

Alkalinity measurement in mine-impacted wetland sediments using gas chromatography

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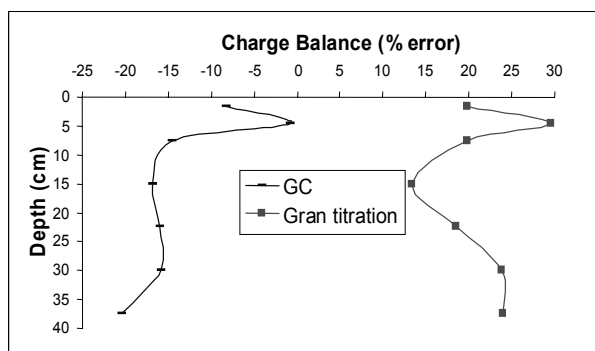
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Introduction

Obtaining accurate carbonate alkalinity measurements in anaerobic, iron-rich wetland sediment porewaters using Gran titration is problematic due to rapid changes in carbonate equilibria that occur after sample collection. Inaccurate alkalinity measurements result in unacceptable charge balance calculations. Porewaters from mine-waste impacted wetlands along the Coeur d'Alene River located in northern Idaho, USA were collected and characterized. Carbonate alkalinity was determined using Gran titration and compared with a newly developed gas chromatographic (GC) technique.

Results

Charge balances calculated using GC-derived alkalinity values were within +/- 10 % for porewaters obtained from the top 5 cm of sediment and within +/- 20 % throughout the remainder of the sediment profile. In contrast, samples analyzed using Gran titration methods resulted in charge balances of +/- 14-30 %.



Conclusions

Loss of CO₂ after sample collection raises the pH and affects carbonate equilibria by reducing the total carbonate alkalinity. The increase in pH is offset by iron oxide precipitation. The GC method minimizes changes in dissolved CO₂ upon sample extraction and transport, enabling a more accurate and reproducible measurement of alkalinity as seen in the increased ability to obtain a charge balance.

Silicon - aluminum MAS-NMR TRAPDOR of natural silica minerals

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Siliceous sinters are an important site for the preservation of microfossils of ancient microbial lineages. Therefore, understanding how and when microfossils are preserved in the geological record is critical to unraveling the authenticity of purported fossil organisms. Solid-state silicon and aluminum NMR spectra are distinct for siliceous sinters formed under different thermal and chemical conditions. Most recently, Hinman et al. (2004 Astrobiology Science Conference) reported that silicon bridges to two other silicon atoms via oxygen (Q2) or to three other silicon atoms via oxygen (Q3) in siliceous sinters as determined by cross-polarization experiments. Both types of sites, Q2 and Q3, have significant amounts of silanol (Si-O-H) groups in network-modifying sites but it is not known whether other ions populate neighboring cation sites. Other cations could modify the silica network either by terminating silicate chains, as would H, or by substituting for silicon in the structure, as would Al. Hypothetically, if differences are noted in the number and type of neighboring cations, then subsequent silica phase reactivity and transition rates would be affected. This is important to potential microbial preservation in hot-spring environments. Using a triple-resonance probe, Si-Al TRAPDOR experiments were conducted to determine the proximity of Al and Si in siliceous sinter samples as well as known samples with and without Si-O-Al bridges. Si-O-Al bridges should be detectable by monitoring the Si NMR frequency while pulsing at the Al NMR frequency. If a reduction in signal occurs during TRAPDOR pulsing experiments, then Al is bridged to Si. The experiment is challenging because the similar NMR frequencies of Al and Si. Nevertheless, TRAPDOR signals were observed for all siliceous sinters, zeolites, and clay minerals studied, but not for a mechanical mixture of alumina and silica. This work demonstrates the success of the Si-Al TRAPDOR experiment, and will enable future experiments on the atomic structure, and therefore reactivity, of silicon in siliceous sinters. We thank the Nuclear Magnetic Resonance User Facility of the Wiley Environmental and Molecular Science Laboratory, Pacific Northwest National Laboratory, for their support.