after 45 s milling, and in B37 after 120 s milling. However, in G30, up to 120 s milling did not affect its Zn level, a phenomenon that has been previously reported (Juliano, 1972; Villareal et al., 1991). With some milled rice samples even higher Zn levels were reported than in the initial brown rice (Heinemann et al., 2005). In the three cultivars studied here, Zn levels after 300 s milling were 4-38% lower than that of initial values.

Location and distribution of phytic acid and Zn in brown rice

In order to visualize the distribution of phytic acid and Zn in brown rice, X-ray fluorescent microscope imaging techniques were used. Images of location of phytic acid (indicated as phosphorus, P) and Zn obtained with X-ray fluorescent scanning, as well as the distribution of phytic acid and Zn in brown rice kernels obtained by abrasive milling are shown in figures 2a, 2b and 2c and demonstrate the location of P and Zn in rice kernels.

In all three cultivars, the density of phosphorus decreased from the surface region inward. This agrees with data from abrasive milling experiments (Bryant et al., 2005). The peripheral embryo region did not show high phosphorus intensities, whereas much higher densities were observed near or at the interface of embryo and endosperm. We observed that whereas in B37 (figure 2a) and G30 (figure 2c), the distribution of phosphorus was similar; the distribution in Z752 (figure 2b) was different, having no distinct layer with higher phosphorus concentration. Notably, at the side of the embryo, we could not observe the high density of phosphorus as observed in figures 2a and 2c. The distribution of phosphorus 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 phosphorus occurs as phytic acid in rice.

The location of Zn in the three cultivars was similar. All three cultivars had the highest density of Zn in the embryo whereas Zn was relatively evenly distributed in the other regions. This helps us to understand earlier reports, that milling degrees higher than 10% had little effect on Zn levels in milled rice (Bryant et al., 2005). The location of Zn indicates that it may be beneficial to retain more embryo to obtain higher final levels of Zn.

We observed an inverse relation: y = a-bx (a=7.7-8.3, b=0.03, R^2=0.82-0.91) between phytic acid levels (y, mg g^{-1}) and milling duration (x, s) (figure 2a, 2b, 2c). This relation shows some similarity with that between milling degree and surface lipid, and phenolic acids observed elsewhere (Perdon et al., 2001; Zhou, 2003). In B37 and Z752, about 23 to 33% of total phytic acid was located in the surface outer layer of kernel (2-3% weight percent of brown rice). In all cultivars, about 23-25% of total phytic acid was located in the sub-surface layer, which accounted for 3.4-4.5% of total weight. Less than 2% of total phytic acid was located in the 75-80% of central portion of kernel. The remaining 40-50% of phytic acid was located in the peripheral layers of brown rice, representing 13-15% of kernel weight. The distribution of phytic acid observed from milling experiments is very well supported by images obtained from X-ray scanning. Differences in the distribution of phytic acid location in cultivars mainly occurred in the outermost layer. In this region, distribution of phytic acid in B37 and Z752 was similar, and relatively even at the outermost surface with a steep decrease inward. However, the distribution in G30 was quite different, showing a steep decrease already at the outermost surface layer, followed by a relatively even distribution. This distribution pattern was similar to the distribution of phosphorus in other rice cultivars (Bajaj et al., 1989). The perisperm is another layer of the kernel, removed at the interval of milling duration from 60 s to 120 s. Phytic acid located here varied by 20-40%, with weight percent at 4-6% in different cultivars.

The distribution of Zn in the three cultivars was different. For B37, distribution of Zn was relatively even in the layer occupied 30% of the total kernel weight, with a steep decrease in next region, and followed with another even distribution in the central part. In contrast, in Z752, a steep decrease of Zn occurred at sub-surface layer, at the milling interval from 30 to 60 s (occupied about 4% of total weight of kernel), and with an even distribution in other parts. For G30, the distribution of Zn was relatively even from the surface to the central part of the kernel. The highest decrease occurred at the interval of 60-120 s. Further analysis of regression showed there was no correlation between Zn contents and milling duration. Figures 2 also showed that more than 60-70% of total phytic acid was located in the 10% of surface layer, and less than 40% of Zn was in the same layer. The different distribution patterns of phosphorus and Zn should enable an optimized milling, removing as much as possible phytate while retaining relevant levels (at least 50%) of Zn.

Molar ratios of phytic acid to Zn varied with regions in kernel and cultivars. For all cultivars, only when more than 20% of outer layer was removed, molar ratios of phytic acid to Zn could decrease to less than 1. This was achieved only after 300 s milling, which is considerably longer than the standard commercial practice.

Discussion

Milling consequences, such as mass loss and breakage, could be affected by intrinsic factors (e.g., cultivar, kernel shape) as well as extrinsic factors (e.g., milling equipment). Under identical processing conditions, rice can display different processing properties. These can be caused by cultivar, maturity, and cultivating conditions, and can influence mass loss and breakage because of different shape, hardness of kernels, and thickness of the aleurone layer (Juliano, 1972; Zhou, 2003). Different bran loss rates by milling have been attributed to shape and hardness of grains, as well as pericarp thickness, oil bodies, cellulose, and hemicelluloses in bran layers (Juliano, 1972; Mohapatra, Bal, 2004; Singh Gujral et al., 2002; Singh et al., 2000). These would contribute to the differences observed for the three cultivars and the higher mass loss rate after short milling periods. Cultivars differ in thickness of the aleurone layer and in hardness distribution in the endosperm. *Japonica* (bold or coarse short-grain) kernels tend to have more cell layers than *indica* (slender long- or medium- grain) kernels. The central core and the mesocarp in *indica* and *japonica*, respectively are hard, and kernel hardness is negatively correlated to length-to-breadth ratio (Juliano, 1972). Combined effects of such factors may have caused the relatively high mass loss of Z752 from milling.

In addition to the effect of equipment and process conditions, the composition, structure and thickness of rice kernels also affect the extent of breakage from milling (Siebenmorgen, Qin, 2005; Zhou, 2003). Whereas breakage could not be related to kernel width or length (Siebenmorgen, Qin, 2005), the susceptibility to relative humidity and fissuring could play a role in breakage (Lloyd, Siebenmorgen, 1999). Further investigation is required to help understand the mechanism for the high extent of breakage from milling in Z752.

Phytic acid is an important storage of phosphorus and minerals present in seeds. It usually occurs as a mixed salt of potassium and magnesium, and may also contain calcium, Zn and/or iron. Phytate has a different accumulation pattern from protein reserves which are mainly deposited within the numerous protein bodies in seed storage cells (Liu et al., 2004; Liu et al., 2005b). Studies on *japonica* rice indicated that phytic acid levels were not related to protein levels, which were significantly influenced by genetic and environmental factors (Juliano, 1972; Liu et al., 2005a; Liu et al., 2005b). Our milling experiment indicated that about 25% of the phytic acid is located in the perisperm of the kernel, which differs from earlier findings that phytic acid was only present in the aleurone layer after embryo removal (Liu et al., 2004). This difference suggests that although phytic acid is approximately located in the outer layer of kernel, the precise distribution might differ among rice cultivars. In order to obtain milled rice with minimum weight losses but maximum removal of phytic acid, the distribution of phytic acid in the kernel should be established first, and this should form the basis to determine the appropriate milling treatment. Our X-ray microscope images indicate that in absolute terms, very little phosphorus is located in the embryo itself, which differs from the observation made earlier (Liu et al., 2004) that phosphorus concentration in embryos was about 5 times higher than in whole kernels. Both abrasive milling experiments and X-ray images indicate that Zn was not mainly located in rice bran, unlike total ash or other minerals (Dikeman et al., 1980; Doesthale et al., 1979; Kennedy et al., 2002; Resurreccion et al., 1979).

From our X-ray images, it can be observed that the embryo has the highest concentration of Zn. It however represents a very small fraction of the total grain and in absolute terms, does not contribute very much to the total Zn in milled rice.

The different distributions of phytic acid and Zn in rice kernels confirmed earlier statements that phytic acid is primarily present in the potassium or magnesium form instead of the Zn form (Dikeman et al., 1980). Further research is required to assess the effects of other factors such as environmental conditions and agricultural practice, on the distribution of phytic acid and minerals in rice.

Conclusion

From this study we conclude that milling characteristics, including mass loss and breakage, varied among the rice cultivars having different kernel shapes. This indicates an opportunity for optimized milling, dedicated to improve the quality of white rice.

In the cultivars studied, we observed that whereas the distribution of phytic acid differed, most of it was located in the outermost layer. In contrast, Zn distribution in the 3 cultivars was quite similar, characterized by an even distribution throughout the kernel with the exception of a higher concentration in the embryo. The results give us the possibility to process brown rice to obtain low phytic acid contents at a relatively high Zn content.

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Table 1

Cultivar	Collection	PC (g 100g^{-1})[a]	Length (mm)	RLW[b]	KSA (mm^2)[c]	TKW (g)[d]	YBR (%)[e]	Breakage (%)[f]
Bijing 37 (Yu et al., 2001)	Guizhou	8.8	5.2	1.8	68	25.5	80.6	3.7
Zhongyou 752 (Centre of China Crop Science and Technology, 2006)	Jiangxi	10.9	6.4	2.8	50	26.5	71.9	16.2
Gangwanxian30 (Information of Jiangxi foodstuff-oil and soil-fertilizer, 2006)	Jiangxi	8.5	7.6	3.4	52	27.6	73.6	28.0

Table 2

Milling time (s)	Bijing 37		Zhongyou 752		Ganwanxian 30	
	PA* (g kg^{-1})	Zn (mg kg^{-1})	PA (g kg^{-1})	Zn (mg kg^{-1})	PA (g kg^{-1})	Zn (mg kg^{-1})
0	8.9 ± 0.1^{a}	22.1 ± 0.7^{a}	7.8 ± 0.1^{a}	22.8 ± 1.0^{a}	11.1 ± 0.1^{a}	19.3 ± 4.9^{a}
6	9.0 ± 0.3^{a}	20.8 ± 2.5^{a}	7.6 ± 0.1^{a}	20.7 ± 0.1^{a}	8.1 ± 0.3^{b}	20.3 ± 4.8^{a}
10	8.9 ± 0.2^{a}	20.0 ± 0.6^{a}	7.9 ± 0.2^{a}	22.6 ± 0.3^{a}	7.5 ± 0.3^{b}	20.0 ± 3.6^{a}
20	6.9 ± 0.3^{b}	19.8 ± 0.5^{a}	8.7 ± 0.3^{a}	22.6 ± 0.8^{a}	7.5 ± 0.4^{b}	19.0 ± 2.9^{a}
30	6.5 ± 0.2^{b}	21.7 ± 1.3^{a}	6.8 ± 0.2^{b}	21.5 ± 1.2^{a}	8.0 ± 0.3^{b}	22.7 ± 1.4^{a}
45	6.3 ± 0.2^{b}	22.3 ± 2.6^{a}	6.5 ± 0.3^{b}	18.1 ± 0.8^{ab}	5.9 ± 0.6^{c}	21.9 ± 0.7^{a}
60	4.8 ± 0.1^{c}	21.2 ± 1.3^{a}	6.3 ± 0.5^{b}	17.7 ± 0.9^{bc}	5.3 ± 0.6^{cd}	21.3 ± 2.2^{a}
90	3.1 ± 0.1^{d}	20.1 ± 1.8^{a}	4.7 ± 0.2^{c}	16.3 ± 0.2^{c}	4.9 ± 0.2^{d}	25.8 ± 4.0^{a}
120	2.1 ± 0.1^{e}	15.0 ± 1.0^{b}	3.2 ± 0.4^{d}	16.4 ± 0.2^{c}	3.3 ± 0.1^{e}	20.5 ± 1.1^{a}
180	0.7 ± 0.0^{f}	14.8 ± 0.7^{b}	0.9 ± 0.0^{e}	15.9 ± 0.3^{c}	1.2 ± 0.1^{f}	21.2 ± 0.3^{a}
300	0.2 ± 0.0^{g}	13.7 ± 1.7^{b}	0.1 ± 0.0^{f}	16.7 ± 1.1^{c}	0.2 ± 0.1^{g}	18.5 ± 2.8^{a}

Figure 1a

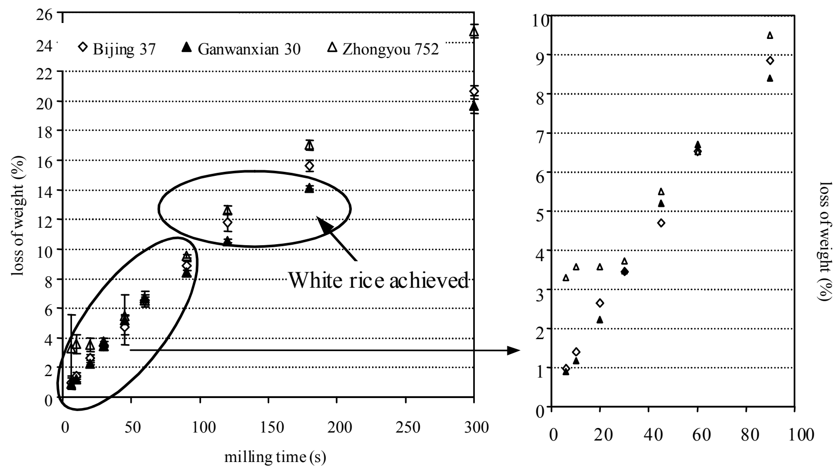
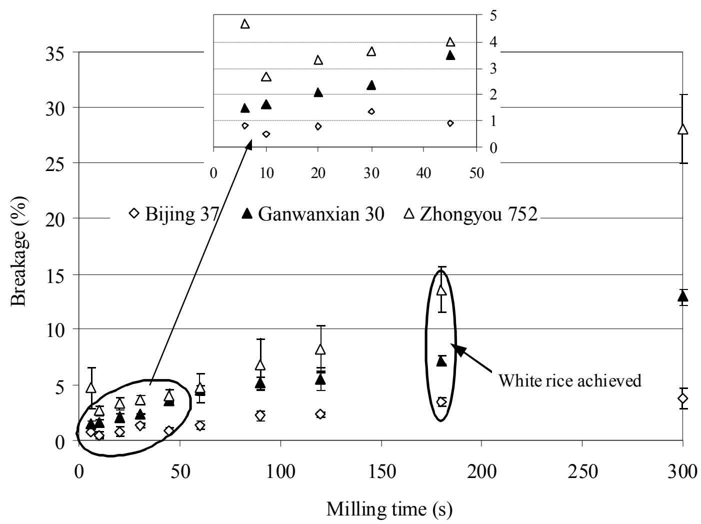
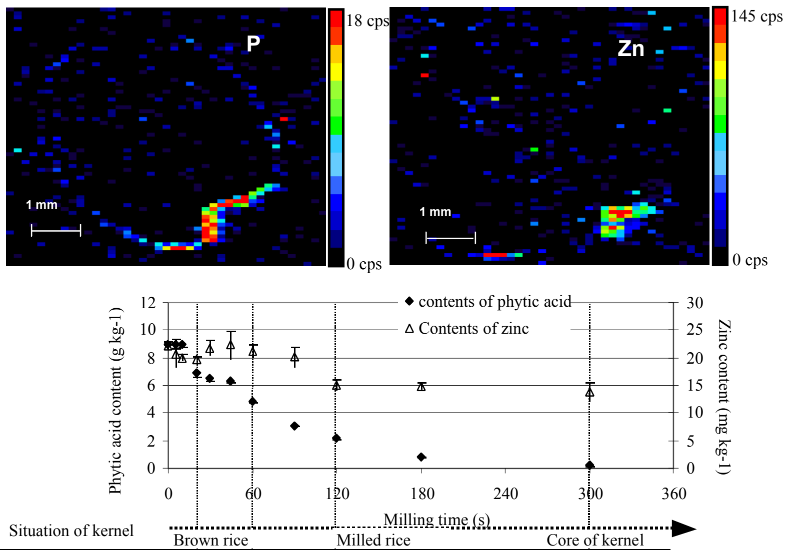

Bijing 37
Ganwanxian 30
Zhongyou 752
loss of weight (%)
milling time (s)
White rice achieved
loss of weight (%)

Figure 1b



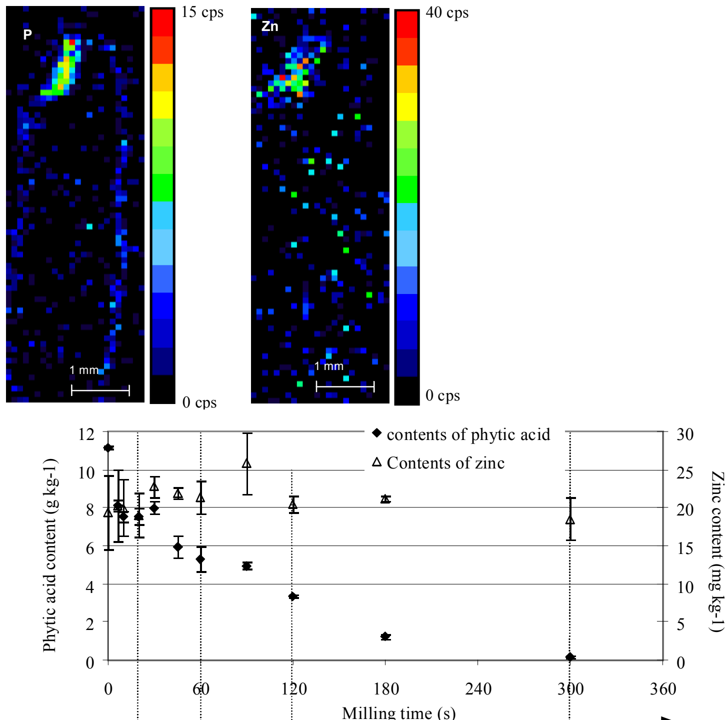
Breakage (%)
Milling time (s)
◇ Bijing 37
▲ Ganwanxian 30
△ Zhongyou 752
White rice achieved
0
5
10
15
20
25
30
35
0
50
100
150
200
250
300
0
1
2
3
4
5
0
10
20
30
40
50

Figure 2a



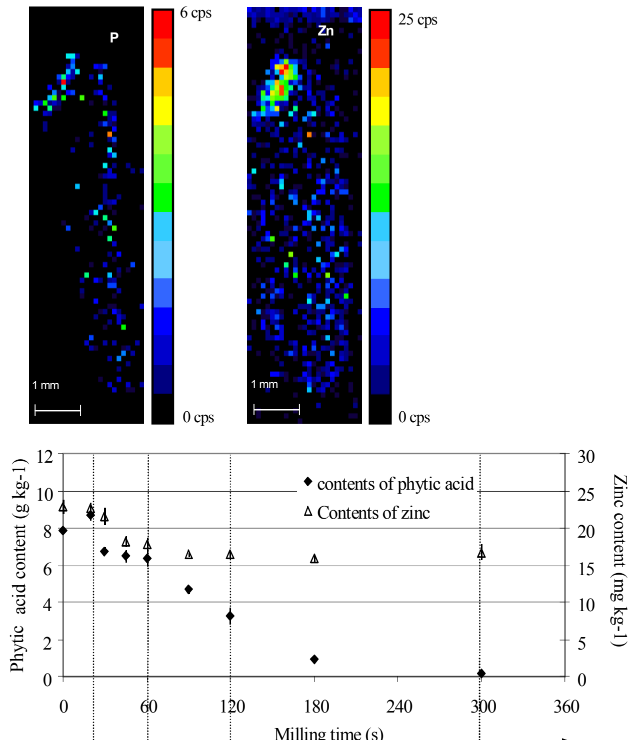
Milling time (s)	20	60	120	300
Mass loss (%)	2.7	6.5	11.8	20.7
Loss of PA (%)	23	46	76	98
Loss of zinc (%)	13	10	40	51
Molar ratio of PA/Zn	23	15	9	<1
Regression of PA (y, %) retention to milling time (x, s)	y = -0.0322 x + 7.7374	R^2 = 0.8236		

Figure 2c



Situation of kernel	Brown rice		Milled rice	Core of kernel
Milling time (s)	20	60	120	300
Mass loss (%)	2.2	6.7	10.5	19.7
Loss of PA (%)	33	52	70	99
Loss of zinc (%)	4	---	6	23
Molar ratio of PA/Zn	39	24	16	<1
Regression of PA (y, %) retention to milling time (x, s)	y = -0.0304 x + 7.907		R^2 = 0.9106	

Figure 2b



Situation of kernel	Brown rice		Milled rice	Core of kernel
Milling time (s)	20	60	120	300
Mass loss (%)	3.1	6.5	12.6	24.7
Loss of PA (%)	---	25	64	99
Loss of zinc (%)	4	27	37	45
Molar ratio of PA/Zn	38	35	20	<1
Regression of PA (y, %) retention to milling time (x, s)	$y = -0.0322 x + 8.2556$ $R^2 = 0.8456$			

TITLES AND LEGENDS FOR TABLES AND FIGURES

Table 1 General characteristics of brown rice samples

a: PC: protein contents (provided by supplier, see reference)

b: RLW: ratios of length to width (analysed in this study)

c: KSA: kernel surface area, assumed that the shape of integral kernels were separated into two semi-sphere and a cylinder. Surface area was calculated with $4^* (\text{width}/2)^2 \times \pi + 0.9 \times \pi \times \text{width} \times \text{length}$ (analysed in this study)

d: TKW: thousand-kernel weight (provided by supplier, see reference)

e: YBR: yield of brown rice, on wet mass basis.

f: Breakage caused by dehulling: percentage of broken brown rice weight to total brown rice weight (analysed in this study)

Table 2 Contents of phytic acid and zinc in milled rice*

* All data are based on dry mass weight and are presented as average ± standard deviations (n=3). Within columns, different superscripts indicate significant differences ($P < 0.05$, two-tailed t-test).

Figure 1a Mass loss during milling

Figure 1b Breakage during milling

Figure 2a Distribution of phytic acid and Zn in Bijing 37 (short-grain)

Figure 2b Distribution of phytic acid and Zn in Zhongyou 752 (medium-grain)

Figure 2c Distribution of phytic acid and Zn in Ganwanxian 30 (long-grain)

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