Rare earth element and yttrium (REY) geochemistry of 3.46-2.40 Ga greenalite-bearing banded iron formations: New insights into iron deposition and ancient ocean chemistry

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Finely laminated chert enclosing nanoparticles of greenalite and apatite are ubiquitous in Archean-Paleoproterozoic ferruginous cherts, jaspilites and Banded Iron Formations (BIFs) and are considered to be primary deposits. The cherts and BIFs are chemical sedimentary rocks interpreted to have been precipitated in marine settings prior to the first permanent rise in atmospheric oxygen at the Great Oxidation Event (GOE) ca. 2.45-2.32 M.y. ago. As chemical sediments, they are potential archives of the solutions from which they precipitated, incorporating signals from hydrothermal fluids and ambient seawater. Previous studies of rare earth elements and Y (REY) in pre-GOE BIFs have found an "Archean seawater signature" with positive Eu anomalies, attributed to the influence of hightemperature hydrothermal processes, and positive anomalies for La, Gd and Y, ascribed to seawater. REY abundances and profiles are presented of well-preserved, laminated greenalitebearing cherts from ten formations of pre-GOE ferruginous cherts and BIFs from Western Australia. The samples come from a wide range of depositional environments, e.g., submarine proximal volcanic environments, basin floor, slope and deep marine shelf, and are between 3.46 Ga to 2.45 Ga in age. Five groups with different REY profiles are identified, namely (i) mafic volcanic vent-proximal chert; (ii) felsic volcanic- and sediment-associated chert, (iii) ferruginous cherts in shelf sediments, (iv) the Nammuldi Member of the Marra Mamba Iron Formation and Joffre Member of the Brockman Iron Formation, and (v) the Dales Gorge Member of the Brockman Iron Formation. Of these, only the Dales Gorge Member BIF has a typical Archean seawater signature while the others have REY patterns likely reflecting differing source fluids and environments of deposition. In situ LA-ICP-MS analyses of chert containing sub-micron-sized particles of greenalite and apatite indicate that the likely hosts of the REEs are apatite, siderite and possibly greenalite. The REY profiles of the greenalite-bearing cherts are generally different from those of bulk samples of the same formations, perhaps reflecting a diagenetic overprint in the bulk samples, whereas the greenalite-bearing cherts likely preserve their depositional compositions, locked in by early silicification.