

Speciation of lead in aqueous solutions

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Introduction

Lead (Pb^{2+}) has been widely studied because of its toxicity to organisms. Since it is the chemical form that is important, rather than the total concentration, in determining the bioavailability, behavior and fate of the metal in natural waters, an accurate knowledge of speciation is required. Speciation is determined by complexation with organic and inorganic ligands, which is a function of temperature, ionic strength, and media; therefore reliable formation constants over a range of temperature, ionic strength, and media are essential. In most natural waters, the inorganic speciation of lead is dominated by chloride and carbonate complexes. To date only a limited number of lead formation constants (β_i) have been made due to difficulty in their determination as a result of the limited solubility of lead. Instead, formation constants have often been estimated from correlations with other metals; direct measurements are limited. Recently several studies of lead chloride and lead carbonate complexation have been done over a large range of ionic strength and in several different media [1,2]. We've combined these previous measurements of lead chloride complexes in various media and lead carbonate complexes in $NaClO_4^-$ with new measurements of $PbCO_3$ in $NaCl$ to model the speciation of lead in natural waters using a Pitzer model.

Pitzer Model

The formation constant of $PbCO_3$ in $NaCl$ was measured using a spectrophotometric method since $PbCO_3$ is known to absorb in the ultraviolet, with a peak in the ultraviolet wavelengths. Measurements were made from 0.001-6 m $NaCl$ at various $[CO_3^{2-}]$. The β_{PbCO_3} was determined through nonlinear least-squares regressions using the global curve-fitting function in OriginPro 8.6. These formation constants were combined with earlier measurements of $PbCl$ complexation (critically reviewed by [1]) and recent measurements of $PbCO_3$ in $NaClO_4^-$ [2] into a Pitzer model. These Pitzer coefficients allow for the inorganic speciation of lead to be determined in many natural waters including brines and seawater.

[1] Powell et al. (2009) Pure Appl. Chem. **81**(12) 2425-2476.

[2] Easley and Byrne (2011) Geochim. et Cosmochim. Acta **75**(19) 5638-5647.

Magnesium isotope cycling within *Acer saccharum* (sugar maple)

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Magnesium (Mg) serves as an important macronutrient for plants being involved with metabolic functions, respiration and most importantly, photosynthesis. Previous studies have demonstrated mass dependent fractionation of Mg within laboratory grown vegetation [1,2] while there has been only one confirmed case of plant fractionation in the field [3]. This study builds on previous work by coupling laboratory and field based investigations of Mg isotope fractionation within *Acer saccharum* (sugar maple) plants. Our main objective is to determine whether Mg isotopes might serve as useful tracers of a forest Mg-cycle.

The study site consists of a sugar maple stand within a first-order catchment located in southern Québec, Canada. Significant Mg isotope fractionation has been established between different tree tissues such as roots, stemwood, and leaves (both senescent and photosynthesizing) as well as other reservoirs including soil waters, precipitation, throughfall, and stream water. The total range of $\delta^{26}Mg$ ($^{26}Mg/^{24}Mg$) values within the study plot is 1.37‰_{DSM3} (approximately 30% of reported terrestrial variation).

Earlier laboratory based studies of potted plants have demonstrated a light isotope enrichment of Mg in the soil pool, complementing heavy isotope uptake and incorporation into plant material [1,2]. In contrast to these reported data trends, we do not see light isotope enrichment within the soil pool in nature when whole seedlings are analyzed as analogues of adult trees. We are conducting our own pot experiment with sugar maple to investigate this effect, which will guide our interpretations of this field study. Full results will be presented and discussed in detail regarding factors influencing Mg isotope cycling within a sugar maple dominated catchment.

[1] Black et al. (2008) Environ. Sci. Technol. **42**, 7831-7836. [2]

Bolou-Bi et al. (2010) Geochim. Cosmochim. Acta **74**, 2523-2537.

[3] Tipper et al. (2010) Geochim. Cosmochim. Acta **74**, 3883-3896.