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Testing the Precambrian reverse weathering hypothesis using a 1-billion-year record of marine shales.

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With solar luminosity 10-15% lower than present, the Precambrian Earth should have been vulnerable to glaciation, yet the Proterozoic sedimentary record indicates largely ice-free conditions. It has been proposed that elevated marine Si levels favored reverse weathering during this time, helping maintain sufficiently elevated atmospheric carbon dioxide to compensate for the reduced solar luminosity [1]. Reverse weathering can be defined as a marine clay authigenesis process that involves the consumption of alkalinity, metal ions and dissolved silica to precipitate clay minerals, releasing and acidity [2] i.e. the opposite of weathering reaction.

Whether the Si enriched Precambrian oceans featured widespread reverse weathering remains largely untested because authigenic clays cannot be readily differentiated from detrital or burial diagenetic clays using conventional mineralogical or geochemical approaches. We employed a novel, scanning electron microscope based mineral mapping approach [3] to identify and quantify the proportion of authigenic clays in twelve well preserved Proterozoic marine shales from the Vindhyan and Chhattisgarh basins of India, spanning ~ 1-billion years. We find that eight out of twelve formations contain unambiguous authigenic clays, with up to 45 wt% of these shales being comprised of authigenic illite, possibly formed via a smectite precursor. We conclude that the widespread occurrence and high abundance of authigenic illite provides strong empirical support for enhanced reverse weathering throughout much of the Proterozoic.

[1] Isson & Planavsky (2018), *Nature* 560, 1-19.
[2] Mackenzie & Garrels (1966), *J. Sediment. Petrol.*36, 1075.
[3] Rafiei et al., (2020), *Precambrian Res.* 350, 1-16.

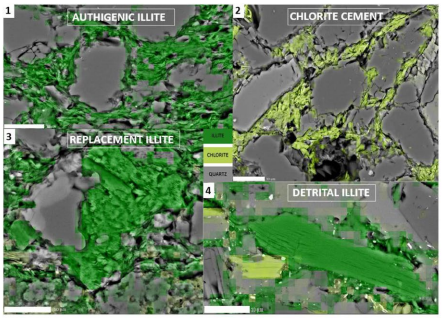

Fig. Backscatter electron images with false colour SEM-EDS mineral map overlay (Nanomin) identify the typical morphology of 1) wavy, fibrous authigenic illite that is variably deformed around silt size quartz grains by burial compaction 2) flaky chlorite cement occupying the intergranular spaces between silt size quartz grains 3) illite replaced feldspar, as inferred from euhedral shape and traceable boundaries of the replacement illite and 4) detrital illite and chlorite with distinct grain boundary, sharp edges, discernable cleavage running along the mineral length.

A general reverse weathering reaction can be depicted as [4]-

$$X^{+2} + 2H_4SiO_4 + 6HCO_3^- \rightarrow X_3Si_2O_5(OH)_4 + 6CO_2 + 5H_2O$$

[4] Isson et al., (2019), *Glob. Biogeochem. Cycles*, 34, 1-28.