

## Modelling long term carbon and sulphur cycling over the Proterozoic

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Current zero-dimensional carbon and sulphur cycle models provide estimates of O<sub>2</sub> and CO<sub>2</sub> concentration over the Phanerozoic eon, and show a reasonable correlation with available proxys [1][2].

In this work we attempt to further extend these techniques to address conditions throughout the Proterozoic. As well as the controlling processes in the Phanerozoic, this model must include the interaction of the surface system with the mantle, the steady accumulation of carbon in the crust and the change in removal pathways as the continental area expands – processes which have been addressed individually in previous work [3][4][5].

Initial results show that the accumulation of crustal carbon in the combined model agrees well with previous modelling, and the predicted surface temperature and isotopic fractionation fall within reasonable limits. However, the baseline model does not predict the expected low oxygen concentration throughout the Proterozoic, instead predicting a stable concentration of around 0.2-0.5 PAL (present atmospheric level). The conclusion is that important processes may be missing.

Thankfully there are many candidates for the missing process (e.g. reduced organic burial due to limited nutrient delievey [6]), and we therefore use our model framework as an assesment tool: for each possibility, model predictions for O<sub>2</sub>, CO<sub>2</sub>, temperature and the isotopic fractionation of carbon and sulphur are compared to all available geochemical proxies, allowing the evaluation of these mechanisms, and hopefully the beginnings of a combined model for Earth evolution.

[1] Bergman *et al.* (2004) *Am. J. Sci.* **304**, 397-437. [2] Berner (2006) *Geochim. Cosmochim.* **70**, 5653-5664. [3] Hayes and Waldbauer (2006) *Phil. Trans. R. Soc. B* **361**, 931-950. [4] Bjerrum and Canfield (2004) *Geochem. Geophys. Geosyst.* **5**, Q08001. [5] Sleep and Zahnle (2001) *J. Geophys. Res.* **106**, 1373-1399. [6] Lenton and Watson (2004) *Geophys. Res. Lett.* **31**, L05202.

## Concentration and transport of solutes drive by transpiration at the edge of a Prairie Pothole wetland

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The Prairie Potholes region (~715,000 km<sup>2</sup>) extends from Alberta, Canada to Iowa, USA. Retreat of Pleistocene glaciers left millions of pothole-like depressions that are internally drained. Topographically low, groundwater discharge wetlands tend to be saline (often Ca-Mg-SO<sub>4</sub>-HCO<sub>3</sub>) due to reaction of groundwater with glacial till rich in pyrite, gypsum, and calcite. However, several other processes influence discharge wetland chemistry, including plant transpiration at the wetland edge. This process can concentrate solutes and change hydrologic gradients at the wetland margin causing it to alternate between a source and sink of water and solutes to the wetland. We used δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub>, δ<sup>2</sup>H<sub>H<sub>2</sub>O</sub>, and δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values of groundwater and wetland water to investigate this process at the edge of wetland P1 in the Cottonwood Lake study area near Jamestown, North Dakota (USA).

Solutes (including SO<sub>4</sub>) were least concentrated in wetland P1 water and deep (several meters below ground surface) groundwater upgradient of P1. Solutes were more concentrated in mid-depth (150 cm) to shallow (60 to 90 cm) groundwater at the edge of the wetland due to plant transpiration. Transpiration did not affect δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub>/ δ<sup>2</sup>H<sub>H<sub>2</sub>O</sub> values of mid-depth groundwater samples which were similar to deep, upgradient groundwater and fell on the meteoric water line (δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub> from -14.6 to -12.0‰). Deep and mid-depth groundwater samples also shared similar δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values (-18.2 to -15.1‰). Water from P1 fell below the meteoric water line (δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub>=-4.6‰) and had more positive δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values (-4.2‰).

Shallow groundwater from the wetland edge had δ<sup>18</sup>O<sub>H<sub>2</sub>O</sub>/ δ<sup>2</sup>H<sub>H<sub>2</sub>O</sub> and δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> values that were intermediate between deeper groundwater and wetland water. A plot of δ<sup>34</sup>S<sub>SO<sub>4</sub></sub> versus the deuterium offset showed shallow groundwater to be a mixture of deeper groundwater and wetland water. Samples taken at different times of day located differently along the mixing line indicating dynamic mixing. Samples collected earlier in the day showed a smaller contribution of wetland water than samples collected later in the day. This may be a result of a diurnal cycle of the hydrological gradient at the wetland edge due to plant transpiration. This study clearly demonstrated the use of natural abundance isotope systems for investigating this hydrochemical process and the potential impact of plant physiology on wetland geochemistry.