Archean "whiffs of oxygen" go Poof!

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NASA's scientific drillcore ABDP-9 penetrated ~90 m of strata from the Archean-Paleoproterozoic boundary interval in the mid-Hamersley Basin of the Pilbara craton, Western Australia beneath ~100 m of regolith. A series of geochemical studies of the core in the past 5 years starting with [1, 2] have reported Mo and Re concentration enrichments, mass-independent sulfur isotope fractionations, ^{15}N-enrichments, and iron speciation that were argued to represent "whiffs" of atmospheric oxygen. These datasets have lent support to controversial traces of biomarkers in both this unit and strata elsewhere in the Hamersley Basin that have been interpreted to contain evidence for cyanobacteria and eukaryotes inhabiting widespread late Archean niches. Similar, though less conspicuous Mo, Re, S, N, Fe, and lipid biomarker anomalies in ~2.7-2.5 Ga marine strata of South Africa's Kaapvaal cratonic margin have been interpreted in context of ABDP-9 "whiffs" of oxygen to suggest even "pervasive" Late Archean oxygenation. These interpretations are surprising because they appear to conflict with other longstanding geological proxies (e.g. red beds, redox-sensitive detrital grains, mass independent S fractionation) that suggest the rise of oxygen occurred several hundred million years later. If correct, these data solicit a complete reevaluation of our knowledge of how solid Earth and surface Earth processes operate to keep oxygen in balance over geological time. It is reasonable to ask whether the inferences made from elemental and isotopic relationships captured in these rocks are sufficiently strong to warrant such reevaluation.

We present new observations from ABDP-9 that reveal significant open-system, post-depositional alteration of the sedimentary rocks in this region of the Hammersley Basin: these include observations of widespread highly-crystalline, high-temperature, late-stage chlorite veins, preferentially developed within shale lithologies and concentrated in the "whiff" interval, locally associated with iron and sulfur metasomatism; and regionally set in ~300-450 °C burial metamorphic, multiply-deformed terrane. Preliminary micro-scale work to measure isotopic and elemental abundances show clear texture-specific differences that may allow untangling of several episodes of diagenesis and metasomatism to provide a framework for better interpreting the bulk data.

These post-depositional features in ABDP-9 argue that the 'whiffs' are metasomatic artifacts. We suspect similar problems in other Archean cores, which are sulfide-remagnetized during orogenic episodes associated with Pb-Zn-mineralizing crustal fluids in the foreland. We note that a late origin of oxygenic photosynthesis can explain the Lomagundi-Jutali event, the Makganyene snowball, the Kalahari Mn field, the Sishen iron deposit, and Shungite deposition [3]. The timing is consistent with recent molecular clock estimates for the radiation of the Eukaryotes, which post-date 2 Ga. [4].

[1] Kaufman et al., Science **317**(2007): 1900-1903. [2] Anbar et al., Science **317**(2007): 1903-1906. [3] Kirschvink et al., GCA **73,** A662-A662. [4] Parfrey et al., PNAS **108** (2011): 13624-13629.

Nitrate transformation and immobilization: effects of biotic-abiotic and oxic-anoxic conditions

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Biogeochemistry under redox-dynamic conditions: processes, speciation, and fluxes

It has been hypothesized that incorporation of dissolved inorganic nitrogen into organic matter (OM) via abiotic (chemical) prossesses is one of the mechanisms that account for the high N retention observed in temperate forest soils [1]. Soil incubations under sterile conditions have shown that N from nitrate ($N\text{-}NO_3^-$) is rapidly transformed to organic nitrogen [2, 3]. Transformation of $N\text{-}NO_3^-$ to organic nitrogen involves a decrease in N oxidation state. Hence, NO_3^- reduction to nitrite (NO_2^-) or other more reduced species may be a required step prior to N immobilization. In this study, solid OM was spiked with $^{15}NO_3^-$ and incubated in suspensions in four combinations of biotic-abiotic and oxic-anoxic conditions at pH 6.5 for five days. Our objectives are to elucidate how biotic-abiotic and redox conditions affect NO_3^- transformations and to determine whether $N\text{-}NO_3^-$ will be incorporated into solid OM under abiotic conditions.

Within the first hour, the experimental (NO_3^- spiked) system incubated under biotic and oxic (Bio-Ox) conditions showed a drastic decrese (22%) in NO_3^- concentration, which increased again towards the end of incubation. Increases in the concentrations of NH_4^+ and dissolved organic nitrogen (DON) in the experimental system were of the same magnitude as in the blank (no NO_3^- spiked) systems. However, significant increases did not occur until after ~3 days in the blank. These results suggest that NO_3^- addition accelerates microbial activity, which facilitates N mineralization to NH_4^+. Incubations of experimental and blank systems under abiotic oxic (Abio-Ox) conditions showed no significant change in NH_4^+ with time; but a steady increase, of the same magnitude, was observed for DON. The experimental system showed a steady decrease in NO_3^- of 8% with time under Abio-Ox conditions. Comparison of Bio-Ox and Abio-Ox systems thus suggests that microbial activity is not required for the production of DON, but seem to be needed for DON mineralization to NH_4^+.

We also performed incubations under anoxic conditions to test whether the same mechanisms are operative in reduced environments, e.g., in the interior of soil aggregates or wetlands. Under anoxic conditions, the spiked NO_3^- disappeared within the first 24 h in both the biotic and abiotic experimental systems. In these systems, NO_2^- was detected; its concentration first increased then droped to zero. Biotic anoxic (Bio-Anox) systems showed an increase in the concentration of NH_4^+ with time. However, the increase of NH_4^+ in the experimental system was twice that of the blank. Another striking result is that DON in the blank increased with time whereas it remained constant in the experimental system. Under abiotic anoxic (Abio-Anox) conditions, the experimental and blank systems showed the same trend and magnitude in DON decrease and NH_4^- increase.

Disappearance of NO_3^- and NO_2^- detection under anoxic conditions suggest that NO_3^- is reduced to NO_2^- which is either volatized or incorporated into the solid OM. Under biotic conditions, immobilization (microbial and chemical) seems to be the primary pathway for NO_3^- disappearance. Our interpreation of the fate of NO_3^- under various conditions will be further verified by ^{15}N measurements.

[1] Aber *et al.* (1998) *Bioscience* **48**, (11), 921-934. [2] Dail *et al.* (2001) *Biogeochemistry* **54**, (2), 131-146. [3] Fitzhugh *et al.* (2003) *Global Change Biology* **9**, (11), 1591-1601.