



# Reply to Jones and Crowe: Correcting mistaken views of sedimentary geology, Mn-oxidation rates, and molecular clocks

Jones and Crowe (1) raise issues already addressed in our article (2) based on an inaccurate grasp of the literature and several logical misconceptions. The authors suggest that inputs we chose in our kinetic calculations are unsuitable because we used values only from the Black Sea. As described, we made an extremely conservative estimate because the Black Sea is the most rapid Mn-oxidizing environment in the literature. Other locations have oxidation rates orders-of-magnitude lower (3). Jones and Crowe also propose sedimentation rates in our Mn-oxidation calculations were too high, citing a reference for incorrect rocks: different lithologies, environments, process sedimentology, geodynamic setting, and age. The paper they cite estimated long-term rates for the 2642–2521 Ma Campbellrand Subgroup, deposited >100 million y earlier on a marine platform rather than Koegas continental margin deltaic sediments. Using correct sedimentary geology is important (2).

In our report  $O_2$  was eliminated as the Mn oxidant by several independent observations. Detrital pyrite is rapidly destroyed by dissolved oxygen, enabling assessment of environmental  $O_2$ . Jones and Crowe (1) suggest that detrital pyrite is preserved at 1  $\mu M$  dissolved  $O_2$ , but this statement is unreferenced and unsupported. Several studies [cited in our report (2)] determined that detrital pyrite is sensitive to far lower dissolved  $O_2$ , calculating that pyrite would erode at 2.5 nM. Detrital pyrites throughout Koegas sandstones are discordant with micromolar-level  $O_2$  concentrations. Although current understanding of mass-independent fractionation (MIF) of sulfur isotopes is incomplete, dozens of studies have indicated that preservation of these

fractionations requires low  $O_2$  ( $\ll 2.5$  nM) (see references in ref. 2). Regardless of whether models can find solutions with high  $O_2$  in the Archean environment, such conditions conflict with observations of detrital pyrite and MIF from the same sedimentary basin as our repeated and widespread (>50 km) Mn enrichments (see ref. 2 page 5 and pages 3–4 in our Supporting Information). It is often said Earth history is about what happened, not what should have happened; observations here supersede box models.

Finally, Jones and Crowe (1) argue that molecular clocks (MC) date cyanobacteria to before 2.415 Ga, but don't appreciate that MCs give a wide range of results, and shouldn't be considered like radiometric dates (4). MCs come with challenges. First, the phylogenies must be correct; this is still uncertain for cyanobacteria. The study they reference only uses one gene, encoding 16S rRNA, and express appropriate caution. The authors did not include the nonphototrophic deeply branching cyanobacteria, which impacts estimates because the divergence time between cyanobacteria and other phyla is not synonymous with the origin of oxygenic photosynthesis (Fig. 1) (5). A more recent MC approach suggested cyanobacteria postdate 2.415 Ga (6). Second, MC studies require accurate models of evolution, which are not known a priori. Third, precise clocks demand many robust calibration points, requiring an unambiguous fossil record, complicated by widespread morphological homoplasy in cyanobacteria (6). Because of these uncertainties, the 95% confidence intervals for these divergences include the age of the Earth (4). MCs offer a valuable

comparison with the geological record, but not a substitute for it.

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**1** Jones C, Crowe SA (2013) No evidence for manganese-oxidizing photosynthesis. *Proc Natl Acad Sci USA* 110:E4118.

**2** Johnson JE, et al. (2013) Manganese-oxidizing photosynthesis before the rise of cyanobacteria. *Proc Natl Acad Sci USA* 110(28):11238–11243.

**3** Dick GJ, et al. (2009) Enzymatic microbial Mn(II) oxidation and Mn biooxide production in the Guaymas Basin deep-sea hydrothermal plume. *Geochim Cosmochim Acta* 73(21):6517–6530.

**4** Graur D, Martin W (2004) Reading the entrails of chickens: Molecular timescales of evolution and the illusion of precision. *Trends Genet* 20(2):80–86.

**5** Fischer WW, Hemp J, Johnson JE (2014) Evolution of oxygenic photosynthesis. *Annu Rev Earth Planet Sci*, in press.

**6** Shih PM, Matzke NJ (2013) Primary endosymbiosis events date to the later Proterozoic with cross-calibrated phylogenetic dating of duplicated ATPase proteins. *Proc Natl Acad Sci USA* 110(30):12355–12360.

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