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Contents and the biogeochemical characteristics of rare earth elements in wheat seeds

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Abstract. Contents of fifteen rare earth elements (REEs) in the seeds of sixty breeds of wheat collected from a seed bank were measured by inductively coupled plasma mass spectrometry (ICP-MS). The distribution patterns of contents of REEs in wheat seeds (n = 58) were observed and compared with their average level in soils (n = 364). Differences among regions and between spring and winter wheat were tested. Comparison with literature data was also made. The results show that the content of REEs in wheat seed ranges between 10^{-11} g · g^{-1} and 10^{-8} g · g^{-1}, 3–4 order of magnitudes lower than that in soils. The distribution patterns are that light REEs enriched and the Eu-anomaly is weak, similar to the soil case. No obvious differences were found among different regions and breeds. The data obtained in this study represent the contents of the fifteen REEs in wheat seeds.

Introduction

In the past decades, much research dealing with contents, distribution, accumulation, transportation as well as ecological effects of rare earth elements (REEs) in agriculture ecosystem, have been carried out (Laul et al. 1979, 1982; Guo 1988; Xie et al. 1991; Wyttenbach et al. 1998). A series of investigations showed the positive effects on increasing photosynthesis rate, raising output and improving the quality of crops, but confirmation is still lacking (Wang et al. 1989; Welch 1995; Wang et al. 1998). However, widespread use of REEs in China has resulted in residues and accumulation in crops and may cause serious environmental issues, which have attracted the attention of the environmental scientists (Liu SJ et al. 1997).

REEs can be taken up through the leaf surface after spraying (Sun et al. 1994), but normally uptake is exclusively by roots. As with most trace elements, REE concentrations decrease in the order of roots > leaves > seeds.

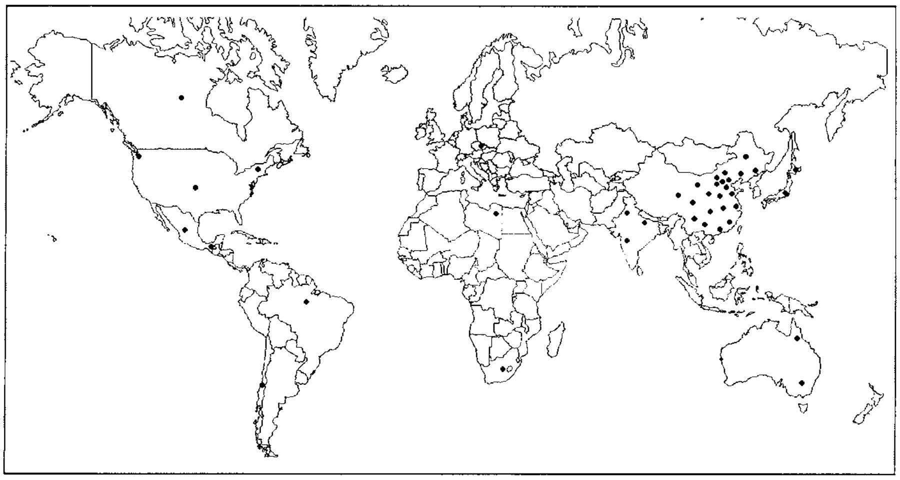

Figure 1. Map of sample locations.

Considering the importance of wheat in food chain and its close relationship with human health, it is important to clarify the amount of REEs in wheat seeds by examining contents and biogeochemical characteristics (Zhang et al. 1994). Many comparative studies of REE contents and distribution between crops and soils have been made (Wang et al. 1997; Lu et al. 1997; Hideki et al. 1992). Only few reports focused on contents in wheat seeds.

The aims of the present work are to determine the contents of REEs in sixty representative samples of wheat of varying places of origin or breeds using inductively coupled plasma mass spectrometry (ICP-MS), and make comparison with soil related contents and patterns. It will supply basic data for long-term accumulation of REEs and risk assessment in agriculture.

Materials and methods

Sampling protocol

Sixty samples were collected from seed banks of the Institute of Genetics, Chinese Academy of Sciences and Institute of Breed Resources, Chinese Academy of Agricultural Sciences in Beijing. It includes 42 domestic samples from 35 cities in 14 provinces, and 18 overseas samples from 12 countries. Sample locations are shown in Figure 1.

364 soil samples were collected far away from industrial pollution affected areas around China, including 18 samples from the South of China, 36 samples from the North of China, 96 samples from the Northeast of China,

96 samples from Central China, and 118 samples from the Northwest of China.

Analytical methods

Seeds of wheat were firstly washed by hot water, air dried, ground in agate mortar, then dried to constant weight at 80 °C. After putting 0.5g sample to 15ml digest beaker, they were digested in 5ml HNO_3 and 0.5ml $HC1O_4$ mixture. The digested samples were then transferred to a container, adding 20 μl 2.5 $\mu g \cdot ml^{-1}$ Re solution for measurement. Contents of 15 REEs in 60 samples were analyzed by ICP-MS (Elan 5000 made by Perkin-Elmer Sciex Co.). The parameters and conditions were described by Liu HS 1997.

Collected soils were pretreated by air drying, crushing, grinding and being passed through a sieve (100 Mu). The 50 mg sample was then taken for analyzing. Contents for REEs in soils were analyzed by instrumental neutron activation analysis (INAA). Detailed parameters, conditions and precision were described by Wang 1991.

Quality assurance

All reagents in the experiment are high purity. Water is 18MΩ cm super-pure water. Results are analyzed with Statistica 5.0 and Excel 97.

To test the method's reliability, a recovery experiment was carried out (Table 1).

Upon adding standard to the digested mixture solution, the measured recovery rates of 15 REEs are in the range from 81% to 100.8% with an average of 92.4%. Repeatability of sample analysis is n = 6. Variances are from 0.88 to 1.84. The recovery experiment shows that the method is reliable.

Results and discussion

Contents of REEs in wheat seeds

Before the analysis of the contents of REEs in wheat seeds, abnormal value processing and distribution tests were carried out (Tao 1994). According to the traditional Area method ($\mu \pm 3\ \delta$), two abnormal values were deleted. Results of Kurtosis and Skewness tests show that contents of REEs in wheat seeds did not agree with normal distribution but approximated a log-normal distribution. Geometric mean and standard deviation can properly represent the characteristics of amount and scatter of REE contents in wheat seeds. The statistical results are shown in Table 2.

Table 1. Results of recovery experiment by adding standard to digested mixture solution (ng · ml^{-1}) [n = 6]

REE	Content in mixture	Standard added	Mixture + Standard added	Standard recovery measured	Recovery rate (%)
La	1.40	15.00	15.80	14.40	96
Ce	2.91	20.00	23.50	20.60	103
Pr	0.14	3.00	3.11	2.97	99
Nd	0.52	15.00	14.17	13.64	91
Sm	0.08	2.00	2.06	1.97	98
Eu	0.06	2.00	2.08	2.01	101
Gd	0.08	3.00	2.88	2.79	93
Tb	0.04	0.50	0.43	0.41	82
Dy	0.048	2.50	2.30	2.25	90
Ho	0.011	0.50	0.47	0.46	92
Er	0.021	1.00	0.89	0.87	87
Tm	0.005	0.50	0.41	0.405	81
Yb	0.030	1.00	0.97	0.90	94
Lu	0.007	0.50	0.43	0.423	84
Y	0.310	10.00	9.89	9.58	95

Table 2 indicates that the contents in wheat seeds are not only very low (10^{-11} g · g^{-1} ∼ 10^{-8} g · g^{-1}) but also unevenly distributed (wide ranges of contents). This reflects either the features of seeds, the portion of the plant with the lowest REE content, or the different wheat varieties and places of origin.

Distribution pattern of REEs in wheat seeds

Following the general method of geochemistry (Wang et al. 1989), contents of REEs in seeds and soils are standardized with contents of REEs in chondrite. The distribution patterns are shown in Figure 2. To further describe the characteristics of seed REE distribution, parameters of seed and soil REE distributions are calculated separately (Table 3).

The curve in Figure 2 and data in Table 3 describe the REE contents and distribution in wheat seeds. The distribution pattern of REE contents in wheat seed shows a negative slope. Contents of light REEs are signficantly higher than those of heavy REEs. The anomaly of Eu is insignificant. Compared with soil REEs, the contents in wheat seeds are 3–4 orders of magnitude lower.

Table 2. Contents of 15 REEs in wheat seeds (ng · g^{-1}) [n = 58]

REE	Contents Range	Geometric mean	Geometric SD
La	4.90 ~ 84.30	16.80	2.19
Ce	6.40 ~ 71.90	29.96	1.75
Pr	0.63 ~ 6.60	1.90	1.69
Nd	1.20 ~ 22.60	6.76	1.82
Sm	0.27 ~ 3.80	1.11	1.70
Eu	0.11 ~ 0.81	0.29	1.52
Gd	0.43 ~ 3.3	1.16	1.52
Tb	0.03 ~ 0.4	0.13	1.72
Dy	0.23 ~ 1.90	0.73	1.60
Ho	0.02 ~ 0.64	0.11	1.81
Er	0.04 ~ 0.87	0.34	1.78
Tm	0.01 ~ 0.24	0.06	1.75
Yb	0.11 ~ 0.75	0.39	1.53
Lu	0.02 ~ 0.14	0.07	1.47
Y	0.93 ~ 13.20	4.40	1.62

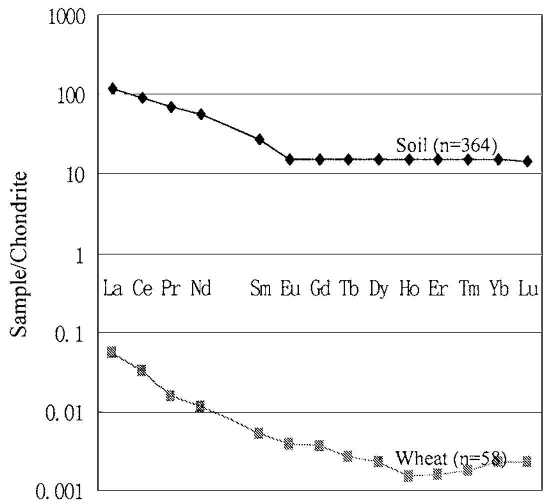

Figure 2. Comparison of soil and seed REE distribution pattern.

Table 3. Comparison of parameters on distribution patterns of REEs in seed and soil ($ng \cdot g^{-1}$)

Parameters	Seed	Soil
Σ REE	56.81	176800
Σ LREE	53.82	157200
Σ HREE	2.99	19600
Σ LR/Σ HR	18.00	8.01
δ Eu	0.88	0.66

Σ REE: total contents of 14 REEs (except Pm);
Σ LREE: total contents of light REEs (La-Eu);
Σ HREE: total contents of heavy REEs (Gd-Lu);
Σ LR/Σ HR: the ratio of light REE to heavy REE;
Δ Eu: Eu-anomaly.

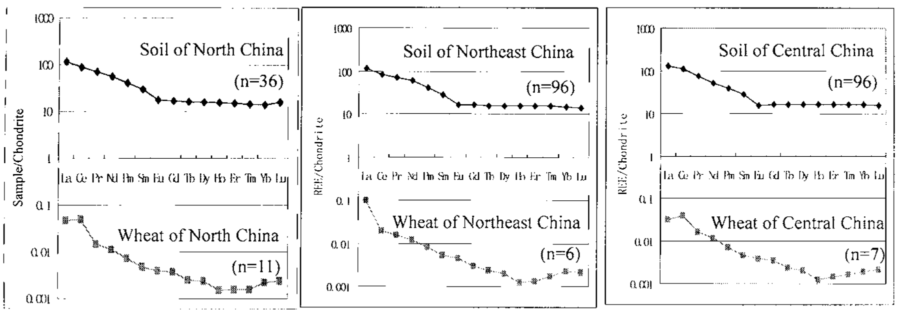

Figure 3. Comparison of regional distribution patterns.

There are some similarities in distribution patterns between seeds and soils. Further comparisons show that the ratio of LREE to HREE is much higher in seed (18.00) than in soil (8.01). That is to say, LREE is more abundant in seeds than in soils. The Eu deficit in seeds is slight (0.88) and in soils it is moderate (0.66). Similar results were found in the comparisons between soil and wheat in three different regions of China (see Figure 3).

Although REEs in wheat originate from soil (distribution pattern of wheat and soil are quite similar), the process of transportation and accumulation in wheat is very complicated, and the abilities of REE absorption of different varieties of wheat vary. To describe the REE content in wheat seeds more effectively, a geometric mean of all samples was used.

Content comparison between spring wheat and winter wheat

Using classical statistical method, the REE contents of spring wheat and winter wheat were compared. To exclude the effects caused by regional differences, three regions (1: North, 2: Central, 3: Northwest) in China were selected and tested separately. Contents of both single element and total amount have been tested using t-test ($n_1 = 11$, $n_2 = 6$, $n_3 = 6$, $\alpha = 0.05$).

For both single REE or total REE content, test results do not show significant difference between spring wheat and winter wheat, except some elements in North China, such as Pr, Sm, Gd and Dy. The conditions of climate and soil are very similar in each region, so it can be concluded that the difference in contents between spring wheat and winter wheat is insignificant.

Contrast between our results and literature reports

Only a few publications deal with the contents of REEs in wheat seeds, and most of them are based on one variety or few samples. In addition, much of the analytical work is done by INAA which measured only 8 elements. In a previous study, the purposes of the measurement of REEs are either for making comparisons of REE accumulation before and after REE fertilization, or determining the standard content of National Standard Material (NSM) of China.

To offer a more accurate background of REEs in wheat seeds, Table 4 provides existing literature data obtained in previous studies in China for comparison. Because the analytical methods and purpose of the study are quite different from each other, the results show that measurements of each case are not at the same order of magnitude. However, Table 4 contents of REEs from the present study (the second columns) are ranging between different literature reports. It is lower than NSM 08503 (third column) but higher than the others (fourth and fifth columns). Comparing the total amount of REEs (Σ REE), it can be found that Σ REE in this study (56.81 ng $\cdot$ g^{-1}) is lower than related reports in Chinese (260∼3150 ng $\cdot$ g^{-1}) and international (110∼1970 ng $\cdot$ g^{-1}) samples (Su et al. 1985). Due to the large amount of samples of different varieties and global locations, and with the aid of ICP-MS, the contents of REEs in wheat seeds can be comprehensively described.

Conclusion

Based on 60 samples collected from a seed bank, total amount of 15 REEs in wheat seeds are averaged 61.21 ng $\cdot$ g^{-1}. The distribution pattern of REEs in wheat seeds shows a relative high content of LREEs and a negative anomaly of Eu. The contents in wheat seed show no significant difference between spring wheat and winter wheat. Data of this result can be used as contents of REEs for related studies.

Table 4. Comparison with literature data ($ng \cdot g^{-1}$)

REEs	Present study	Liu HS et al. 1997	Sun et al. 1994	Liu SJ et al. 1997
La	16.80	15.5	3.19	5.0
Ce	26.96	28.7	N.D.	< 7.5
Pr	1.90	3.15	–	–
Nd	6.76	15.5	N.D.	< 40
Sm	1.11	2.4	0.48	0.70
Eu	0.29	1.2	0.11	0.60
Gd	1.16	2.4	–	–
Tb	0.13	0.31	N.D.	< 0.20
Dy	0.73	2.01	–	–
Ho	0.11	0.28	–	–
Er	0.34	0.86	–	–
Tm	0.06	0.11	–	–
Yb	0.39	0.85	< 0.8	< 0.80
Lu	0.07	0.12	< 0.2	< 0.20
Methods	ICP-MS	ICP-MS	INAA	INAA

(1) Data in the third column are means of 7 repeated samples in standard material (NSM 08503); Data in the fourth column are means of 8 repeated samples in one location; Data in the fifth column are means of 6 repeated samples in one location;
(2) N.D. denotes the content is below the limit of detection;
(3) – denotes this REE of the column has not been measured.

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