Copper in banded iron formations as a redox proxy for Precambrian paleoceanography

FANNY THIBON[1], JANNE BLICHERT-TOFT[1], FRANCIS ALBAREDE[1], JOHN FODEN[2], AND HARILAOS TSIKOS[3]

[1] Ecole Normale Supérieure de Lyon, 69007 Lyon, France (fanny.thibon@ens-lyon.fr)
[2] University of Adelaide, SA 5005, Adelaide, Australia
[3] Rhodes University, Grahamstown 6140, South Africa

Trace metals and their stable isotope ratios in iron formations (IF) have been used to reconstruct the redox evolution of the past oceans and atmosphere, specifically around the Great Oxydation Event (GOE). A number of studies have utilised redox-sensitive elements such as Mo [1], Cr [2], and U [3]. By comparison, Cu has been one of the least studied trace metals, with a single study documenting temporal evolution of δ^{65}Cu in black shales around the GOE [4]. Fractionation effects from coeval IF deposition have been implicated to explain the observed shale δ^{65}Cu variations. Here we focus on Cu from four pre-GOE IF sequences from the Neoarchean-Paleoproterozoic Transvaal and Hamersley Supergroups in, respectively, South Africa (Kuruman – Griquatown – Hotazel) and Australia (Joffre). The aim is to critically asses the potential of Cu and its stable isotope ratio in IF to constrain redox processes in the pre-GOE ocean.

Whole-rock Cu contents in IF are lower than in average continental crust, and much lower than in modern oceanic ferromanganese deposits. They show no relationship with the mineralogy of IF, and no statistical correlation with bulk-rock Fe and Mn abundances. Instead, Cu contents show positive correlations with Ti in the Joffre IF and with Cr, V, and Ni in the Transvaal IF. Additionally, all four IF record shale-like Cu/Ti ratios. Copper isotope compositions are statistically invariant for all Transvaal IF (~0‰), while the Joffre IF differs in that it has a slightly negative average δ^{65}Cu value of -0.24‰. Our results suggest that Cu in IF represents an inapt proxy for water-column processes of primary Fe and Mn precipitation and rather records isotopically homogeneous, minor particulate inputs from a predominantly volcanic (ash) source. Copper abundances and δ^{65}Cu in IF therefore appear to be unsuitable records of secular oceanic redox evolution in the early Precambrian oceans, particularly with respect to the GOE.

[1] Planavsky et al. (2014) *Nat. Geosci.* **7**, 283-286 [2] Crowe et al. (2013) *Nature* **501**, 535-538 [3] Wang et al. (2018) *GCA* **238**, 438-452 [4] Chi Fru et al. (2016) *PNAS* **113**, 4941-4946.