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"Constraining Redox Conditions and Their Potential Role in Climactic Variations of the Mesoarchean as Recorded in the South African Witwatersrand and Pontola Supergroups of the Kaapvaal Craton"

Project Report

Fieldwork was carried out in the Pongola and Witwatersrand Supergroups of the Kaapvaal Craton, South Africa. Over 130 drill core samples were collected from these correlative Supergroups. The majority of the Pongola Supergroup stratigraphy was visited in the field, giving extra context to the samples that were collected (Figure 1). Samples included sandstones, siltstones, shales, magnetic mudstones, and banded iron formations.

One outstanding feature about the Witwatersrand-Pongola Supergroups is that a complete depositional basin is preserved, which allows us to test basin-wide questions on these Mesoarchean (~3 b.y.) rocks. For the first project on these samples, it was tested whether the deeply rooted metabolism of Dissimilatory Iron Reduction (DIR) left a basin-wide footprint in the Witwatersrand Supergroup. Based on modern marine systems, it has been proposed that DIR may pump aqueous Fe (II), the product of DIR, on a basin-wide scale—a process termed a benthic iron shuttle.

For this project, we have analyzed Fe isotope compositions from samples of the Mesoarchean Witwatersrand Supergroup. These analyses consist of microdrilled pyrite, bulk whole rocks, and magnetite separates. Results on Fe isotope compositions of microdrilled pyrite and whole-rock samples show a trend of increasingly light iron isotope signatures (decreasing d^{56}Fe) moving from the proximal to distal marine settings—in tandem with whole-rock Fe enrichment in the distal basin (Figure 2). In Severmann et al (2008)'s study of the Black Sea, a similar trend was observed. Measuring the Fe isotopes and concentrations of sediments across the basin, it was found that there was an inverse correlation between δ^{56}Fe and the Fe/Al ratio of whole rock samples. This formed the basis for proposing the benthic iron shuttle, where reactive Fe produced by DIR is preferentially removed from the shelf and sequestered in the deeper depofacies. Sequestration of this benthic iron flux is required in order to observe a negative correlation between δ^{56}Fe and whole rock iron content. In order to keep this iron in the distal basin, a trapping mechanism is required. In all previously studied benthic iron shuttles, this trapping mechanism is a water-column redox boundary, where the benthic iron flux is trapped below oxic surface waters in an anoxic or euxinic basin. Therefore, the expression of a benthic shuttle not only informs us about the microbial ecology of iron reducing microbes of this time, it could also imply an ephemeral oxidation of the Mesoarchean atmosphere.

The fractionation factor between aqueous Fe (II) and pyrite is very different from the fractionation factor between aqueous Fe (II) and iron oxides (Johnson et al., 2008). To produce whole-rock δ^{56}Fe values that are similar to those for pyrite, as seen in preliminary data, is unexpected for equilibrium conditions, and suggests that pyrite was formed by sulfidation of iron oxides. This trend is also observed with in situ laser ablation MC-ICPMS on magnetite, where magnetite δ^{56}Fe signatures similar to those obtained for microdrilled pyrite. Magnetic separates made from whole rock powders were also analyzed for iron isotopes, and they were found to have isotopically light negative δ^{56}Fe signatures. We therefore hypothesize that the main sink for a benthic iron flux signature in the distal basin could be magnetite.

This work demonstrates, for the first time, that DIR left a basin-wide footprint in the Mesoarchean Witwatersrand-Pongola basin. This is the oldest evidence for a benthic iron shuttle, which indicates that a vigorous Fe reducing microbial community was present around 3 billion years ago. As well as informing us about early life, this work also indirectly informs us about the Mesoarchean environment. Since a redox stratified water column is required to preserve the inverse correlation between iron isotopes and iron concentrations, the presence of a Mesoarchean benthic iron shuttle suggests that oxygen concentrations were sufficiently high to have oxygenated surface waters. To continue investigating the Mesoarchean biosphere and environment, samples collected from this field expedition will be used to fuel future studies over the next two years.

Severmann, S. Lyons, T.W., Anbar, A., McManus, J., Gordon., G., 2008, Modern iron isotope perspective on the benthic iron shuttle and the redox evolution of ancient oceans: Geology, v. 36, p. 487-490

Publications

Hashman, B. M., Guy, B. M., Beukes, N. J., Beard, B. L., Johnson, C. M., 2014, A microbial iron shuttle in a redox-stratified ocean 2.9 billion years ago: Abstract presented at 2014 Astrobiology Graduate Conference (Abgradcon).

Figures

Figure 1. Field stop at the Izermijn Banded Iron Formation (BIF), which is the oldest BIF of the Pongola Supergroup.

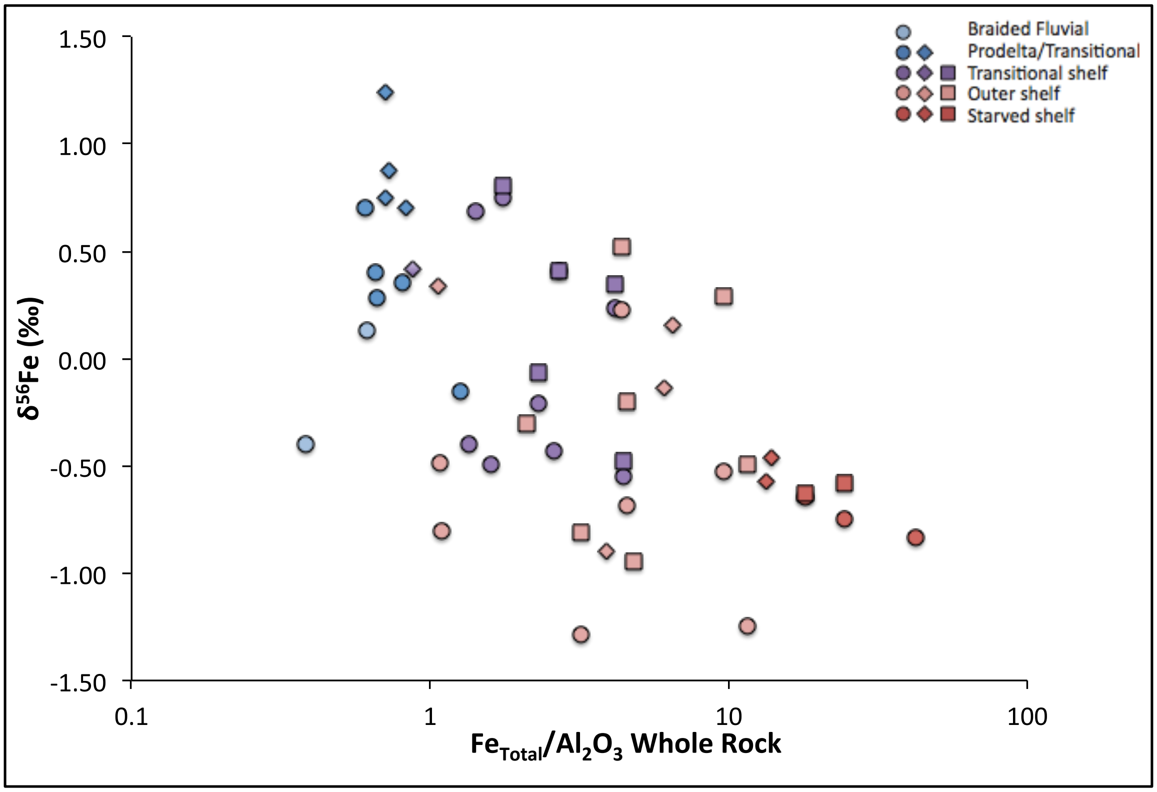

Figure 2. This graph shows δ^{56}Fe plotted against the aluminum normalized iron concentrations. Fe total is as Fe_2O_3 weight %. Diamonds are microdrilled pyrite, squares are magnetite separates, and circles are whole rock samples. This inverse

correlation is indicative of a benthic iron shuttle. Blue colors are proximal, with warmer colors representing more distal depofacies.