

Temperature dependence of ^{13}C - ^{18}O clumping in synthetic aragonite: Laboratory calibration

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A paleothermometer has recently been proposed, based on the abundance of the doubly-substituted CO_3^{2-} isotopologue, $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$, in carbonate minerals [1, 2]. This carbonate 'clumped' isotope thermometer requires only the carbonate mineral to estimate its formation temperature, in contrast to the conventional carbonate-water paleothermometer which requires the oxygen isotope compositions of both the carbonate and parent water.

Given that only a limited number of calibration studies of the carbonate clumped isotope paleothermometer are currently available in the literature and, most importantly, previous calibrations of aragonite have included only biogenic specimens, we synthesized more than 30 inorganic aragonite samples under well-controlled laboratory conditions to obtain a aragonite clumped isotope paleothermometer. Subsequently, all of the inorganic aragonite samples were examined for their oxygen isotope fractionation with respect to their parent solution, for comparison with the previous calibration of the aragonite-water fractionation relationship [3]. We then examined the clumped isotope compositions of these samples through measurements of the abundance of $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ in CO_2 liberated by phosphoric acid digestion, focusing on those new samples that have $\delta^{18}\text{O}$ values within 0.3 ‰ of the previous calibration of the oxygen isotope equilibrium [3]. Our results indicate a temperature dependence of ^{13}C - ^{18}O clumping in synthetic aragonite that agrees with that of Ghosh *et al.* [1] at 25 °C, but exhibits lower temperature sensitivity and departs significantly from that calibration at higher and lower temperatures. Possible reasons for this discrepancy will be discussed.

[1] Ghosh *et al.* (2006) *GCA* **70**, 1439–1456. [2] Schauble *et al.* (2006) *GCA* **70**, 2510–2529. [3] Kim *et al.* (2007) *GCA* **71**, 4704–4715.

Effects of road salts on pore water geochemistry of lake sediments

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Salt de-icer is commonly applied to roads to promote safer motor vehicle and pedestrian travel during the winter season. The fate of millions of tons of roadsalt is of growing concern. Most prior study has focused on the effects of salt on roadside vegetation, but the influence of these salts on lake sediment geochemistry remains poorly understood. Therefore, the effects on lake sediment porewater geochemistry of two commonly used de-icers, NaCl and CaCl_2 , were investigated.

Intact lake sediment cores (d. i 5 cm, length 15 cm) were collected from the shoreline of Asylum Lake (Kalamazoo, MI, USA), and incubated in distilled water (control), NaCl (5 g/L) or CaCl_2 (5 g/L). A suite of redox sensitive species (pH, alkalinity, ammonium, Mn (II), Fe (II), sulfide, sulfate, phosphate), together with selected major (Ca, Mg, Na, K) and trace (Pb, Ni, Co, Cr) elements were analysed at 3 depths using 3 replicate cores for initial conditions and for each treatment after 30 and 60 days of incubation.

Some parameters were influenced little by the addition of NaCl or CaCl_2 . Alkalinity increased steadily with incubation time, while ammonium and sulfide increased only slightly for all three treatments. Phosphate, sulfate and trace element concentrations were typically low in all samples.

pH, Fe, Mn, Mg, Na and Ca were significantly influenced by NaCl or CaCl_2 addition. The control pH was invariant at ~7.5-8 compared to ~7-7.5 with NaCl treatment and ~6.5 with CaCl_2 . Fe (II) and Mn (II) increased dramatically with time in the CaCl_2 incubations, suggesting stimulation of anaerobic Fe (III) and Mn (IV) respiration. NaCl treatments resulted in large increases with time in Mn (II), but not Fe (II), compared to controls. Na levels were significantly elevated relative to controls in the CaCl_2 treatments, while Ca increased greatly with addition of NaCl, consistent with promotion of ion exchange from salt addition. Mg concentrations were increased by ~5x in NaCl experiments, and by nearly 10x in CaCl_2 experiments. Furthermore, visual inspection of cores suggests that some of the differences in geochemistry may be due to differential growth of algal mats on the surface of the cores, which appeared to be enhanced by the application of CaCl_2 . Further study will be required to elucidate the role of these algal mats in altering the pore water geochemistry of these sediments.