Fe isotopes in primary hematite constrain marine redox conditions at the base of the 2.4 Ga Hotazel Fm

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Recent dating of the Ongeluk Formation basalts at 2426 ± 3 Ma [1] has resolved years of discussion [2, 3, 4], and now confidently places the overlying hematite- and manganese-rich Hotazel iron formation of the Griqualand West basin, South Africa, right at the onset of the first rise in atmospheric oxygen. The so-called Great Oxygenation Event (GOE) took place somewhere between 2.4 and 2.3 Ga [5]. The Hotazel strata may therefore yield valuable insight into oceanic redox conditions during this still poorly understood time interval.

The basal part of the Hotazel Fm. forms the missing link between the large-scale Ongeluk volcanism and extensive Mn precipitation. However, no extensive research has been carried out to date on this contact due to poor exposure. Here we conducted a detailed petrographic, geochemical and Fe isotopic study of a 3-metre-thick drill-core section that uniquely exposes the Hotazel / Ongeluk contact.

Our results show that following cessation of Ongeluk volcanism, sedimentation was controlled by primary seawater precipitation of Fe(III) oxyhydroxides. Negative δ^{56}Fe values (between -0.26 and -0.50 ‰), measured in micro-drilled hematite-chert, indicate that upper water column δ^{56}Fe was significantly more depleted than lower down in the stratigraphy of the basin. Yet, δ^{56}Fe and bulk-rock Fe/Mn values are still substantially higher (1-2 ‰) than those reported higher up in the Mn-rich layers of the Hotazel sequence [4]. Apparently, redox potentials were still comparatively limited at the earliest stages of the Hotazel depositional environment. Our rocks thus seem to form a transitional interval between deposition from essentially ferruginous waters to precipitation from highly evolved surface waters. Continuous production of photosynthetic O_2 in the shallowest parts of the basin may ultimately have provided a strong signal for the onset of the GOE in Hotazel times.

[1] Gumsley *et al*. (2017) *PNAS* **114**, 1811-1816. [2] Cornell *et al*. (1996) *Prec. Res*. **79,** 101-123. [3] Bau *et al*. (1999) *EPSL* **174**, 43-57. [4] Tsikos *et al*. (2010) *EPSL* **298**, 125-134. [5] Bekker *et al*. (2004) *Nature* **427**, 117.