Sulfides from the Huronian Supergroup, Ontario, Canada: a key to understanding Paleoproterozoic oxygenation and Snowball Earth

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The mass-independent isotopic fractionations (MIF) in sulfur isotopes (32S, 33S, 34S, and 36S) in the Archean and Paleoproterozoic rocks have been attributed to the low oxygen content in the atmosphere [e.g., 1-3]. It has been suggested that the atmospheric oxygen level was extremely low before 2.45 billion years ago (Ga) when the degree of MIF for 33S, expressed by D33S = d33S - 0.515 d34S, ranged from -2.5 to +8 permil and that the oxygen level raised to a considerable level by 1.9 Ga, after which rocks lost the MIF signatures (D33S = 0 permil) [1].

It is important to determine the timing of the raise of atmospheric oxygen level because it is closely related to the evolutions of the surface environment and the early life. The recent finding of very little sulfur-MIF in pyrites from 2.32-Gyr-old organic-rich shales of the Rooihoogte and Timeball Hill formations, South Africa, have led to the conclusion that the atmospheric oxygen had reached a significant level (10-5 PAL) by 2.32 Ga [4]. However, the database for sulfur-MIF in the Paleoproterozoic is still limited in size, and not enough for comprehensive understanding of the great oxygenation event.

The Huronian Supergroup, South Ontario, Canada, deposited about 2.4-2.2 Ga, contemporary with the deposition of the Rooihoogte and Timeball Hill Formations, and preserves a record of three Paleoproterozoic glaciations, one of which may represent a global-scale glacial event, i.e., Snowball Earth. The sulfur isotopic compositions from the Huronian Supergroup will give additional information on the Paleoproterozoic sulfur-MIF, which may or may not provide a supporting evidence for 2.32-Ga global oxygenation implied from the Rooihoogte and Timeball Hill Formations. Although there have been a couple of reports that showed small sulfur-MIFs (D33S is smaller than 0.5 permil) for the Huronian Supergroup sulfides [1, 5], it is not clear whether or not the origin of sulfides analyzed by [1, 5] are early diagenetic.

We have sampled the Huronian Supergroup rocks during two field trips in 2002 and 2003. Sulfide minerals have been found in most of formations, including glacial diamictites (Bruce and Gowganda Formations). Most of sulfide minerals are pyrites and pyrrhotites, and some formations contain galena or chalcopyrite as a minor phase. The sulfides show a variety of occurrences. Some sulfides are euhedral, suggesting that they probably formed in situ, while a fraction of sulfides are rounded and sometimes aligned parallel to lamination, implying that they are detrital in origin. We will present bulk and trace element compositions of the Huronian Supergroup sulfides and discuss their origins. We are planning to measure sulfur isotopic compositions of early-diagenetic sulfides by ion microprobe with high precision. We will compare the sulfur isotopic compositions with compiled literature data for sulfur-MIF or our carbon isotope data from the Huronian Supergroup carbonates and organic carbon [6] to discuss the Paleoproterozoic sulfur cycle, the oxygenation event, and the Snowball Earth.

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