

## In situ multiple sulfur isotope analyses of a Mesoarchean (2.93 Ga) sulfidic shale, Red Lake, Canada

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The 2.93 Ga Red Lake Greenstone Belt in northwest Ontario, Canada, preserves the earliest known occurrence on Earth of sulfidic black shales containing abundant pyrite and pyrrhotite. These minerals occur as nodules, disseminated cubes, and thin laminae. This project investigates using high-resolution SIMS the multiple sulfur isotope composition ( $\delta^{32}\text{S}$ ,  $\Delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ , and  $\Delta^{36}\text{S}$ ) of Red Lake sulfidic shales containing pyrite and pyrrhotite. Nine epoxy-mounted disks were analyzed and a total of 150 points were obtained using the SwissSIMS Cameca IMS1280 by simultaneous measurements of  $^{32}\text{S}$ ,  $^{33}\text{S}$ ,  $^{34}\text{S}$ , and  $^{36}\text{S}$  in multi-collection mode with three Faraday cups. The  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ , and  $\Delta^{36}\text{S}$  values range from -18‰ to +11‰, -1‰ to +1.4‰, and -4‰ to +3‰, respectively (all values relative to VCDT). The slope value of  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  of most of the samples is within the range of the Archean reference array (-1.5 to -0.9)<sup>1</sup>. The narrow range of  $\Delta^{33}\text{S}$  values is comparable to the mass independent fractionation (MIF) from other Mesoarchean sites<sup>2</sup>. The  $\Delta^{33}\text{S}$  values of most of the samples appear to reflect an elemental sulfur atmospheric contribution ( $\Delta^{33}\text{S} > 0$  ‰), while a smaller number of samples show  $\Delta^{33}\text{S} < 0$  ‰ that would be classically interpreted as reflecting deposition of atmospheric sulfate. Some disseminated pyrite has a negative  $\Delta^{33}\text{S}$  value and large negative  $\delta^{34}\text{S}$  isotopic composition, indicating microbial sulfate reduction to some extent. However, the  $\Delta^{33}\text{S}$  values of some samples represent mass dependent fractionation (MDF) processes which may be attributed to a second generation of pyrite and pyrrhotite. This dataset reveals that the Red Lake sulfidic shales preserve typical Mesoarchean MIF signals, revealing sulfur derived from different sources including juvenile sulfur ( $\Delta^{33}\text{S} = 0 \pm 0.3$  ‰), elemental sulfur, and sulfate.

1. Farquhar, J. *et al. Nature* **449**, 706 (2007).
2. Eickmann, B. *et al. Nat. Geosci.* **11**, 133–138 (2018).