

A YOUNGER GREAT OXIDATION EVENT IN THE HURONIAN SUPERGROUP OF NORTH AMERICA. Huan Cui^{1,2}, Kouki Kitajima^{1,2}, James Farquhar³, Maciej G. Śliwiński², Michael J. Spicuzza^{1,2}, John H. Fournelle², Akizumi Ishida^{1,2}, Philip E. Brown², John W. Valley^{1,2}, ¹WiscSIMS & NASA Astrobiology Institute, University of Wisconsin, Madison, WI 53706, USA (Huan.Cui@wisc.edu), ²Department of Geoscience, University of Wisconsin, Madison, WI 53706, USA, ³Department of Geology and Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20742, USA

Sedimentological observations from the Paleoproterozoic Huronian Supergroup in Ontario, Canada suggest a rise in atmospheric oxygen (i.e., the Great Oxidation Event, GOE) at that time [1,2]. Previous study of S three-isotopes across this interval suggested a weak signal of the transition from mass-independent fractionation (MIF-S) to mass-dependent fractionation (MDF-S) [3]. However, the location of the transition is based upon three analyses of $\Delta^{33}\text{S}$ ($0.45 \pm 0.25\%$, $0.51 \pm 0.23\%$, and $0.88 \pm 0.23\%$) that were proposed to be MIF signals; other data were all near-0 values. Given the limited MIF-S data, the placement of the GOE in Huronian has been ambiguous.

In this study, we revisited two drill cores of the Huronian Supergroup; for the first time, simultaneously analyzed all four S isotopes (thereby $\Delta^{36}\text{S}$ was calculated) for chalcopyrite, pyrrhotite and non-detrital pyrite in situ by secondary ion mass spectrometer (SIMS, 20- μm spot) using a newly developed ion microprobe technique with four Faraday cup detectors [4]; and report improved precision for $\Delta^{33}\text{S}$. Analytical spot-to-spot precisions (2SD) for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$ are $\pm 0.31\%$, $\pm 0.04\%$, $\pm 0.87\%$, respectively, based on the analyses of bracketing UWPpy-1 (Balmat pyrite) standard during the same SIMS session. New $\delta^{34}\text{S}$ data analyzed from two drill cores throughout the lower Huronian are mostly positive values. In drill core 150–4, $\Delta^{33}\text{S}$ values of this study range from +0.01 to +0.38‰, while in drill core 156–1, the $\Delta^{33}\text{S}$ data range from –0.07 to +0.26‰. New $\Delta^{36}\text{S}$ data analyzed from the same Huronian samples range from –3.7 to +0.3‰ in drill core 150–4 and from –4.1 to +1.0‰ in drill core 156–1.

In light of the mineral assemblages and isotopic compositions, we re-interpret the previously proposed “early authigenic” pyrrhotite in the studied drill cores as formed during low-grade metamorphism. The previously identified MDF-S signatures may thus result from homogenization during regional metamorphism. With improved precision, our new SIMS data reveal small but real MIF-S in both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ compositions throughout the entire lower Huronian. In light of the new data, we propose that the GOE is younger (higher in stratigraphy) than previously thought, and most likely right after the deposition of the Gowganda diamictite. Our new SIMS data from Huronian, together with published bulk S isotope data [5] and other well

studied sections in South Africa [6] and Western Australia [7], suggest that the GOE may be a globally synchronized oxidation event followed by a rapid increase in sulfate concentration in the ocean.

Keywords: Great Oxidation Event, GOE, SIMS, Huronian Group, Paleoproterozoic, sulfur isotopes, mass independent fractionation, glaciation

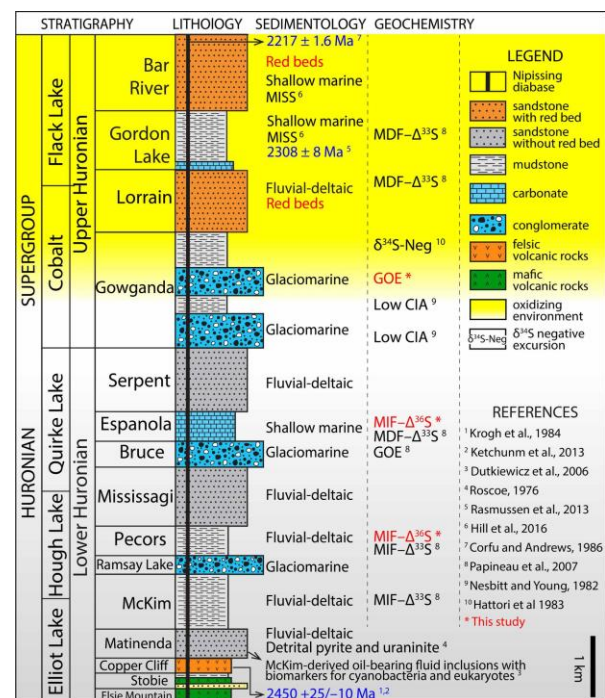


Figure 1. Integrated lithostratigraphy, sedimentology, and geochemical studies of the Huronian Supergroup. Note that the putative MIF-MDF transition has been relocated from the Bruce Formation [3] to Gowganda Formation based on our new data in this study. CIA: chemical index of alteration; MISS: microbially induced sedimentary structure.

References: [1] Roscoe, S. M. (1973) *Geological Association of Canada, Special Paper 12*, 31–47. [2] Holland, H.D. (2006) *Philos. Trans. R. Soc. London, B*, 361, 903, 5686–915. [3] Papineau, D. et al. (2007) *Earth Planet. Sci. Lett.*, 255, 188–212. [4] Ushikubo, T. et al. (2014) *Chem. Geol.*, 383, 86–99. [5] Hattori, K. et al. (1983) *Science* 221, 549–551. [6] Luo, G. et al. (2016) *Science Advances*, 2, e1600134. [7] Williford, K.H., et al. (2011) *Geochim. Cosmochim. Acta* 75, 5686–5705.