

## **Kinetic studies on iron-mediated ROS generation: Resolving the catalytic/inhibitory activity of Fe-DTPA complexes**

JUSTIN M. COPELAND\*,  
DEWAMUNNAGE-MUDITHA C. DIAS, PING LI,  
JOHN L. FERRY AND TIMOTHY J. SHAW

Department of Chemistry and Biochemistry, Univ. of South  
Carolina, Columbia, SC 29208. USA  
(\*correspondance: copelajm@email.sc.edu)

The co-existence of Fe(II), Fe(III), dioxygen ( $O_2$ ), superoxide ( $O_2^-$ ) and hydrogen peroxide ( $H_2O_2$ ) has been demonstrated in many natural waters, including cloudwater, the photic zone of the water column, and points of anoxic groundwater emergence. These mixtures occur as metastable states, usually poised by the input of fresh material or energy maintaining the components at an apparent steady state. The simultaneous measurement of all five species is complicated by their high rates of reaction. Historically, these systems are interrogated by the addition of fast acting, redox-inert ligands to “freeze” the system in place by locking the metals at a fixed oxidation state. Here we present a study of the ligand most widely used for this purpose, diethylenetriaminepentaacetic acid (DTPA), and show the necessity of accounting for reaction(s) with other metals during sample collection. Kinetic studies showed that autoxidation of Fe(II) by  $O_2$  competed with complexation of Fe(II) by DTPA until a 100X excess of DTPA with respect to  $O_2$  was achieved, as indicated by decreased  $H_2O_2$  production rates and  $H_2O_2$  stability. The measured competition between  $O_2$  and DTPA for Fe(II), as well as competition of other cations for DTPA, can explain the apparent contradiction in the literature regarding the catalytic and/or inhibitory nature of DTPA in regards to Fe(II) sequestration. Our results suggest that the rate of iron oxidation by  $O_2$  is comparable to the complexation rate of Fe(II) by DTPA ( $k \sim 10^6 \text{ M}^{-1}\text{s}^{-1}$ ) under relevant environmental conditions. Implications for this work include more reliable analysis of ROS in the presence of redox-sensitive metals.