

## Scaling of critical zone processes in the Praire Pothole region, USA

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The Prairie Pothole Region, which occupies 750,000 km<sup>2</sup> of the north central U.S. and south central Canada is one of the most important ecosystems in North America. It contains millions of small wetlands underlain by glacial till that are internally drained within discrete, km-scale basins. We studied the geochemistry of soils, sediments, wetland water, and groundwater in the 92 hectare Cottonwood Lakes (CWL) area of North Dakota. The CWL area includes upland groundwater recharge wetlands with compositions similar to rainwater (TDS 150 mg/l), and a discharge wetland at a local topographic low only 200m from the recharge wetlands. Oxygenated water interacting with pyrite in surficial glacial till has oxidized the till to depths >10 m. Coupled fluid flow and chemical reaction modeling shows that this oxidation process has taken >10<sup>3</sup> years. The resulting SO<sub>4</sub><sup>2-</sup>-enriched fluids have migrated from upland recharge areas and accumulated in the discharge wetland which has >2500mg/l SO<sub>4</sub><sup>2-</sup>. The drastic variability in recharge and discharge wetland chemistry is reflected by fauna and flora. Sulfur isotope data support the conclusion that isotopically light pyrite, originally from marine shale (mean δ<sup>34</sup>S<sub>SO4</sub> = -16‰) is the source of groundwater sulfate (δ<sup>34</sup>S<sub>SO4</sub> = -7.5 to -15.9‰). Heavier δ<sup>34</sup>S<sub>SO4</sub> values within discharge wetlands (maximum +4‰) is evidence that bacteria are reducing SO<sub>4</sub><sup>2-</sup> to sulfide, a process that drives the precipitation of high Mg calcite.

Our evaluation of literature data on water compositions of 178 wetlands throughout a 10<sup>3</sup> km<sup>2</sup> area surrounding the study site document that oxidation of pyrite and formation of SO<sub>4</sub><sup>2-</sup>-enriched wetlands has occurred over a large area in North Dakota.

## Oxygen isotope variations in the Allende CV3 meteorite

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### Introduction

The Allende (CV3) carbonaceous chondrite consists of mm-sized chondrules, fine-grained matrix, Ca- and Al-rich inclusions (CAIs), dark inclusions (DI) and amoeboid olivine aggregates (AOA). Various components of the Allende meteorite fall on a mixing line in the δ<sup>17</sup>O vs. δ<sup>18</sup>O space [1].

In this study, we investigate isotope variations of small bulk samples (~0.3 – 1.1 g) and compare the variations with chemical data of the same aliquots.

### Samples and Measurement techniques

37 of 39 samples of a 22.5 mm<sup>2</sup> large and 4 mm thick slice of the meteorite were analyzed. One sample (C4) contained a macroscopically visibly CAI, one (F3) a large DI. Oxygen isotopes were analyzed in Göttingen using IR laser fluorination in combination with GC-irmMS using a MAT 253 gas source mass spectrometer. The Δ<sup>17</sup>O is calculated relative to the rocks- and minerals-defined TFL (N > 700) with a slope of β = 0.5151 ± 0.0007 (1σ) and an intercept of γ = -0.0014 ± 0.008 (1σ). The accuracy and precision of a single isotope analysis is ~0.15 ‰ and δ<sup>18</sup>O and ±0.04 ‰ in Δ<sup>17</sup>O.

The chemical analyses were obtained by XRF in Cologne.

### Results

The O-isotope data fall on the AML. The Δ<sup>17</sup>O<sub>TFL</sub> shows a spread from -4.6 ‰ to -2.3 ‰. The lower limit is marked by sample C4 (CAI) and the upper limit by the DI in sample F3. Excluding these 2 samples, a spread in Δ<sup>17</sup>O of -4.1 to -3.0 ‰ is observed. For the remaining samples, no correlation between chemical composition (e.g. Al content) and Δ<sup>17</sup>O is observed. The Al<sub>2</sub>O<sub>3</sub> concentrations range from 2.6 – 4.3 wt.%, with constant Ca/Al-ratios..

### Discussion

A correlation between Δ<sup>17</sup>O and chemistry is expected if variations in Al (and other refractory elements) is caused by addition of CAI-like material. Such a correlation is not observed. This suggests the existence of an oxygen component, independent of the chemical variability. Implications with respect of the correlation between O- and Cr-isotopes [3] will be discussed.

[1] Clayton, R.N. *et al.* (1977) *EPSL*, **34**: 209-224 [2] Young & Russell (1998) *Science*, **282**: 452-455. [3] Trinquier *et al.* (2007) *ApJ*, **655**: 1179-1185.