

decrease in the Cu(II) EPR signal, can be attributed to inter- or intramolecular disproportionation, that is  $2 \text{Cu(I)}-Q \rightleftharpoons \text{Cu(I)}-Q_{\text{red}} + \text{Cu(I)}-Q_{\text{ox}}$ , using the notation of Fig. 3. Copper reduction by substrates was confirmed by circular dichroism (CD) spectroscopy. The Cu(II) ligand-field transitions of pea seedling diamine oxidase and *Arthrobacter* methylamine oxidase are observed in the CD spectra from 600 to 800 nm (ref. 10, and D.M.D., unpublished observations), where the quinone makes no contribution. Fully reduced amine oxidases display no CD bands in this region. Substrate addition under anaerobic conditions produces a 35% decrease in the intensity of the methylamine oxidase Cu(II) CD bands (Fig. 4a), consistent with the EPR results.

The EPR data in Figs 1 and 2 establish that amine oxidase Cu(I)-semiquinones can be generated under conditions that are biologically relevant, in the absence of trapping agents. This permits the development of a plausible mechanism (Fig. 3) featuring well-precedented roles for both copper and the quinone, which circumvents the well-known spin conservation problem associated with two-electron reductions of oxygen<sup>18</sup>. Evidence for a bound superoxide intermediate has been previously described<sup>19,20</sup>. Further, for an amine oxidase isolated from lentil seedlings, Finazzi-Agro and co-workers have shown that a substrate-reduced species with absorption bands at 464, 432 and 360 nm (similar to B in Fig. 4b) is a catalytic intermediate and reacts very rapidly with oxygen<sup>21</sup>. By correlating the room-temperature EPR and absorption spectra, this intermediate can plausibly be assigned as the Cu(I)-semiquinone.

Why has the Cu(I)-semiquinone state of amine oxidases been so elusive? The results in Fig. 4b provide a clue. Anaerobic addition of substrate to methylamine oxidase produces the characteristic semiquinone absorption bands; cooling, without freezing, the enzyme solution bleaches the absorption spectrum and produces a spectrum that represents a mixture of the fully reduced and oxidized quinones. The process is reversible because the semiquinone bands are recovered upon warming the solution to 22 °C. Cyanide prevents the bleaching of the semiquinone spectrum on cooling, probably by stabilizing Cu(I) and preventing back electron-transfer, thereby allowing the semiquinone to be observed even at low temperature. Collectively, the results suggest that the Cu(I)-semiquinone and the Cu(II)-reduced quinone are in equilibrium, and that low temperatures favour the Cu(II) form. Similar effects might be present in other enzymes containing multiple redox centres where intramolecular electron-transfer steps are involved in the mechanism. □

Received 26 September; accepted 16 November 1990.

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ACKNOWLEDGEMENTS. This research was supported by NIH, SERC and the Veterans Administration.

## ERRATUM

### Anticrack-associated faulting at very high pressure in natural olivine

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*Nature* **348**, 720-722 (1990)

IN this letter in the 20/27 December issue, the legend to Fig. 1 should read:

FIG. 1 Low-magnification photomicrograph in obliquely incident light showing a fault traversing specimen 36. The specimen was shortened in approximately the E-W direction. Bright areas on the edges of the specimen are remnants of the rhenium heater. Vertical dimension of specimen is 3 mm.

The printed version referred incorrectly to the 'N-S direction' and the horizontal dimension.

## CORRECTION

### Weak-link-free behaviour of high-angle $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ grain boundaries in high magnetic fields

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*Nature* **347**, 167-169 (1990)

THE expression used to calculate  $J_c$  values throughout the above paper was misquoted in the paper (bottom of left side, page 332) as  $J_c = \Delta M / (2r)$ . The correct expression is  $J_c = 3\Delta M / r$ . The correct expression was used for all the calculations which appear in the text and figures.