Discriminating factors affecting incorporation: Comparison of the fate of Eu³⁺/Cm³⁺ in the Sr carbonate/sulfate system

KIEL HOLLIDAY^{1,2*}, AURÉLIE CHAGNEAU^{1,3,4}, MORITZ SCHMIDT¹, FRANCIS CLARET³, THORSTEN SCHÄFER^{1,4}, AND THORSTEN STUMPF¹

1 Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal, P.O. Box 3640, 76021 Karlsruhe, Germany; E-mail: holliday7@llnl.gov, mschmidt@anl.gov,

thorsten.schaefer@kit.edu, thorsten.stumpf@kit.edu

2 Lawrence Livermore National Lab, 7000 East Ave., Livermore, CA 94551 USA; E-mail: holliday7@llnl.gov

3 Bureau de Recherches Géologiques et Minières, 3 avenue Claude-Guillemin, BP 36009, Orléans Cedex 2, France; E-mail: aurelie.chagneau@kit.edu, f.claret@brgm.fr

4Institute of Geological Sciences, Department of Earth Sciences, Freie Universität Berlin, Berlin, Germany.

The aim of this work is to assess the effect of ligand strength, symmetry, and coordination number on solid solution formation of trivalent actinides and lanthanides in carbonate and sulfate minerals. This is of particular importance in radionuclide migration where trivalent actinides such as Pu, Am, and Cm are responsible for the majority of radiotoxicity after 1,000 years. Time-resolved laser fluorescence spectroscopy was used to study trace concentrations of the dopant ion after interaction with the mineral phase. This study expands on previous work with aragonite and gypsum where it was found that aragonite incorporates Eu³⁺ and Cm³⁺ while only surface sorption is observed in gypsum. This study uses isostructural minerals strontianite (SrCO₃) and celestite (SrSO₄) to decouple the effect of structure from that due to the anion. It is demonstrated that while distribution coefficients can predict the amount of dopant ion associated with the mineral phase, they do not have any correlation with solid solution formation. This substitution mechanism is most likely dictated by the symmetry of the site being substituted and the electronic structure of the dopant atom.

Table 1: Lifetime and position of fluorescence emission in Eu^{3+} and Cm^{3+} doped aragonite, strontianite, and celestite.

Sample	Wavelength (F ₀ or S _{7/2})/nm	Lifetime/ms
Eu-CaCO ₃ ¹	579.4	1.6
Eu-SrCO ₃	578.5	1.6
Eu-SrSO ₄	577.7	3.1
Cm-CaCO ₃ ¹	612.7	0.64
Cm-SrCO ₃	608.5	0.47
Cm-SrSO ₄	596.3	1.1

[1] Schmidt, M., Stumpf, T., Walther, C., Geckeis, H., Fanghänel, T. (2009) *Dalton Trans.* **33**, 6645.

Dissolved organic matter characterization for a Prairie Potholes ecosystem

JOANN M. HOLLOWAY¹*, MARTIN B. GOLDHABER¹, CHRISTOPHER T. MILLS¹, GEORGE R. AIKEN², AND KENNA D. BUTLER²

¹U.S. Geological Survey, Denver, CO, USA, jholloway@usgs.gov

(* presenting author), mgold@usgs.gov, cmills@usgs.gov

²U.S. Geological Survey, Boulder, CO, USA, <u>graiken@usgs.gov</u>, <u>kebutler@usgs.gov</u>

The Prairie Potholes region of the northern Great Plains includes an extensive system of small (< 0.5 hectare), discrete wetlands that occur within a hummocky topography formed by the retreat of Pleistocene glaciers. The Cottonwood Lake Study Area, located in the Prairie Potholes region near Jamestown, North Dakota (USA), includes 16 wetlands. These wetlands receive water primarily from snowmelt and are hydrologically connected by groundwater flow within a 92-hectare basin that lacks surface drainage. The objectives of this study were to 1) determine if different wetland vegetation communities affect the quantity and quality of dissolved organic matter (DOM), and 2) determine the extent to which vegetation-DOM is partitioned into groundwater.

Wetland salinity ranged from 150 mg kg⁻¹ in recharge wetlands receiving only meteoric input to $>3000 \text{ mg kg}^{-1}$ in discharge wetlands receiving groundwater flow from topographically higher wetlands. The pH of individual wetlands ranged from 6.7 to 8.8 and has been linked to variable wetland salinity that supports differing plant community structures. Unusually high concentrations of dissolved organic carbon (DOC) accumulate from the decay of vegetation and algae in wetland waters (27 to 56 mg C L⁻¹), an order of magnitude greater than most natural waters. The hydrologic connection between the wetlands and shallow groundwater was reflected by elevated DOC concentrations (20 to 46 mg $C L^{-1}$) from wells screened within this flow path. Deeper groundwater isolated from direct wetland recharge had lower DOC concentrations (2.5 to 10 mg C L⁻¹). Specific UV absorbance (SUVA₂₅₄) is an index of aromaticity. Wetlands with near neutral pH had a greater SUVA254 than alkaline wetlands, although aromatic dissolved organic matter is generally more soluble in alkaline waters. Thus, we interpret this trend to be in part a function of organic matter source. Groundwater had a lower SUVA254 than the wetlands, indicating a lower proportion of aromatic compounds. We are also applying fluorescence-based techniques in evaluating the quality of DOM associated with these wetlands. These data give insights on how varying vegetation communities can affect types of DOM associated with these wetlands and the exchange of organic matter between surface and groundwater.