

***In vitro* Fe(II) oxidation by *c*-type cytochromes under anoxic conditions**

YING WANG, TONGXU LIU*, XIAOMIN LI,
FANGBAI LI*

Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou, P. R. China 510650.
txliu@soil.gd.cn; cefbli@soil.gd.cn

Although microaerophilic or anaerobic microbial oxidation of Fe(II) has attracted great interests given its significance in iron cycling in many suboxic and anoxic environments, and the *c*-type cytochromes (*c*-Cyts) involvement in the Fe(II) oxidation processes have been proposed, little effort was made on the molecular reaction of *c*-Cyts in the presence of Fe(II). In this study, spectral kinetics and spectroelectrochemistry characteristics of commercial *c*-Cyts were investigated under various environmental conditions (i.e., Fe(II) concentration, pH and ionic strength). The concentrations of reduced *c*-Cyts (*c*-Cyt_{red}) increased gradually over time and then reached a steady stage. The *c*-Cyt_{red} formation rate constants (*k*) increased with increasing initial Fe(II) concentrations (5-1000 μM) and pH (5.5-8.0). The *k* values decreased with increasing NaCl concentrations (0-1.0 M), and then increased slightly when the NaCl increased from 1.0 M to 3.4 M. Spectroelectrochemistry characterization results revealed that the extent of *c*-Cyt_{red} was strongly dependent on pH but not associated with the ionic strength. The reaction equilibrium constant (*K*) of reaction between *c*-Cyts and Fe(II) was determined as $(10.5 \pm 0.9) \times 10^{-3}$ from the average *K* values based on the experimental results of *c*-Cyt_{red} with excess Fe(II) concentrations (i.e., 100-800 μM) at the equilibrium stage. The standard redox potential (*E*⁰) of *c*-Cyts was calculated as 0.65 V according to the kinetic data and Nernst equation. The correlations between the reaction rates and the concentrations/activities of Fe(II) species were discussed with results demonstrating that the Fe²⁺ activity was the major factor influencing the reaction kinetics. This study provides a fundamental understanding of the biologic iron oxidation process under a molecular level.

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