



Investigation of tissue level distribution of functional groups and associated trace metals in rice seeds (*Oryza sativa* L.) using FTIR and LA-ICP-MS



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ABSTRACT

Rice, rich with carbohydrates, proteins, and essential elements such as zinc, has the propensity to bio-accumulate toxic elements. The purpose of this study is to investigate the potential metal–ligand binding sites in the husk, bran and endosperm tissues in rice seeds (*Oryza sativa* L.) collected from contaminated rice fields near the XKS mine in China using ATR-FTIR spectroscopy, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and elemental analysis. Results demonstrate that the polar atom ratio (N + S + O / C) ranged from 0.92–1.16 in both endosperm and husk. The N/C ratio was greater in endosperm (0.02–0.04) than in the husk (0.01). Thus, metals having an affinity to N containing groups would be expected in higher concentrations in the endosperm including embryo. FTIR spectroscopy revealed –OH, >C=O, Si–OH, O–Si–O functional groups in the husk and –OH, >C=O and CONH₂ groups in the endosperm. The tissue-level spatial elemental distribution was unraveled by LA-ICP-MS analysis of rice seed cross-sections. Results showed elevated concentrations of Zn in the embryo and high levels of Sb, As, Pb and Cd on the husk/bran tissues. The rice embryo and edible starch and protein containing endosperm tissues are rich with Zn. It appears that binding sites (i.e. silanol, phenolic and nitrogen containing moieties) in inedible husk tend to localize toxic As, Sb, and Pb in rice seeds.

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1. Introduction

A well-known staple food in many parts of the world, rice is a major source of carbohydrates, proteins [1,2], nutritional elements [3], and it has the propensity to bio-accumulate toxic elements like arsenic [4,5]. Rice is grown in over hundred nations where more than 700 million tons of rice per annum is grown worldwide [6] and China produces more than quarter of the world's rice harvest. The people in developing nations are highly dependent on this cereal as a major source of dietary energy supply (27%), proteins (20%) [7], and fat (3%) [3], and also to facilitate their livelihoods. Over the past decades the rice production [8] and consumption has increased significantly in the US but is still below the rice per capita consumption in other parts of the world [9].

Rice grain is a caryopsis in which the seed is intimately fused with the exterior wall of the mature germ forming a dry seed-like grain. The main tissue components of the rice are the outermost husk, followed by bran, endosperm and embryo. Rice husk (RH) is a unique protective seed layer consisting of 38% cellulose, 22% lignin, 20% inorganic ash,

18% pentose, and 2% other residual organic compounds. Inorganic ash containing silica (SiO₂) is rich with surface silanol group (Si–OH) and siloxane (Si–O–Si) groups [10]. The nutritionally important bran layer contains proteins, vitamins (i.e. vitamin E) and oil composed of oryzanol (esters of trans-ferulic acids, tocotrienols, and triterpene alcohols) [11]. The most prominent endosperm consists of outer oil rich aleurone layer (1–5 cells) and the inner starchy endosperm consists of thin-walled parenchyma cells rich with starch granules [1], and 6%–12% proteins are located in aleurone and embryo tissues [12]. One of the notable proteins in the rice endosperm is the rice globulin which is polymeric and has α -helix secondary structure rich with intermolecular disulfide bonds, and β -sheet and β -turn conformations [13]. Thus, silanol and siloxane groups and lignin in the rice husk, amides, phenolic moieties in bran and embryo, and oxygen, sulfur and nitrogen sites in protein sprinkled starchy endosperm are potential metal binding sites in the rice seeds. Even though rice is an abundant source of carbohydrates, proteins and nutritional elements like zinc, it also has the ability to bioaccumulate toxic elements such as As [4,5,14–16], Cd [17], Pb [18] and Sb [19] in part due to metal–ligand binding [20,21].

Fourier transform infrared spectroscopy (FTIR) is a molecular vibrational technique that offers qualitative identification of important functional groups including metal binding sites in seeds [13,22–24].

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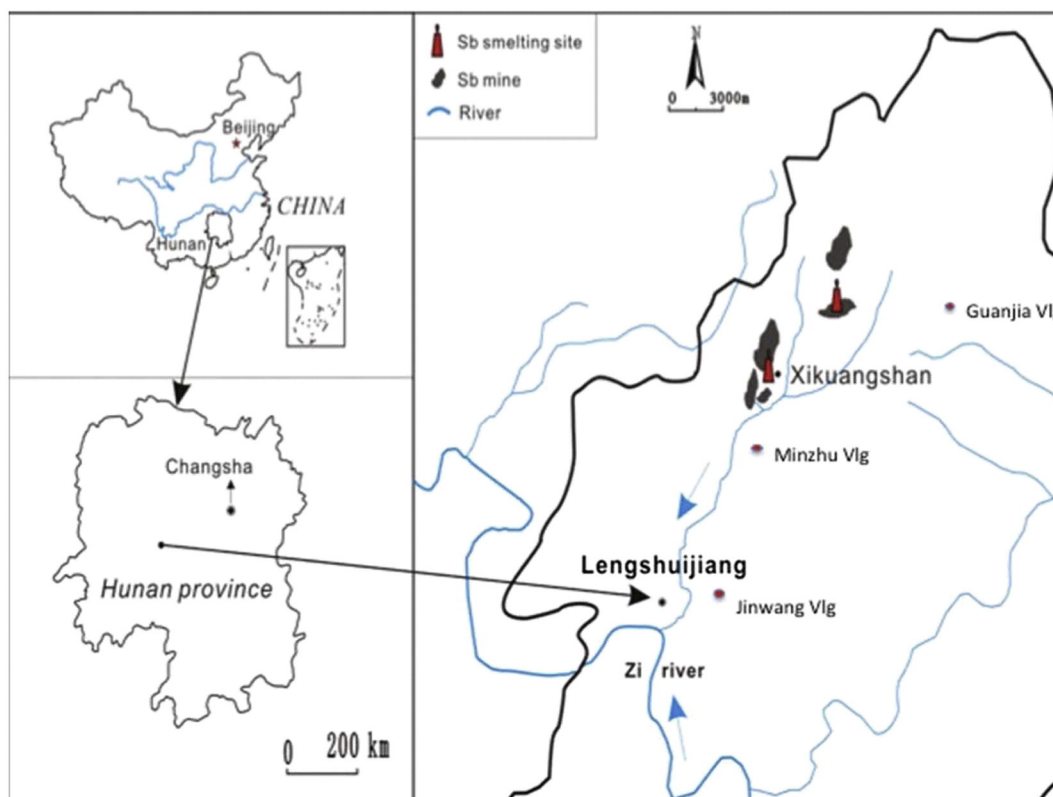


Fig. 1. A map showing location and sampling sites near XKS mine in Hunan province, China (Basnet et al., 2014 [37]; Fig. 1 with permission from Elsevier License number: 3800220245194 and originally modified after Fu et al., 2010 [38]; Fig. 1 with permission from Elsevier license number: 3800491277547).

Wavenumber shifts and changes in IR peak intensities due to metal binding with organic functional groups are well documented [25,26]. Advent of the attenuated total reflectance (ATR) accessory offers ease of sample preparation and FTIR analysis. In this mode incident infrared radiation is focused on a high refractive index crystal such as a diamond where the sample material is in intimate contact with the crystal resulting in a right-angled positioned evanescent wave, which reaches the fraction of the test sample resulting in IR absorption. IR beam reflecting from one or more of the attenuated reflections is directed on to an IR detector to obtain IR absorption or transmission spectra [27].

The visualization of the spatial distribution of trace metals in various biological tissues can be achieved by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). LA is a sub-micrometer spatial resolution laser energy assisted solid sampling device coupled to a sensitive metal detector such as ICP-MS [28,29]. LA-ICP-MS has been effectively applied for elemental bio imaging of variety of plant tissues [30]. For instance, LA-ICP-MS has been used to image Cu distribution in *Elsholtzia splendens*, a copper tolerant plant [31], to determine Pb distribution and bioaccumulation in Antarctic lichen *thalii* [32], as well as accumulation of Sb, Pb in fern rhizomes grown in a shooting field [33]. Semi-quantitative analysis of Ni distribution in Ni hyper accumulating plant (*Berkheya Coddii* L.) roots by LA-ICP-MS revealed that Ni preferentially accumulated in the cortex tissue of the root. Pb and Mg bioaccumulation in sunflower leaves (*Helianthus annuus* L.) was imaged by using LA-ICP-MS and compared with laser induced breakdown spectroscopy (LIBS) [34]. Wang et al. [35] used LA-ICP-MS to map two-dimensional (2D) spatial information on Zn distribution in wheat grains. Arsenic spatial distribution in white and brown rice varieties from Korea was studied by femtosecond (fs) LA-ICP-MS and found that As is concentrated in the husk [36]. LA-ICP-MS was also used for 2D elemental bioimaging (i.e. As, Cd, Pb, Sb and Zn) in whole rice seeds from contaminated mining area in China, and identified major bio accumulating tissues within the rice seeds and suggested that Sb

and Cd may likely be competing with Zn rich regions in the endosperm (i.e. edible part) [37]. Clearly, LA-ICP-MS offers a great potential to investigate the metal bioaccumulation and translocation properties in plant tissues including seeds.

The goal of this study is to investigate the tissue level elemental distribution of As, Cd, Sb, Pb, and Zn within rice seeds and to retrieve information on functional groups by ATR-FTIR spectroscopy to identify the potential metal–ligand binding sites in the husk, bran and endosperm in rice seeds. Xikuangshan (XKS) is a large metal mining operation located in the Hunan province in China and produces bulk of the world's Sb supply [38]. The surrounding water, soil, freshwater plants and fish are contaminated due to dissolution of stibnite (Sb_2S_3) and other accessory sulfide minerals of As, Cd and Zn [17,38,39]. For this purpose we used rice seeds from contaminated rice fields from in the vicinity of the large XKS Sb mine in Hunan province, China and compared with the rice seeds collected from Anhui province in China, as well as Nipponbare rice from Arkansas, USA. To our knowledge very little information is available on elemental association distribution with metal-binding functional groups in rice seeds, and therefore IR spectroscopy of the endosperm, bran and husk of rice seeds were conducted to gain insights on metal–ligand binding sites.

Table 1
Polarity (N + S + O) / C ratio from elemental analysis.

Site	Endosperm (N + S + O) / C	Husk (N + S + O) / C
Guanjia (G)	0.99	0.96
Minzhu (M)	0.96	0.92
Jinwang (J)	0.94	0.96
Nipponbare (Nr)	1.01	1.16
Anhui	0.99	0.93

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