# Shifting transition element abundances in Banded Iron Formations mark the Great Oxidation Event.

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### Summary

Banded Iron Formations, ancient marine deposits originally consisting of iron- and silica-rich chemical sediments, preserve a record of the evolution of seawater by shifts in their composition over time. The Great Oxidation Event some 2.4 - 2.2 billion years ago (Ga) is recorded in the BIF rock record by dramatic excursions in the abundances of certain redox-sensitive trace elements such as molybdenum, chromium, and copper. In this work we present data from new analyses of several BIF as well as from an extensive literature compilation, all of which point towards profound changes in the supply of redox-sensitive trace elements coincident with the first accumulation of free oxygen in Earth's atmosphere.

### Introduction

Before the evolution of silica biomineralization and oxygenation of the deep oceans circa 0.5 Ga, dissolved silica and iron accumulated in seawater at times past the point of saturation, precipitating out as chemical muds that thickly accumulated over large areas of the deep ocean floor to be preserved as BIF. The BIF rock record is extensive, spanning every continent and encompassing sediments from as young as 0.5 Ga to as far back as Earth's earliest known marine deposit (~3.8 Ga BIF in Greenland). Crucially, as pure chemical sediments free of detrital contamination, the precipitates that formed BIF effectively captured elemental and isotopic signatures of evolving ancient seawater by sorption and co-precipitation reactions; it is this property of BIF that arguably makes them one of the richest records of marine geochemistry on the ancient Earth.

# **Theory and/or Method**

In-situ trace element analyses were performed on BIF samples at the University of Alberta using a quadrupole ICP-MS coupled to laser ablation system. NIST 610 and 612 standards and BIF samples were ablated using identical conditions with spot sizes of either 20  $\mu$ m or 60  $\mu$ m, 5 Hz repetition rate and energy density of ~13 J/cm<sup>2</sup>. Quantitative results were obtained via the calibration of relative element sensitivities against the NIST 610 and 612 standards. Data reduction and concentration determinations were obtained using the GLITTER® (XP version, New Wave Research) laser ablation software.

# Conclusions

Banded iron formations deposited prior to the Great Oxidation Event generally possess very low abundances of molybdenum and chromium, in accordance with the low mobility of these elements under anoxic or reducing conditions. Approximately concomitant with independent evidence for the first appearance of free oxygen circa 2.5 Ga, the abundance of these elements in BIF increases dramatically as they became increasingly mobile at Earth's surface as the result of oxidation processes. The BIF record is not entirely straightforward, however; some non-redox-sensitive trace elements also show excursions at this time. Related proxies (e.g., black shales) should provide much needed additional insight into this enigmatic period of Earth's history.