

Trace element and isotopic characterization of Paleoproterozoic BIF in the Black Hills (South Dakota, USA): Timing of deposition straddling the first rise of atmospheric oxygen and the biochemical event between 2.4 to 2.0 Gyr ago.

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The first significant rise of atmospheric oxygen is widely believed to have taken place between ~2.4 and 2.0 Ga ago. There is an ubiquitous world-wide lack of deposition of banded iron formations (BIF) during this time interval. Because of a strong coincidence of several strong and positive excursions of $\delta^{13}\text{C}$ in contemporaneous carbonates - indicative of enhanced bioproductivity and carbon burial - the lack of BIFs could possibly be related to a concomitant change in the rate of biogenic sulfate reduction causing the precipitation of Fe-sulfides rather than Fe-oxyhydroxides. As a consequence, rather anoxic bottom waters might have developed, essentially inhibiting the chemical precipitation of oxide-facies BIFs during this time interval.

BIFs were deposited in the Black Hills, South Dakota, prior to - and after the first main oxygenation of the atmosphere around 2.3-2.4 Ga ago. Oxide-facies, detritus-free BIF with negligible MnO concentrations deposited during the first interval between 2478 – 2559 Ma ago (initial rifting of the Kenorland supercontinent) show rare earth elemental (REE) characteristics typical of ambient seawater signatures (positive La, Eu, Ga and Y anomalies in PAAS normalized REE diagrams) and display variably positive and negative Ce anomalies. These characteristics imply relatively slow rates of sedimentation. Sm-Nd isotopes from individual mesobands of the stratigraphically oldest BIF of this group define early Archean (3.66 - 3.78 Ga) T_{DM} ages, whereas the so-called Benchmark group of BIFs are predominantly characterized by Meso-to Neoproterozoic (2.56 - 3.30 Ga) mixed T_{DM} ages. While these old ages generally are compatible with crustal residence ages known from the adjacent Wyoming craton - thereby suggesting that the Black Hills were likely a part of the latter during the Archean - the variability of these ages (recorded on a mesoband and local sampling scale) may indicate the presence of a rather heterogeneous eroding landmass and the existence of small, restricted intercontinental depositional basins during this time period. Pb isotopes from this group of BIF reflect the generally high- μ ($^{238}\text{U}/^{204}\text{Pb}$) tenor typical of the Wyoming craton and in addition show low $^{208}\text{Pb}/^{204}\text{Pb}$ relative $^{206}\text{Pb}/^{204}\text{Pb}$ ratios implying pronounced fractionation of Th relative to U in the depositional environment during their deposition. These observations are compatible with a locally reducing bottom water mass in which U transported to the sedimentation site by oxidized water masses was effectively stripped by the iron oxyhydroxides. Mixed silicate-carbonate-oxide facies BIF with significant detrital input and elevated MnO concentrations were deposited during younger rifting events related to the brake-up of the Kenorland supercontinent in the time interval between ~2.1 and 2.0

Ga. These BIFs (including the Homestake Fm. as the host of the US largest former gold deposit) are characterized by less fractionated PAAS-normalized REE patterns, by the absence of La anomalies and the presence of only weak positive Eu anomalies. Negative Y/Ho ratios of these BIF are in sharp contrast to the positive Y_{PAAS} anomaly of seawater and reflect the low marine particle reactivity of Y known from hydrous Fe-oxides. Positive Ce anomalies possibly reflect the more oxidative scavenging of Ce (IV) onto Fe-oxyhydroxides and generally point to a more oxidized seawater environment during the deposition of these later BIFs. Pb isotopes are conformable with this in that thorogenic Pb is not significantly fractionated from uraniumogenic Pb in individual mesobands. Sm-Nd isotopes define similarly variable T_{DM} ages (2.51-3.83 Ga) compared to the older rift-sequence BIFs and suggest tapping of at least REEs from essentially the same, continuously prevalent Paleo –to Neoproterozoic continental landmass.

In essence, BIFs in the Black Hills straddle the worldwide 2.0-2.4 Ga BIF depositional gap, which curiously coincides with the coupled first atmospheric – biospheric ($\delta^{13}C$ positive excursion) oxygenation. While Paleoproterozoic BIFs deposited before this major oxygenation event (i.e., those of type “Benchmark Iron Formation”) still indicate prevalence of reducing conditions in the depositional basins, consistent with the occurrence of uranium- and pyrite-rich conglomerates in the stratigraphically associated Boxelder Fm., silicate-carbonate-oxide BIFs straddling the end of the $\delta^{13}C$ positive anomaly were likely deposited in continental margin-like environments that seem to have developed as a consequence of intense rifting periods associated with the break-up of the Kenorland supercontinent. Despite of a contamination with detrital components, the preservation of positive Eu anomalies in these 2.0-2.1 Ga old BIFs, together with the association of these BIFs with volcanic (basaltic) rocks, indicate that reduced elements such as Fe(II) were supplied to the seawater through high hydrothermal and volcanic inputs and subsequently upwelled into shallower, more oxidized surface waters of the continental shelves.