

## Metamorphic history of the pre-3750 Ma Nuvvuagittuq Supracrustal Belt, Québec (Canada)

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The ca. 3750 Ma Nuvvuagittuq Supracrustal Belt (NSB) in northwestern Québec is among the oldest volcano-sedimentary sequences thus far discovered; it overlaps in age with the Eoarchean Isua Supracrustal Belt and the Akilia association supracrustal enclaves in West Greenland [1]. Mapped NSB sequences are dominated by amphibolites ( $\pm$  Gt), ultramafic rocks, granitoid gneisses and leucogranite intrusions, but also comprise both chemical and detrital metasediments such as finely laminated banded iron-formations and quartzite. Like other pre-3600 Ma terranes, the NSB has been thermally metamorphosed and multiply deformed. Our preliminary garnet-biotite and plagioclase-amphibole geothermometry coupled with U-Pb zircon geochronology suggests that the belt last reached the mid- to upper amphibolite facies (550-600°C) in the late Archean.

To explore in detail the timing of events in the NSB, we obtained U-Th-Pb depth profiles for two zircons from a trondhjemitic orthogneiss that shares the entire deformational history of the outcrop. Both zircons were previously analysed via conventional ion microprobe techniques and their core ages correspond with the oldest ages for the NSB ( $3755 \pm 7$  and  $3752 \pm 10$  Ma). Grain IN05022\_26 preserves a thin overgrowth and large core with rhythmic zoning. Our depth profile penetrated 6.7  $\mu\text{m}$  into the zircon and the core was reached within the first 2.25  $\mu\text{m}$ . The weighted mean of all core Pb-Pb ages yields an age of  $3802 \pm 12$  Ma and Th/U (0.31) consistent with igneous growth in a melt of the composition of the host gneiss. Grain IN05003\_18 preserves an unzoned overgrowth over a rhythmically zoned core. The 1  $\mu\text{m}$  thick overgrowth yields an age  $2736 \pm 25$  Ma with very low Th/U (0.009) consistent with growth in a metamorphic fluid. The core age of  $3743 \pm 26$  Ma was reached at a depth of 4.6  $\mu\text{m}$  and has a Th/U (0.39) consistent with igneous growth. A thin (<1  $\mu\text{m}$ ) intermediate age plateau of  $3668 \pm 26$  Ma with somewhat lower Th/U (0.25) than the core may record an earlier metamorphic event for the NSB. The ca. 2700 Ma event in the zircons corresponds to the amalgamation of the Minto block and initiation of widespread igneous activity in the vicinity of the NSB [2]. This is likely recorded by our thermometry which documents mid- to upper-amphibolite facies metamorphism. The 3650 Ma event probably corresponds to the intrusion of the Voizel suite granitoids which surround the NSB [3].

### References

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## Archean methane, oxygen and sulfur

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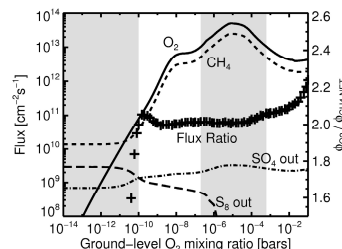
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Mass-independent fractionation (S-MIF) of S isotopes marks the 2.4 Ga division of Earth's anoxic and oxic atmospheres. We emphasize that S-MIF also indicates abundant Archean atmospheric CH<sub>4</sub>. In addition, the magnitude of S-MIF reflects the size of S gas fluxes to the atmosphere. Thus, high amplitude S-MIF in the late Archean may indicate the advent of significant biogenic S gases.

Relatively inert CH<sub>4</sub> leaves little geochemical trace. For many years, the only evidence that Archean CH<sub>4</sub> was abundant came from a global distribution of 2.5-2.8 Ga <sup>12</sup>C-enriched kerogens attributed to methanogenic CH<sub>4</sub> incorporated into methanotrophs. S-MIF now provides independent evidence. S-MIF occurs when S exits the atmosphere in soluble sulfate and insoluble polymerized sulphur (S<sub>8</sub>) [1]. Our models [2] show that O<sub>2</sub> <1 ppmv and a high abundance of CH<sub>4</sub> are required for significant rainout of S<sub>8</sub>. Sufficient CH<sub>4</sub> enables the reduction of S-bearing gases to S<sub>8</sub>. Plentiful H<sub>2</sub> is an alternative but is implausible because H<sub>2</sub> is biologically converted to CH<sub>4</sub>.



**Fig. 1:** Fluxes in a 100 ppmv CH<sub>4</sub> atmosphere. Plus symbols (“+”) indicate the ratio of O<sub>2</sub> ( $\phi_{\text{O}_2}$ ) to CH<sub>4</sub> ( $\phi_{\text{CH}_4}$ ) bio-fluxes, on the R.H. axis. Shaded regions have implausible O<sub>2</sub> fluxes.

After the advent of oxygenic photosynthesis, photochemically-stable anoxic or oxic atmospheres can exist (Fig. 1). A ~3% increase in the ratio of O<sub>2</sub>:CH<sub>4</sub> fluxes to the atmosphere causes a transition to the oxic state. In an anoxic environment, O<sub>2</sub> and CH<sub>4</sub> flux to the atmosphere in a 2:1 redox neutral ratio, according to  $\text{CO}_2 + 2\text{H}_2\text{O} = 2\text{O}_2 + \text{CH}_4$ , the net reaction of photosynthesis + methanogenesis. This ratio increases if sufficient sulfate allows microbial anaerobic oxidation to change the reduced partner of O<sub>2</sub> from gaseous CH<sub>4</sub> to solid sulfide. Alternatively, with increasing sulphate, the reduced partner of O<sub>2</sub> may change from CH<sub>4</sub> to biogenic sulphur gases. These gases, unlike CH<sub>4</sub>, are kinetically more unstable than O<sub>2</sub> and may have left a signal in S-MIF.

### References

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