

**P008** Crystallographic observations of iron mineralization in bacterioferritin

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We have studied the mechanism of iron mineralization in *E. coli* bacterioferritin using a combination of spectroscopic/enzyme kinetics methods and a form of time-resolved X-ray crystallography. Our structural studies have revealed three distinct forms of the ferroxidase centre; the apo-form, which is devoid of iron; the di-ferrous form, in which two irons are bound within the ferroxidase centre (reduced); and the  $\mu$ -oxo bridged di-ferric form (oxidised) in which the two ferric irons are bridged by a single oxygen atom. The structures also reveal a previously unrecognised iron site located on the inside face of the protein, just 10 Å from the ferroxidase centre. This novel site is shown to be accessible to iron even when the ferroxidase centre is blocked by zinc. Furthermore, mutation of the residues that compose the inner-surface iron site impair the rate of mineral core formation, but do not affect the catalytic activity of the ferroxidase centre itself, suggesting a very specific role iron mineralization. Our results show that the mechanism by which bacterioferritin accumulates iron is fundamentally different to that proposed for other ferritins; The ferroxidase centre is not a gated site-of-entry for iron, but acts as a classical catalytic centre, cycling between di-ferrous and  $\mu$ -oxo bridged di-ferric forms as electrons are transferred from ferrous iron within the core to molecular oxygen/hydrogen peroxide in the ferroxidase centre pocket.