Biological controls on oxygenation in the Neoproterozoic and Paleozoic

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The deep oceans were finally oxygenated during the Late Neoproterozoic, and this is widely attributed to a rise in atmospheric oxygen. However, existing data suggests there followed a de-oxygenation of the ocean across the Precambrian-Cambrian boundary. Only later in the Paleozoic did the deep ocean recover a fully oxygenated state. What biogeochemical mechanisms could explain these changes?

It is hypothesised that increases in phosphorus weathering, either due to greening of the land [1] or the aftermath of glaciations [2], fuelled organic carbon burial and thus a Neoproterozoic increase in atmospheric oxygen. However, sustained changes in silicate weathering flux are prevented by the well-known regulator of atmospheric CO_2 and temperature. Thus, increases in phosphorus weathering can only be sustained long enough to affect atmospheric oxygen if there is selective weathering of phosphorus relative to bulk rock (by biology) [1], or a shift in the balance of CO_2 sinks from seafloor weathering to continental weathering [3].

Hence it is worth considering if the Neoproterozoic oxygenation of the ocean could have happened without a rise in atmospheric oxygen. A possible scenario invokes the evolution of eukaryotes in the surface ocean producing larger particles that sank faster [4]. This would have shifted oxygen demand away from the bottom waters of continental shelves (where the majority of phosphorus burial and recycling occurs) to greater depth. Oxygenation of the shelves would have increased the efficiency phosphorus removal from the ocean (in organic matter and adsorbed to iron oxyhydroxides) thus lowering global productivity and lowering oxygen demand in the deep ocean, oxygenating it. The net effect on organic carbon burial is uncertain because less export production was counteracted by faster sinking to sediments.

The subsequent early Paleozoic de-oxygenation of the ocean could be explained by the evolution of animal bioturbation lowering the C/P burial ratio of organic matter in sediments and thus lowering atmospheric oxygen [5].

The later rise of land plants, selectively weathering phosphorus and producing recalcitrant high C/P biomass, increased organic carbon burial and atmospheric oxygen, finally producing a persistent oxygenation of the ocean.

[1] Lenton & Watson (2004) *GRL* **31**, L05202. [2] Planavsky *et al.*. (2010) *Nature* **467**, 1088-90. [3] Mills *et al.*. (submitted). [4] Logan *et al.*. (1995) *Nature* **376**, 53-6. [5] Boyle *et al.*. (submitted).

Orientation-dependent REE^{3+} luminescence: a possible artifact in luminescence imaging

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Luminescence imaging is a sensitive tool for revealing internal zoning patterns of crystals and other geological samples, especially for species containing rare-earth elements (REE^{3+}) [1,2]. In addition to the traditional direct imaging methods, the hyperspectral mapping technique is used increasingly for this [3]. Quantifications of REEs from emission intensities have been proposed for several minerals [3–5]. Note, however, that the orientation-dependence of REE^{3+} emissions is often neglected by Earth scientists [4], even though the phenomenon is well known [5,6].

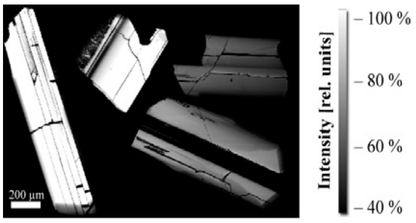

Figure 1: PL map (532 nm excitation with N–S polarisation) of the emission of Nd^{3+}, showing clear intensity differences among chemically uniform but randomly oriented crystals.

As an example, we have studied the orientation-dependence of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission of trace Nd^{3+} in zircon and xenotime–(Y) and their synthetic analogues. We found once again that the emission intensity depends strongly on the direction of the emitted light being analysed (CL and PL). In PL, the intensities observed are further affected by the polarisation of the incident laser beam relative to the crystal (compare Fig. 1).

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