Mass independent isotopic fractionation of sulfur from sulfides in mid-Archean

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Mass-independent isotopic fractionation (MIF) of sulfur found in sedimentary rocks older than 2470 Ma implies that the atmospheric oxygen level was lower than 10-5 PAL (present atmospheric level) in the Archean atmosphere if the MIF was caused by photochemical reactions of volcanic SO2. Sulfides from the Rooihoogte and Timeball Hill Formations, Transvaal Supergroup, South Africa, (2316 +/- 7 Ma; Hannah J. L. et al., 2004) show only a small degree of MIF [Bekker A. et al., 2004a], suggesting that the atmospheric oxygen level reached 0.00001 PAL by 2316 Ma. The Huronian Supergroup in Canada recording three Paleoproterozoic glaciatial events between 2450 and 2220 Ma is correlated with the Rooihootge and Timeball Hill Formations, and may record the evidence of the great oxygenation event. The sulfur isotopic compositions of sulfides in the Matinenda to Gordon Lake Formations of the Lower Huronian Supergroup exhibit D33S, deviation from a mass-dependent fractionation line, of less than 0.5 permil [e.g., Farquhar J. et al., 2000]. This suggests that the atmospheric oxygen reached a level that is high enough to vanish the large MIF signature before the deposition of the Matinenda Formation. In-situ ion microprobe (Cameca ims-1270) measurements showed that most of sulfides have a small degree of sulfur MIF, as seen in other formations, except for sulfide blocks in the polymictic conglomerate of the Livingstone Creek Formation, the lowermost Huronian Supergroup [Tachibana et al., 2005]. The sulfides in the Livingstone sulfide blocks show a clear evidence of MIF (D33S = -1.7+3.6 permil) with d34S of -4-+2 permil. The range of MIF from the sulfide blocks is an order of magnitude larger than that for other sulfides from the Huronian Supergroup. Re-Os age of the sulfide blocks is estimated to be 3074 +/- 220 Ma, indicating that such sulfide blocks did not form contemporaneously with the Livingstone Creek Formation, but formed in mid Archean. Ohmoto et al. (2006) showed little or no sulfur MIF from sulfides with the age of 2920 Ma and suggested that the atmosphere may not have been reducing. However, our present results indicate that sulfur MIF was present in mid Archean and that the atmosphere was not globally oxidizing.