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Effects of Manganese Deficiency and Added Cerium on Photochemical Efficiency of Maize Chloroplasts

Chunxiang Qu · Xiaolan Gong · Chao Liu · Mengmeng Hong · Ling Wang · Fashui Hong

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Abstract The mechanism of the fact that manganese deprivation and cerium addition affect the photochemical efficiency of plants is unclear. In this study, we investigated the improvement by cerium of the damage of the photochemical function of maize chloroplasts under manganese-deprived stress. Chlorophyll fluorescence induction measurements showed that the ratio of variable to maximum fluorescence (Fv/Fm) underwent great decreases under manganese deficiency, which was attributed to the reduction of intrinsic quantum efficiency of the photosystem II units. The electron flow between the two photosystems, activities of Mg^{2+}–ATPase and Ca^{2+}–ATPase, and rate of photophosphorylation on the thylakoid membrane of maize chloroplasts were reduced significantly by exposure to manganese deprivation. Furthermore, the inhibition of cyclic photophosphorylation was more severe than noncyclic photophosphorylation under manganese deficiency. However, added cerium could relieve the inhibition of the photochemical reaction caused by manganese deprivation in maize chloroplasts. It implied that manganese deprivation could disturb photochemical reaction of chloroplasts strongly, which could be improved by cerium addition.

Keyword Manganese deprivation · Cerium · Maize · Photophosphorylation · Chlorophyll fluorescence

Introduction

As a micronutrient, manganese (Mn) is a transition metal that can exist in several different valence states, and therefore, in photosynthesis, the four Mn atom-containing oxygen-evolving complex catalyzes water oxidation to oxygen in photosystem II (PSII) [1]. Mn is also an important constituent of essential metalloenzymes, including oxidases and dehydrogenases, DNA and RNA polymerases, kinases, decarboxylases, and sugar transferases [2, 3]. Mn deficiency resulted in destruction of the thylakoid structure, chlorophyll (Chl) a fluorescence kinetics and gas exchange, loss of PS II and MnSOD function, and sensitivity to peroxides [4, 5]. Our previous work confirmed that growth of Mn-deprived maize seedlings was inhibited, especially the photosynthetic ability [6, 7].

Rare earth elements (REEs), such as lanthanum (La), neodymium (Nd), and cerium (Ce), of optimal concentrations typically had been proved to improve spinach growth, especially photosynthesis, including Chl formation, the absorption, transport, and conversion efficiency of light energy of spinach [8–17]. In terms of Mn-deprived maize seedlings, we conducted the experiments by adding Ce to Mn-deprived maize seedlings to study its effect on CO_2 assimilation [18]. However, whether Ce affected the photochemical reaction of Mn-deprived maize seedlings is unclear.

In this paper, therefore, we carried out experiments to evaluate whether Mn deficiency affected photochemical reaction of maize seedlings and Ce addition improved the photochemical reaction of plants by exposure to Mn-deficient

Chunxiang Qu and Xiaolan Gong contributed equally to this work.

C. Qu · X. Gong · C. Liu · M. Hong · F. Hong (✉)
Medical College of Soochow University,
215123 Suzhou, People's Republic of China
e-mail: Hongfsh_cn@sina.com

C. Qu
College of Chemistry, Chemical Engineering and Materials Science, Soochow University,
Suzhou 215123, People's Republic of China

L. Wang
Library of Soochow University,
215123 Suzhou, People's Republic of China

media, and assayed parameters involved in photochemical reaction including Chl fluorescence, activities of $K_3Fe(CN)_6$ (FeCy) reduction rate, Mg^{2+}–ATPase and Ca^{2+}-ATPase, photophosphorylation (PSP) rate and electron flow in maize seedlings. Our findings will be of benefit to the underlying Mn deficiency-induced photosynthetic effects in plants and arouse attention to Mn deficiency in fields.

Materials and Methods

Material Treatment and Culture

Seeds of *Zea mays* (L. cv.) were planted in a quartz sand-containing pot and placed in porcelain dishes, to which 1 L each of the following culture solutions were added: (1) Mn-containing Hoagland's nutrient solution, (2) 15 μM $CeCl_3$+ Mn-containing Hoagland's nutrient solution, (3) Mn-deprived Hoagland's nutrient solution, and (4) 15 μM $CeCl_3$+Mn-deprived Hoagland's nutrient solution. Mn-containing Hoagland's nutrient solution and Mn-deprived Hoagland's nutrient solution were prepared as described in Arnon and Hoagland's method [19]. In the preparation of Mn-deprived Hoagland's nutrient solution, the macronutrient concentrations were the same as the Mn-containing Hoagland's nutrient solution; no $MnCl_2$ was added in micronutrient solution. Plants were grown at 25°C using a 16/8-h light/dark cycle in a growth chamber under 500 μmol m^{-2} s^{-1} of cool fluorescent light for 30 days. The nutrient solution was renewed every week. Maize seedlings at the age of two leaves and four leaves were sprayed with 15 μM $CeCl_3$ solution and deionized water for control.

Assay of Chl Fluorescence

Chl fluorescence and P700 parameters were measured at room temperature (25°C) with a dual-wavelength pulse-amplitude-modulated fluorescence monitoring system (Dual-PAM, Heinz Walz, Effeltrich, Germany) according to Schreiber et al. [20] and the manufacturer's instructions. Samples were dark adapted in the sample chamber for a minimum of 20 min prior to all measurements. The light intensity was 500 μmol photons m^{-2} s^{-1} photosynthetic active radiation (PAR). With repetitive application of saturation pulses (SP) for assessment of fluorescence and P700 parameters, the intrinsic fluorescence (Fo) was determined after keeping the tissue in darkness for 30 min. Saturating actinic light pulses (SP) were applied to obtain maximum fluorescence (Fm) in the dark-adapted samples. The maximum quantum efficiency of PSII primary photochemistry (Fv/Fm) was then determined by application of a 1-s pulse of red saturation flash (800 μmol photons m^{-2} s^{-1} PAR); Fv/Fm was estimated as (Fm−Fo)/Fm.

All fluorometer measurements were taken on the uppermost two leaves of each seedling and averaged to standardize within-plant variations.

Chloroplast Preparation

All leaves of maize plants were used as experimental materials. The leaves were homogenized in a prechilled mortar and pestle in ice-cold isolation buffer, which contained 400 mM sucrose, 10 mM NaCl, and 20 mM tricine (pH 7.8). The slurry was filtered through five layers of cheesecloth, and the chloroplasts were sedimented at 3,000×*g* for 5 min at 4°C. The supernatant was carefully discarded and the pellet retained. The pellet was washed and resuspended in a small volume of chilled suspension buffer that contained 100 mM sucrose, 10 mM NaCl, 2 mM $MgCl_2$, and 20 mM HEPES (pH 7.5). The whole procedure was completely done in ice-cold conditions as quickly as possible to inactivate and prevent the degradation of chloroplast by proteolytic enzymes. Chl was extracted in chilled 80% acetone and estimated spectrophotometrically [21].

Assay of FeCy Reduction Rate

The reduction rate of FeCy of the chloroplasts was measured photometrically by following the absorbance change at 420 nm, using a dual-beam spectrophotometer (UV-3010, Hitachi Co., Japan). The above measurement methods were described in Allen and Holmes [22].

Assay of Photophosphorylation Rate

PSP activity of chloroplasts was assayed by the luciferin–luciferase method to measure the amount of ATP synthesized within 2 min at saturating irradiance of about 1,500 μmol m^{-2} s^{-1} and 25°C according to Allnutt et al. with some modification [23]. Cyclic-PSP (C-PSP) activity was determined in 1 cm^3 of reaction mixture containing 50 mM tricine–KOH (pH 8.0), 2 mM $MgCl_2$, 1 mM ADP, 5 mM phosphate (Pi), 0.05 mM phenazine methosulfate (PMS), and the chloroplasts containing about 10 μg chlorophyll. Non-cyclic-PSP (NC-PSP) activity was assayed similarly to C-PSP except that PMS was replaced by 1 mM FeCy or methyl viologen (MV). By putting the test tubes for 3 min into boiling water, the reactions were stopped.

Assay of the Activity of Mg^{2+}–ATPase and Ca^{2+}–ATPase

Mg^{2+}–ATPase on the thylakoid membranes was extracted and assayed according to MoCarty's method [24]. Activated solution, 0.6 ml, was added into 0.4 ml suspension of chloroplasts (containing 50 μM Tris–HCl, pH 8.0; 50 μM

NaCl; 5 μM $MgCl_2$; 5 μM dithiothreitol), then activated it with light of 500 μmol m^{-2} s^{-1} for 6 min in room temperature. About 0.5 ml reaction solution (containing 50 μM Tris–HCl, pH 8.0; 5 μM $MgCl_2$; 20 μM ATP) was added into 0.5 ml activated suspension of the chloroplasts above and incubated at 37°C for 10 min, then 0.1 ml 20% trichloroacetic acid (TCA) was added to stop the reaction. The inorganic phosphorus content was determined by Ames's method [24].

Ca^{2+}–ATPase was extracted from maize chloroplasts according to Li's method [25] and assayed with the method of Shi et al. [26]. About 100 μl of Ca^{2+}–ATPase samples was mixed with 1 ml of reaction buffer (50 mM Tris–HCl, 5 mM ATP, 5 mM $CaCl_2$, 25% CH_3OH, 20 mM NaCl, pH 8.8) and incubated at 37°C for 2 min. The reaction was stopped by adding 0.2 ml 20% TCA, and the inorganic phosphorus content was determined by Ames's method [27].

Statistical Analysis

Each biochemical indicator was replicated five times. All data were expressed as mean ± standard deviation (SD) and were analyzed by an analysis of variance (ANOVA). If significance was found in ANOVA, group means were compared using Student's *t* test. Differences were considered significant when $p \leq 0.05$.

Results

Chl Fluorescence Measurements

Chl fluorescence not only can reflect the photosynthetic primary reaction process, such as light energy absorption, excitation energy transfer, photochemical reaction, but also relates to the processes of photosynthetic electron transport, proton gradient establishment, carbon dioxide fixation, and so on. We detected Chl fluorescence parameters of maize seedlings under various culture conditions; the results are listed in Table 1. It can be see that Fv/Fm in the Mn-deprived maize seedlings was decreased by 21.39%, as compared to the control, and added Ce made it recover back to 98.40% of the control level. The quantum yields of PSII, PSI (Y(II), and Y(I)) in the Mn-deprived seedlings decreased significantly by 14.98% and 7.61% as compared to the control; added Ce relieved the damage by 8.37% and 6.37% reduction, respectively, compared with the control. The electron transport rates of PSII (ETR(II)) and PSI (ETR (I)) of Mn-deprived maize seedlings were 16.66% and 12.90% lower than those of the control. After Ce treatment, those were decreased by 9.73% and 7.47%. The photochemical quenching (qP) of maize seedlings grown in the Mn-deprived Hoagland's media decreased by 18.54%, and added Ce promoted qP value. Conversely, the non-photochemical quenching (qN) grown in the Mn-deprived Hoagland's media increased obviously by 40.88% compared with the control, and that of the added Ce group increased by 13.63%. In terms of Ce-added Mn-present maize seedlings, the values of Y(II), Y(I), ETR(I), and qP were increased respectively by 11.89%, 11.48%, 6.22%, and 10.49%, while qN was decreased by 6.93%, and the values of Fv/Fm and ETR(II) showed no significant increase.

FeCy Reduction Rate of Chloroplasts

To further confirm changes of electron transport rate caused by Mn deficiency and added Ce, we detected the FeCy reduction rate of chloroplasts. As shown in Fig. 1, the FeCy reduction rate from Mn-deprived maize seedlings decreased by 54.44%, as compared to those of the control. However, added Ce alleviated the inhibition of Mn deprivation, making the upper indices decreased by 11.21% compared with that of the control. Additionally, Ce enhanced significantly the FeCy reduction rate of maize grown in

Table 1 Effects of Ce on Chl fluorescenes of maize chloroplast under Mn deprivation

Culture	1	2	3	4
Fv/Fm	0.784±0.004	0.754±0.002	0.732±0.005*	0.736±0.004*
Y(II)	0.227±0.010	0.254±0.003**	0.193±0.006**	0.208±0.002*
Y(I)	0.565±0.003	0.582±0.004	0.522±0.007*	0.529±0.006*
ETR(II)	47.90±1.800	53.40±0.880**	39.92±1.376**	43.24±0.872*
ETR(I)	115.54±2.232	122.73±2.546*	100.64±2.448**	106.91±2.548*
qP	0.410±0.024	0.453±0.015**	0.334±0.009**	0.343±0.014**
qN	0.433±0.017	0.0403±0.009**	0.610±0.054**	0.492±0.009**

Lines marked with a star or double stars were different from Hoagland's solution in that panel at the 5% or 1% confidence level, respectively. Values represent means±SD, $n=5$

1 Hoagland's solution (control), *2* Hoagland's solution+Ce, *3* Mn-deprived Hoagland's solution, *4* Mn-deprived Hoagland's solution+Ce

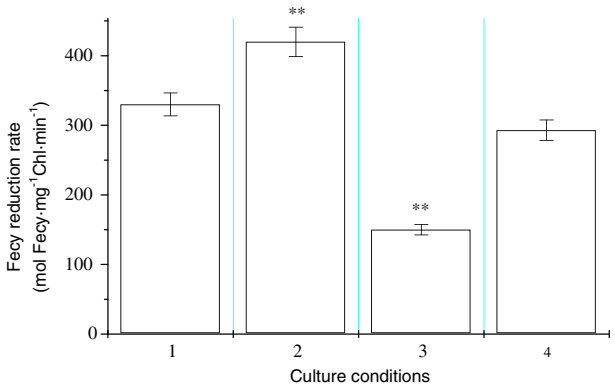

Fig. 1 Effects of Ce on electron transport of maize chloroplast under Mn deprivation. *1* Hoagland's solution (control), *2* Hoagland's solution+Ce, *3* Mn-deprived Hoagland's solution, *4* Mn-deprived Hoagland's solution+Ce. *Bars marked with double stars* were different from Hoagland's solution in that panel at the 1% confidence level. Values represent means ± SD, $n=5$

Mn-present Hoagland's media. Indeed, Mn deficiency and added Ce did affect electron transport in the chloroplast.

PSP Rate of Chloroplasts

Adding $NADP^+$ and Hill oxidizing agent FeCy to the reaction media makes the electron transport follow the non-cyclic pathway, while by adding PMS, a cyclic electron carrier, to the reaction media, the electron transport then follows the cyclic pathway, without oxygen evolving and $NADP^+$ reduction.

Figure 2 shows the NC-PSP (+ MV or FeCy) and C-PSP (+ PMS) rates of Ce-treated chloroplasts grown in Mn-present Hoagland's media and Mn-deprived Hoagland's media were increased significantly. The NC-PSP (+ MV) and C-PSP (+ PMS) rates of Ce-treated chloroplasts grown in Mn-present Hoagland's media were elevated by 13.08% and 15.58%, respectively, compared with those of the control; Mn-deprived chloroplasts were significantly inhibited by 50.33% and 37.14% reduction compared with those of the control; after Ce addition, these two rates were improved, showing 26.75% and 20.50% reduction compared with those of the control. The results also revealed that added Ce could improve both NC-PSP and C-PSP rates and had more pronounced effect on the NC-PSP rate, indicating the influence of added Ce on PSII was greater than that of PSI.

To determine the details about effects of added Ce on PSII, dibromothymoquinone (DBMIB) and benzoquinone (BQ) were used (Fig. 3) [9]. After adding DBMIB, which blocked the electron transfer between the two photosystems, the NC-PSP (+ FeCy) rate of Mn-deprived maize was inhibited significantly by 54.03% compared with the control, and added Ce improved it by 30.26% reduction to the control. Besides, Ce improved the NC-PSP rate of maize seedlings grown in Mn-present Hoagland's media by 11.66%. Instead of FeCy, hydrophobic electron acceptor was used as artificial electron acceptor, finding that NC-PSP (+ FeCy) rate of Mn-deprived maize was decreased by 47.64%, and added Ce improved it by 30.26% reduction compared to the control. Meanwhile, Ce increased the NC-PSP rate of Mn-present maize seedlings by 22.67%, indicating that added Ce could influence both of the two photosystems positively.

Mg^{2+}–ATPase and Ca^{2+}–ATPase Activities of Chloroplasts

It is observed in Fig. 4 that the activities of Mg^{2+}–ATPase and Ca^{2+}–ATPase of Ce-treated groups grown in Mn-present

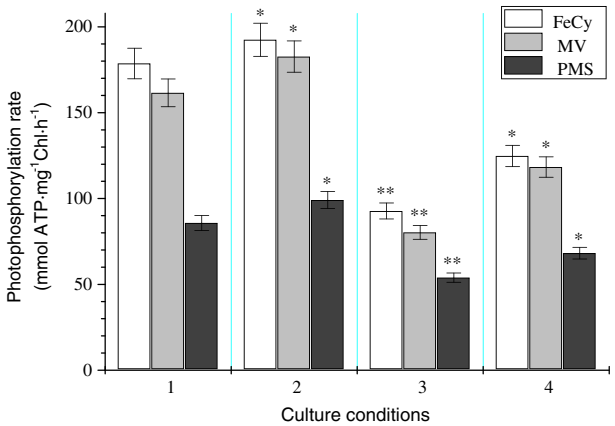

Fig. 2 Effects of Ce on NC-PSP and C-PSP activity of maize chloroplast under Mn deprivation. *1* Hoagland's solution (control), *2* Hoagland's solution+Ce, *3* Mn-deprived Hoagland's solution, *4* Mn-deprived Hoagland's solution+Ce. *Bars marked with single star or double ones* were different from Hoagland's solution in that panel at the 5% or 1% confidence level, respectively. Values represent means ± SD, $n=5$

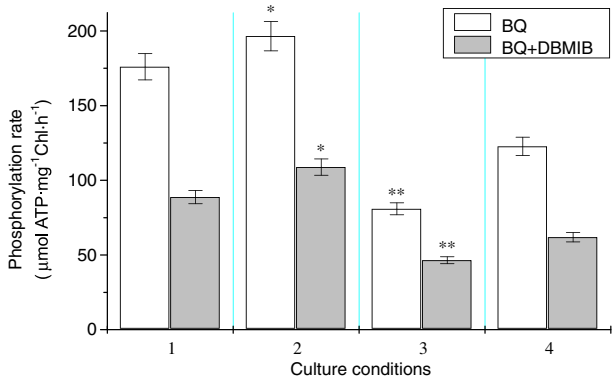

Fig. 3 Effects of Ce on photophosphorylation activity of both PSII and PSI maize chloroplast under Mn deprivation. *1* Hoagland's solution (control), *2* Hoagland's solution+Ce, *3* Mn-deprived Hoagland's solution, *4* Mn-deprived Hoagland's solution+Ce. *Bars marked with single star or double ones* were different from Hoagland's solution in that panel at the 5% or 1% confidence level, respectively. Values represent means ± SD, $n=5$

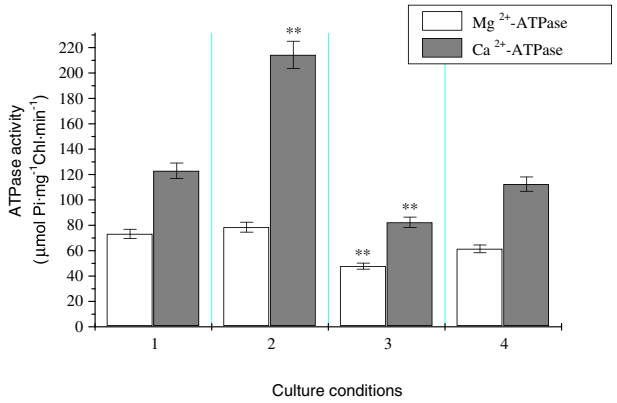

Fig. 4 Effects of Ce on Mg^{2+}–ATPase activity and Ca^{2+}–ATPase activity of maize chloroplast under Mn deprivation. *1* Hoagland's solution (control), *2* Hoagland's solution+Ce, *3* Mn-deprived Hoagland's solution, *4* Mn-deprived Hoagland's solution+Ce. *Bars marked with double stars* were different from Hoagland's solution in that panel at the 1% confidence level. Values represent means ± SD, n=5

Hoagland's media were increased only by 7.24% and 74.34% contrasted to those of the control. But under Mn-deprived stress, the activities of Mg^{2+}–ATPase and Ca^{2+}–ATPase were declined by 34.74% and 32.99%. Furthermore, the two enzyme activities of Ce-treated groups grown in Mn-deprived Hoagland's media were 28.63% and 36.54% higher than those of Mn-deprived condition. It was apparently that Mn deprivation exerted more inhibition on Mg^{2+}–ATPase activity than that of Ca^{2+}–ATPase, and Ca^{2+}–ATPase displayed more activity recovery since Ce was added.

Discussion

Mn is key to the electron transfer for its construction to the structure of PSII ($Mn_4O_xCaCl_y$ cluster), where four electrons are transferred to oxidative water. No other metal ions have been found to date that can replace it according to Dasgupa et al. [28]. Our previous work revealed that Mn deprivation made light absorption, transmission, and oxygen evolution of chloroplast damaged by spectral methods [6], and resulted in extensive declines in PSP rate and key enzymes of CO_2 assimilation [7]. In this paper, the electron transport rate (FeCy reduction rate) (Fig. 1) from the Mn-deprived maize seedlings decreased sharply, and the total electron flow, involving both of the two photosystems, was inhibited, indicating Mn deprivation had a significant impact on the electron harvesting from the primary reaction in PSII or PSI, thus reducing the conversion efficiency from light energy to electric energy. However, added Ce may relieve the inhibition of FeCy reduction rate and the electron flow involving both PSII and PSI caused by Mn deficiency, speculating that Ce might enter the chloroplast and bind to PSII, then repaired the PSII damage caused by Mn deprivation. Moreover, added Ce could promote the oxygen evolution and CO_2 assimilation [18]. Besides, previous researches implied that Ce had the similar function as Ca in the oxygen evolution center so that it could accelerate the electronic transfer and oxygen evolution of chloroplast of spinach grown in Ca^{2+}-deficient media [17].

The extent of Mn-deprived stress can be monitored by measuring Fv/Fm of PSII. The dark-adapted value of Fv/Fm reflects photosynthetic performance, and the potential quantum efficiency of PSII [29] and values that are lower than the optimal value of 0.83 indicate a decrease in PSII efficiency [30, 31]. Fv/Fm value of Mn-deprived maize seedlings was significantly decreased (Table 1), indicating that Mn-deprived stress disturbed severely the photosynthetic electron transport or damage to the thylakoid structure in the donor side of PSII [32]. Furthermore, lower Fv/Fm resulted in the significant reduction electron transport rate (ETR II) of PSII caused by Mn-deprived stress. Y(II) is proportional to the product of qP and the efficiency of excitation capture by open PSII centers, denoted as Fv/Fm [33]. Coincident with Fv/Fm, lower Y(II) and qP were observed in Mn-deprived maize seedlings, suggesting that lower efficiency of photochemical energy conversion and dissipation were associated with inhibition of PSII electron transport. Related to heat dissipation and protect photosynthesis, the non-photochemical quenching (qN) increases in environments in which light energy absorption exceeds the capacity for light utilization. qN value of Mn-deprived maize seedlings was higher than that of the control, which was coincident with the previous result of photosynthetic pigments reduction under Mn deprivation [6, 7], indicating a significant reduction of photosynthetic protection of Mn-deprived maize seedlings. For PSI (P700), compared to the control, the obvious reduction of Y(I) (PSI photochemical efficiency) from the Mn-deprived maize seedlings was observed, which then resulted in the reduction of PSI electron transport rate (ETRI), suggesting that PSI function was damaged by Mn-deprived stress. But the mechanisms still need further study in the future. However, added Ce could significantly relieve reduction of Fv/Fm, Y(II), Y(I), ETR(II), and ETR(I) as well as qP caused by Mn deprivation, while qN was lower compared to those of the control, suggesting that added Ce may improve the function of PSI and PSII under Mn-deprived stress.

It is well established that photosynthetic plants convert electron energy into ATP from ADP, and NADPH: In cyclic electron flow, ATP synthesis is coupled to light-induced electron flow in a closed system around PSI without the net production of NADPH, whereas in non-cyclic electron flow, oxygen, ATP, and a strong reductant, NADPH, are simultaneously synthesized. Various demands for ATP caused by variability of environmental conditions could be compensated through establishment of ΔpH gradient by

the cyclic electron transport. Our results showed that PSII was more sensitive to both Mn deprivation and added Ce than PSI (Figs. 2 and 3). Both NC-PSP and C-PSP were decreased due to Mn deprivation, especially NC-PSP, but added Ce significantly increased both NC-PSP and C-PSP rates and had more pronounced effects on the NC-PSP rate, indicating the influence of added Ce on PSII is greater than that of PSI, which could be supported by our previous work about the conspicuous effect of Ce on oxygen evolution of Mn-deprived maize seedlings [18]), since OEC ($Mn_4O_xCaCl_y$ cluster) is the core of PSII. Besides, other REEs, such as La, Ce, Nd, and praseodymium (Pr), had been demonstrated to accelerate oxygen-evolving and hydrogen-evolving of photosynthesis, and increase the concentration of chlorophyll protein complexes and the activities of Hill reaction, Mg^{2+}–ATPase, and the rate of PSP in chloroplast of some plant species [34, 35].

Photosynthesis is flexibility in meeting different metabolic demands for ATP, which is probably required for photosynthetic assimilation of CO_2 into carbohydrates and other cellular material, including macromolecules. Photosynthetic electron transport is coupled to ATP synthesis. Mg^{2+}–ATPase and Ca^{2+}–ATPase are the terminal points of the whole PSP. According to our researches (Fig. 4), the reduction of ATPase activities was significant, particularly the Ca^{2+}–ATPase activity on the thylakoid membrane caused by Mn deficiency. The enhancement of photosynthesis was coupled with the increase of the amount of ATP by spraying $CeCl_3$ on the leaf of spinach [17]. Added Ce made the activity of Ca^{2+}–ATPase of Mn-deprived maize recover to 91.99% of the control (Fig. 4), which was of benefit to the improvement of CO_2 assimilation of Mn-deprived maize. Chen and Pan et al. added La and Pr to pot-cultured tobacco and spinach, demonstrating that they could promote the cyclic and non-cyclic PSP of chloroplasts, and improve the couple level of chloroplasts and activate Mg^{2+}–ATPase and Ca^{2+}–ATPase [36–38]. Huang et al. demonstrated that added Ce decreased the inhibition of the activities of Mg^{2+}–ATPase and Ca^{2+}–ATPase of Ca^{2+}-deprived spinach chloroplasts [17], which are coincident with our results. The results indicated that added Ce could positively affect photophosphorylation by activating the photophosphorylation coupling factor.

In conclusion, the results of the present study showed that added Ce significantly decreased the inhibition of the photochemical reaction of both PSII and PSI, including Fv/Fm, Y(II), Y(I), ETR(II), ETR(I), qP, NC-PSP, and C-PSP, in maize seedlings caused by Mn deprivation. Added Ce might partly substitute for Mn and improve photosynthesis under Mn-deficient conditions, but the mechanisms need further study in the future.

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References

1. Merchant S, Sawaya MR (2005) The light reactions: a guide to recent acquisitions for the picture gallery. Plant Cell 17:648–663
2. Crowley JD, Traynor DA, Weatherburn DC (2000) Enzymes and proteins containing manganese: an overview. Met Ions Biol Syst 37:209–278
3. Culotta VC, Yang M, Matthew D (2005) Manganese transport and trafficking: lessons learned from *Saccharomyces cerevisiae*. Eukaryotic Cell 4:1159–1165
4. Shenker M, Plessner OE, Tel-Or E (2004) Manganese nutrition effects on tomato growth, chlorophyll concentration, and superoxide dismutase activity. J Plant Physiol 161:197–202
5. Allen MD, Kropat J, Tottey S, Del Campo JA, Merchant SS (2007) Manganese deficiency in *Chlamydomonas* results in loss of photosystem II and MnSOD function, sensitivity to peroxides, and secondary phosphorus and iron deficiency. Plant Physiol 143:263–277
6. Gong XL, Liu C, Wang Y, Zhao XY, Zhou M, Hong MM, Wang S, Li N, Hong FS (2010) Inhibition of the photosynthesis in maize caused by Mn deficiency. Cereal Res Commun 38(3):353–365
7. Gong XL, Wang Y, Liu C, Wang SS, Zhao XY, Zhou M, Li N, Lu Y, Hong FS (2010) Effects of manganese deficiency on spectral characteristics and oxygen evolution in maize chloroplasts. Biol Trace Elem Res 136(3):372–382
8. Hong FS (2002) Study on the mechanism of cerium nitrate effects on germination of aged rice seed. Biol Trace Elem Res 87(1–3):191–200
9. Hong FS, Liu C, Zheng L, Wang XF, Wu K, Song WP, Lü SP, Tao Y, Zhao GW (2005) Formation of complexes of rubisco-rubisco activase from La^{3+}, Ce^{3+} treatment spinach. Sci China Ser B 48:67–74
10. Hong FS, Wang L, Liu C (2003) Study of lanthanum on seeds germination and growth of rice. Biol Trace Elem Res 94(3):273–286
11. Hong FS, Wang L, Meng XX, Wei Z, Zhao WG (2002) The effect of cerium (III) on the chlorophyll formation of spinach. Biol Trace Elem Res 89:263–277
12. Hong FS, Wei ZG, Zhao GW (2000) Effect of lanthanum on aged seed germination of rice. Biol Trace Elem Res 75:205–213
13. Hong FS, Wei ZG, Zhao GW (2002) Mechanism of lanthanum effect on the chlorophyll of spinach. Sci China Ser C 45(2):166–176
14. Hong FS, Zhou J, Liu C, Yang F, Wu C, Zheng L, Yang P (2005) Effect of nano-Tio_2 on photochemical reaction of chloroplasts of spinach. Biol Trace Elem Res 105:269–279
15. Liu XQ, Su MY, Liu C, Zhang Y, Si WH, Hong FS (2007) Effects of 4f electron characteristic and alternation valence of rare earths on photosynthesis: regulating distribution of energy and activities of spinach chloroplast. J Rare Earths 25(2):495–501
16. Liu XQ, Su MY, Liu C, Zhang L, Si WH, Hong FS (2007) Effects of $CeCl_3$ on energy transfer and oxygen evolution within spinach photosystem II. J Rare Earths 25(5):624–631
17. Huang H, Liu XQ, Qu CX, Liu C, Chen L, Hong FS (2008) Influences of calcium deficiency and cerium on the conversion efficiency of light energy of spinach. Biometals 21:553–561
18. Gong XL, Hong MM, Wang Y, Zhou M, Cai JW, Liu C, Gong SJ, Hong FS (2011) Cerium relieves the inhibition of photosynthesis

of maize caused by Mn deficiency. Biol Trace Elem Res 141 (1):305–316
19. Arnon DI, Hoagland DR (1940) Crop production in artificial solutions and in soil with special reference to factors affecting yields and absorption of inorganic nutrients. Soil Sci 50:463–484
20. Schreiber U, Klughammer C (2008) Saturation pulse method for assessment of energy conversion in PS I. PAM Application Notes 1:11–14
21. Arnon DI (1949) Copper enzymes in isolated chloroplasts: polyphenol oxidase in *Beta vulgaris*. Plant Physiol 24:1–15
22. Allen JF, Holmes NG (1986) Electron transport and redox titration. In: Hipkins MF, Baker NR (eds) Photosynthesis, energy transduction: a practical approach. IRL Press, Oxford, pp 103–141
23. Allnutt FC, Ewy RG, Renganathan M, Pan RS, Dilley RA (1991) Nigericin and hexylamine effects on localized proton gradients in thylakoid. Biochem Biophys Acta 1059:28–36
24. MoCarty RE, Racker E (1968) Partial resolution of the enzymes catalyzing photosphorylation. J Biol Chem 243:129–137
25. Li SJ, Cai JP, Wan GQ et al (1978) Studies on structure and function of chloroplasts II isolation and interchangeability of pure coupling factors. Acta Bot Sin 20(2):103–107
26. Shi XB, Wei JM, Shen YK (2001) Effects of sequential deletions of residues from the N- or C-terminus on the function of subunit of the chloroplast ATP synthase. Biochemistry 40:10825–10831
27. Ames BN (1966) Assay of inorganic phosphate, Pi total phosphate and phosphatases. In: Colowick SP, Kaplan NO (eds) Methods in enzymology, vol 8. Academic, New York, p 115
28. Dasgupa J, Ananyev GM, Dismukes GC (2008) Photoassembly of the water–oxidizing complex in photosystem II. Coordination Chemistry Review 252:347–360
29. Lichtenthaler HK, Babani F (2004) Light adaptation and senescence of the photosynthetic apparatus. Changes in pigment composition chlorophyll fluorescence parameters and photosynthetic activity. In: Papageorgiou GC, Govindjee (eds) Chlorophyll fluorescence: a signature of photosynthesis. Springer, Dordrecht. p. 713–736
30. Björkman O, Deming B (1987) Photon yield of O_2 evolution and chlorophyll fluorescence at 77 k among vascular plants of diverse origins. Planta 170:489–504
31. Maxwell K, Johnson GN (2000) Chlorophyll fluorescence-a practical guide. J Exp Bot 51:659–668
32. Skórzyńska-Polit E, Baszyński T (1995) Photochemical activity of primary leaves in cadmium stressed *Phaseolus coccineus* depends on their growth stages. Acta Soc Bot Pol 64:273–279
33. Genty B, Briantais JM, Baker NR (1989) The relationship between the quantum yield of photosynthetic electron transport and quenching of chlorophyll fluorescence. Biochim Biophys Acta 990:87–92
34. Zeng FL, An Y, Ren L, Deng RW, Zhang MF (2000) Effect of lanthanum and calcium on photoelectron transport activity and the related protein complexes in chloroplast of cucumber leaves. Biol Trace Elem Res 77:83–91
35. Zhang AQ, Wang LX, Wu XY (1988) Effect of rare earth elements on photosynthesis growth and hydrogen evolution of *Spirulina platensis*. J Rare Earths 6(4):55–58
36. Chen WJ, Gu YH, Wang SB, Zhan GW (2001) Effects of lamhanum on RuBPase activity in tobacco seedlings. J Rare Earths 19(2):129–133
37. Chen WJ, Wei ZG, Tao Y, Gu YH, Zhao GW (2001) Effects of La $(NO_3)_3$ on photosynthetic light reaction in chloroplast of tobacco plants. Acta Agron Sin 27(4):506–511 (in Chin)
38. Pan DK, Wang YG, Zhang JT (2003) Effect of $LaCl_3$, $PrCl_3$ on photophosphorylation of spinach chloroplasts. J Chin Rare Earth Soc 21(1):77–81