Photodissolution of Rare Earth Elements and Dissolved Organic Carbon from Subbituminous Coal: Effects of Environmental Variables and Implications for Biogeochemical Cycling

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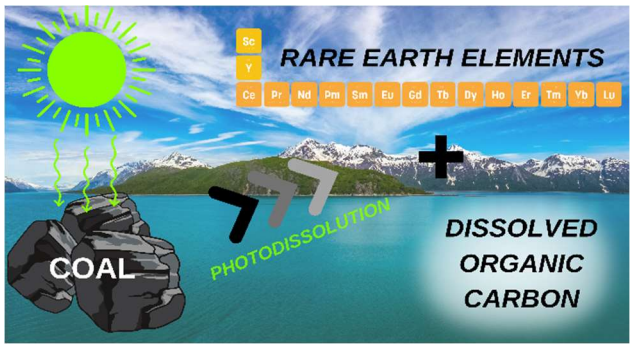

Abstract:

Rare earth elements (REEs) are a group of unique elements with diverse applications in energy, medicine, and technology. Increasing global demand and limited supplies has led to exploring the economic viability of domestic feedstock extraction from sources such as coal. Little is known about the release of REEs from coal due to the environmentally-driven processes of

photodissolution. In this study, the photodissolution of water-soluble REEs and dissolved organic carbon (DOC) from subbituminous coal was investigated using laboratory simulated sunlight exposures. The effects of solar intensity, temperature, and exposure time on photodissolution were also examined. Following irradiation, water-soluble REE and DOC concentrations increased significantly above non-irradiated controls, indicating photodissolution is a significant process. Both solar intensity and exposure time influenced photodissolution rates, while temperature did not. Results from this study provide motivation to further investigate photodissolution pathways of REEs from subbituminous coal and interaction with DOC ligands, given that photosolubilized REEs may be organic-associated. These findings may have implications, both positive and negative, for the environmental impact of REEs.

Keywords:

biogeochemical processing, photochemistry, lanthanides, environmental variability, aquatic ecosystems, ICP-MS, environmental fate

Synopsis:

The photodissolution of rare earth elements and dissolved organic carbon from subbituminous coal was explored to provide insight into biogeochemical cycling.

Introduction:

Rare earth elements (REEs) are a group of elements that make up the lanthanide series, along with scandium and yttrium.[1] REEs can be further classified into light rare earth elements (LREEs) and heavy rare earth elements (HREEs) based on electronic and chemical characteristics.[2] There is no consensus in the literature about the exact distinction between LREEs and HREEs, but for the purpose of this study LREEs are La-Eu and HREEs are Gd-Lu

plus Sc and Y.[3-5] REEs are in high demand as they are utilized in various applications, such as renewable energy, healthcare, electronics, and transportation due to their unique magnetic, electronic, and optical properties.[4, 6, 7] REEs in coal are well studied for industrial application.[8] There has been extensive work completed in characterizing REEs in various coals and by-products.[8-14] In general, most REEs found in coal are associated with inorganic matter (minerals), minor amounts are associated with organic matter, and small to none are readily water-soluble.[10, 15-20] This study aims to examine REEs in coal through a fundamental environmental perspective rather than a potential industrial application.

Anthropogenic exposures of REEs in the environment is of growing concern due to increased refining, development, and use.[6, 21] Bioavailability and environmental fate of REEs is dependent upon factors such as speciation, pH, ligand (organic and inorganic), salinity, redox potential, and cation exchange capacity.[4, 22-25] REEs are reported to have toxicological effects on terrestrial and aquatic biota, as well as humans.[4, 21, 26-31] Except for an enzymatic pathway of methanotrophic bacteria, there is currently no known biological role of REEs.[32-35] Although the exact biological action of REEs is not fully understood, previous studies suggested several mechanisms of toxicity, including intracellular membrane crossing, generation of reactive oxygen species, lipid peroxidation, and modulation of anti-oxidation pathways.[36] The photodissolution of REEs from coal coupled with the toxicological impacts of REEs and the potential for increased prevalence due to climate change, underscores the importance of understanding this environmental process.

Little is known about the release of REEs from coal due to environmentally driven processes. To our knowledge, the photodissolution of REEs from coal is not reported. Photodissolution is a principal environmental weathering process driven by sunlight and influenced by environmental conditions such as temperature, solar intensity, and exposure length.[37] Understanding the

photodissolution pathway of coal is relevant in the context of climate change, as increased temperature, erosion, and runoff can potentially increase interactions between coal, water, and sunlight, leading to subsequent photodissolution. Photoproduced dissolved organic carbon (DOC, defined as non-volatile and passes through a 0.2 - 0.7 μm filter) from particulate organic matter is reported and recognized as an important process in carbon cycling.[37-41] We hypothesize coal in the environment can be exposed to water and sunlight and release photoproduced DOC and REEs into the water column. Examining the photodissolution of REEs and DOC from coal can uncover fundamental pathways of global biogeochemical cycling that are currently unknown.

In this study, we report the photodissolution of REEs and DOC from subbituminous coal (SBC) utilizing a laboratory simulated experimental approach. We investigate the role of environmental variables, such as solar intensity, temperature, and exposure length, on the photodissolution of subbituminous coal. We have also identified the relationships between the photoproduction of REEs and DOC from SBC, and their potential implications for the environment.

Materials and Methods:

Photodissolution Experiments

SBC (a low rank coal) sourced from Cook Inlet, Alaska[41] was ground into a powder, surface area = 0.151 m^2/g (supplementary information), using a mortar and pestle. 500 mg of coal was added to 70 mL of Milli-Q water (18.2 MΩ cm) in a 100 mL thermostatically controlled jacked beaker to create a thin coal film. Samples were then covered with quartz lids and secured with Teflon tape to reduce evaporation. A solar simulator (Atlas Suntest XLS+, calibrated annually) was used to complete simulated outdoor daylight solar radiation exposures at 300 – 800 nm. Photon flux of

the solar simulator was calculated by 2-nitrobenzaldehyde actinometry (Figure S1). Variability in solar intensity (250 W/m^2 - 765 W/m^2), temperature (5.5 °C - 20 °C), and exposure time (1 - 4 days) was utilized to study environmental effects on the photodissolution of REEs and DOC from SBC. Each irradiation treatment group was also completed in the dark as a control. All sample treatments and dark controls were completed in triplicate.

Rare Earth Element (REE) Analysis

Inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ) was utilized to measure the water-soluble photoproduced REEs. After each exposure, a 10 mL aliquot of each sample was filtered through 0.45-µm polypropylene syringe filters (Agilent Technologies) and acidified to a concentration of 2% (v/v) trace-metal grade nitric acid (Fisher Scientific) and 0.5% (v/v) trace-metal grade hydrochloric acid (VWR International). REEs in the coal filtrate were analyzed using ICP-QQQ (Agilent Technologies 8900) in MS/MS mass-shift mode, using oxygen as the reaction gas.[42-44] Specific operating conditions are outlined in the supplementary information.

Dissolved Organic Carbon (DOC) Analysis

The remaining volume of each sample was filtered through a pre-combusted (550 °C > 4 hours) Advantec GF-75 0.3 µm glass fiber filter. Each filtrate was then pH adjusted to below 2 using ultrapure hydrochloric acid (VWR International). To measure the concentration of DOC, a Shimadzu TOC-V system with an autosampler was utilized. Potassium hydrogen phthalate (VWR International) was used to calibrate the instrument.

Statistical Analyses

*S*tatistical analyses were performed using JMP, Version 17 (SAS Institute Inc.). Cauchy robust outlier analysis was performed to remove outlier data. P-values were calculated by student's t-test pairwise at 95% confidence. Correlation determined by Spearman's rank correlation coefficient (ρ) and similarity determined by Tucker's congruence coefficient (TCC). Percent relative abundance was utilized as a normalization technique for comparison between REEs and DOC concentrations. Principal component analysis was conducted to examine variation between different treatment groups.

Results and Discussion:

Photochemical Formation of REEs and DOC

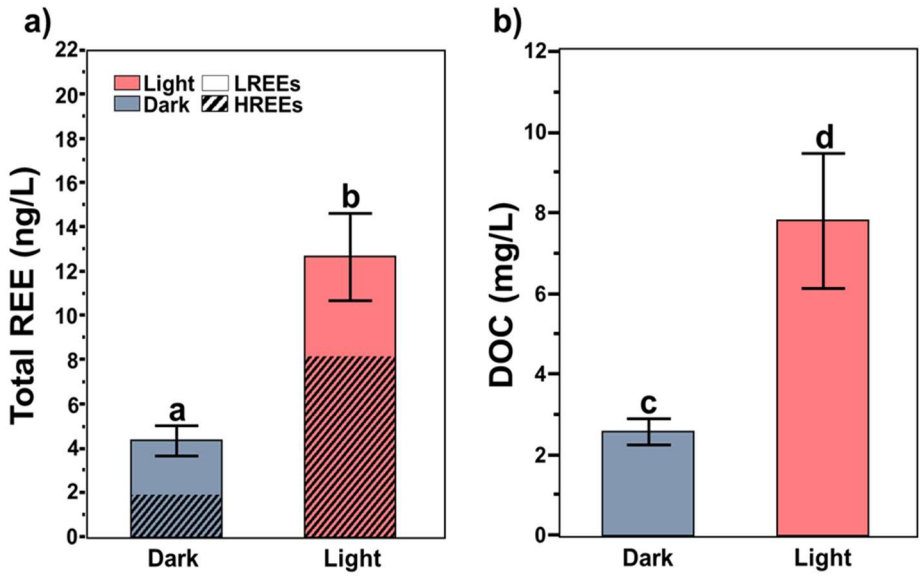

Figure 1. Average overall irradiance comparison for Total REE and DOC (N = See Table S3, ± 1 SE). Connecting letters for Total REE (a,b) and DOC (c,d) are Student's t-test pairwise comparisons at 95% confidence.

Irradiated SBC produces more water-soluble REEs compared to non-irradiated treatments ($p < 0.05$) (Figure 1a). The overall REE distribution follows the Oddo-Harkins rule, where even atomic number REEs are more abundant than odd atomic REEs (Figure S2).[45, 46] Pm is not typically included as a REE because it does not naturally exist, as such it will not be discussed in this study.[47, 48] Sc and Y were produced in the largest amount, 10.5 ± 1.70 ng/L (765 W/m^2, 5.5 °C, Day 4) and 6.73 ± 1.21 ng/L (20 °C, Day 4), respectively (Figure S3). The maximum REEs produced in irradiated samples was 29.3 ± 1.87 ng/L (765 W/m^2, 5.5 °C, Day 4) and 3.23 ± 1.63 ng/L (20 °C, Day 4) for the dark controls. The low concentration of REEs in the dark control corroborates with previous studies that only a small amount of REEs in coal are readily water-soluble, absent of sunlight.[18] Irradiated SBC produces more water-soluble HREEs than LREEs ($p < 0.05$), confirming previous findings that low rank coals have higher proportions of HREEs.[16, 18, 49] A previous study by Gupta et al. reports the concentration of total REEs in Alaskan SBC to be up to ~247 times more than the photoproduced water-soluble REEs in this study.[50] These data provide evidence of organic associated REEs in coal.[10, 15-20] Irradiated SBC produces more DOC compared with dark controls ($p < 0.05$) (Figure 1b). The maximum DOC produced in irradiated samples was 30.5 ± 5.69 mg/L (765 W/m^2, 5.5 °C, Day 4) and 1.74 ± 0.155 mg/L (5.5 °C, Day 1) for the dark treatment groups. These results agree with previous studies that report the photochemical formation of DOC from particulate organic matter.[37-41, 51] The relatively small concentration of DOC in the dark controls represent the readily water-soluble organic matter in coal. An increase in DOC after irradiation could be explained by the photooxidation of hydrocarbons in coal that produces water-soluble organic compounds.

Effects of Environmental Variables on Photodissolution

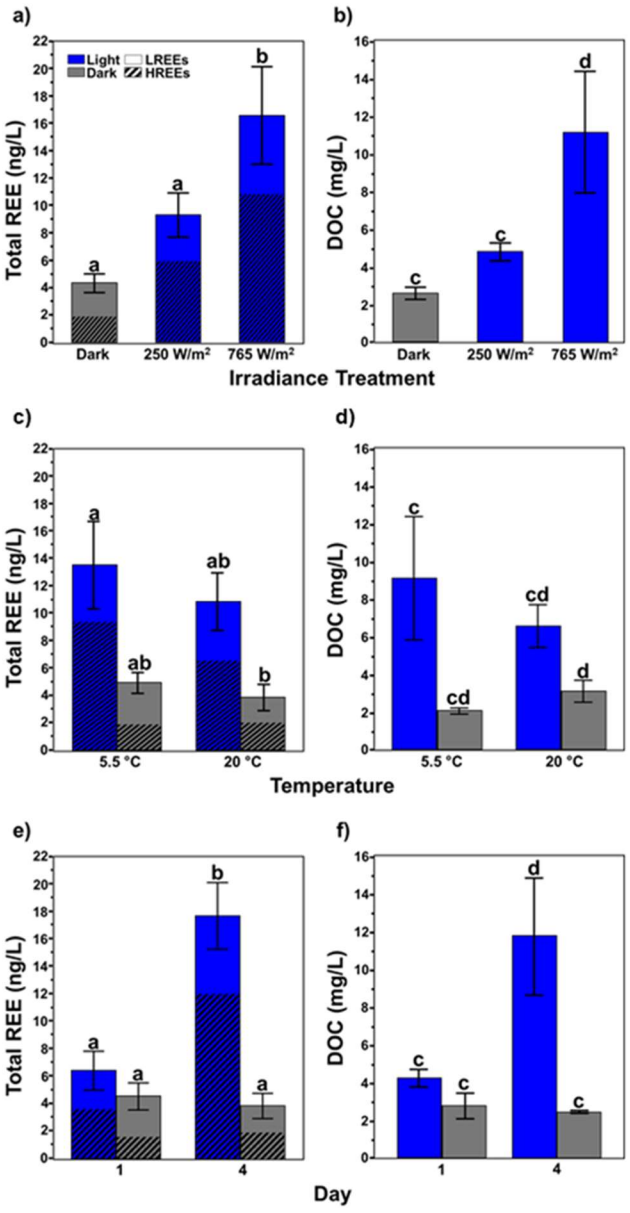

Figure 2. Total REE and DOC photodissolution dependence on solar intensity (a-b), temperature (c-d), and exposure time (e-f) (N = See Table S3, ± 1 SE). Connecting letters for Total REE (a,b) and DOC (c,d) are Student's t-test pairwise comparisons at 95% confidence.

Solar intensity (irradiance) is a significant driver of the photodissolution of REE and DOC in SBC ($p < 0.05$) (Figure 2a,b). REE concentrations range from 4.17 ± 0.642 ng/L (dark control) to 15.9 ± 3.43 ng/L (765 W/m^2) and DOC concentrations range from 2.59 ± 0.331 mg/L (dark

control) to 11.1 ± 3.23 mg/L (765 W/m^2). Increasing irradiance is positively correlated with the concentration of total REE, LREE, HREE, and DOC (ρ_{REE}=0.613, ρ_{LREE}=0.482, ρ_{HREE}=0.653, ρ_{DOC}=0.621). HREEs have a stronger correlation with increasing irradiance in comparison to LREEs, this result is expected as low rank coals have been reported to have a higher abundance of HREEs. 765 W/m^2 is the only significantly different irradiance treatment group, where the dark controls and 250 W/m^2 treatment group are not. Photodissolution of REEs and DOC is affected by solar intensity, as shown by these results. For example, the photodissolution of coal at a high latitude ecosystem (low irradiance) will produce REEs and DOC differently than a low latitude ecosystem (high irradiance).

The dataset revealed no differences between temperature groups in the production of water-soluble REEs and DOC, suggesting that temperature was not a significant factor of the photodissolution of SBC in this experiment (Figure 2c,d). REE concentrations range from 3.73 ± 0.961 ng/L (dark control, 20 °C) to 13.4 ± 3.19 ng/L (irradiated, 5.5 °C) and DOC concentrations range from 2.07 ± 0.162 mg/L (dark control, 5.5 °C) to 9.17 ± 3.30 mg/L (irradiated, 5.5 °C). These results are unexpected, as photoproduced DOC from particulate organic matter has reported to increase with temperature (Mayer et al. 2006). Future work will comprehensively investigate the interactive effects of temperature on the photodissolution rates of DOC and REEs in coal, to better understand this relationship.

Exposure time was a significant driver in the photodissolution of REE and DOC in this experiment ($p < 0.05$) (Figure 2e,f). REE concentrations range from 3.91 ± 0.912 ng/L (dark control, day 4) to 17.7 ± 2.43 ng/L (irradiated, day 4) and DOC concentrations range from 2.42 ± 0.0730 mg/L (dark control, day 4) to 11.8 ± 3.10 mg/L (irradiated, day 4). Increasing time is positively correlated with the concentration of total REE, LREE, HREE, and DOC in light-

treated samples (ρ_{REE}= 0.728, ρ_{LREE}= 0.572, ρ_{HREE}= 0.798, ρ_{DOC}= 0.591). Photoproduced HREEs have a stronger correlation with increasing time than LREEs in light-treated samples, verifying the irradiance variable trend and previous reports on the prevalence of HREEs in low rank coals.[16, 18, 49] The only significant time point is after four days of irradiation. These results could suggest that the photodissolution of REE and DOC may increase with longer irradiation times, but further investigation is needed to uncover a more comprehensive understanding of temporal trends in photodissolution.

Principal component analysis further illustrates the positive correlation between solar intensity, exposure time, and the photodissolution of REE and DOC from SBC (Figure S4). Longer irradiation periods and irradiance are closely related to the photodissolution of REEs and DOC. These trends demonstrate the susceptibility of photodissolution of REEs and DOC to location in the environment. While this report does not focus on a specific environmental setting, the findings presented reveal general patterns that contribute to the fundamental understanding of coal photodissolution.

Implications of Photoproduced REE and DOC in the Environment

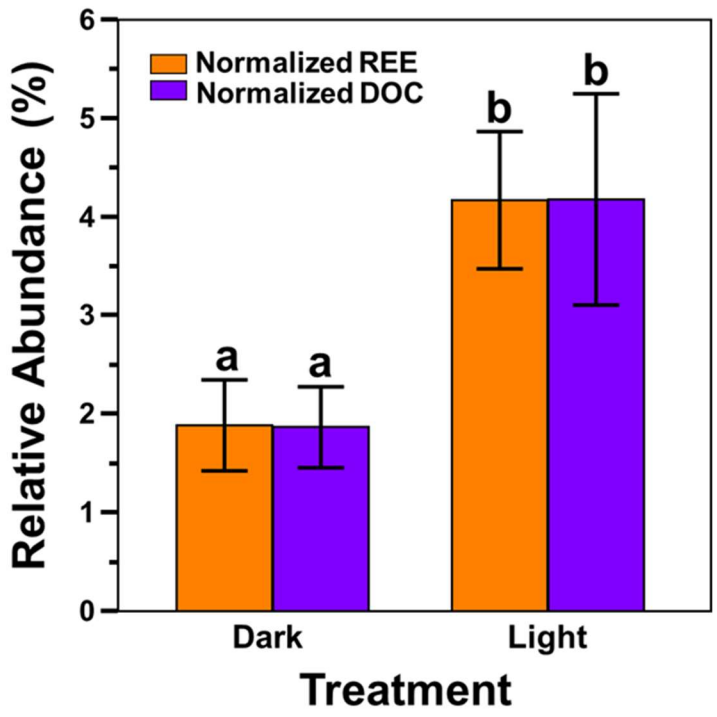

Figure 3. Irradiation affects the normalized (percent relative abundance) REE and DOC concentrations (N = See Table S3, ± 1 SE). Connecting letters for Total REE (a) and DOC (b) are Student's t-test pairwise comparisons at 95% confidence.

Normalized (percent relative abundance) results suggest the pathway of photodissolution of REEs from SBC is linked to DOC dissolution rate, an indicator that photosolubilized REEs may be complexed with DOC (TCC = 0.914) (Figure 3). Such REE-DOC complexes are reported with carboxyl groups being a primary factor affecting the binding capacity.[52-57] SBC, a low rank coal, contains higher abundances of organic matter with carboxyl functionalities.[10, 16, 18] HREEs have a more robust complexing ability than LREEs due to their smaller ion radius.[4] Analysis of the results from this study are correlative and should be considered as a fundamental baseline. Further work is necessary to obtain a tangible understanding of the relationship between photoproduced REEs and DOC from coal.

Recent studies report the presence of REE-DOC complexes in natural waters, sediment, and soil.[50, 58-63] The majority of dissolved REEs present in natural water are complexed with DOC.[53, 54, 57, 64-70] The complexation of REEs and DOC is dependent on the specific REE and amount and composition of DOC involved. For instance, low molecular weight DOC is shown to preferentially complex with HREEs, whereas high molecular weight DOC preferentially complexes with middle REEs.[53] Environmental factors such as pH, temperature, and salinity also affect the complexing of REEs and DOC.[67, 71] While photochemical processes are of particular importance in this study, the effects of photooxidation on REE-DOC complexes are not well understood. Shiller et al. reports the photooxidation of trace element-DOC complexes results in a change in speciation of the trace element, causing a release from organic ligands.[72] DOC complexation has also been reported as a potential remediator of toxic heavy metals in the environment, but not understood for REEs.[73] Both of these relationships could potentially be pathways for REE-DOC complexes, but further research is needed to fully understand the fate of these complexes in aquatic ecosystems.

Little is known about the toxicity of REE-DOC complexes in aquatic ecosystems. Recent studies reported the complexing to organic ligands significantly reduce the bioavailability, bioaccumulation, and toxicity of REEs in aquatic ecosystems.[21, 74-77] These reports highlight the significance of accounting for REE speciation in toxicity experiments, which is largely neglected in the literature,[75] and further ecotoxicity studies on REEs are needed can help develop a environmental risk assessment criteria.[78] REE-DOC interactions are another factor needing further research; DOM composition drives a wide range of global biogeochemical cycles,[79-83] metal complexation can affect DOM-mediated processes,[84-88] and photochemistry is an environmental driver of DOM composition.[38, 51, 64, 89, 90] There is considerable uncertainty over

how boreal soil–aquatic-marine system interactions will change over the coming years due to onset of rapid deglaciation and permafrost thaw.[91-95] As new stores of subbituminous coal are released from landslides and terrestrial throughfall into the marine environment, photochemistry, as a process, may affect increased REE bioavailability in the oceans.

REEs are mobilized into the environment through various other processes than photodissolution, such as hydrolysis, mineral weathering, and biological recycling. Hydrolysis is the dominant process of mobilizing REEs from parent sources, involving the oxidation of minerals at low pH values.[96] This process can be accelerated by anthropogenic activities, such as mining and processing, though natural processes are observed.[60] There is growing concern that climate change may increase the natural mechanisms of hydrolysis mobilization of metals from rocks.[35] Mineral weathering is the largest natural pathway of mobilized REEs in the environment. REE-rich primary minerals undergo weathering, leading to the formation of secondary REE complexes with inorganic ligands.[97, 98] These processes are dependent on specific minerals and weathering conditions.[99] Biological driven processes, such as plant uptake, account for only small fraction of mobilized REEs and is highly dependent on species and pH.[98, 99] While there are various mechanisms of REE mobilization in the environment, the major contributor to REE mobilization into natural waters is the complexation of REEs with organic ligands.[64, 100-104] The photodissolution of coal may represent a significant pathway for the release of these complexes. Therefore, the photodissolution process of REEs and DOC from coal and the potential subsequent formation of REE-DOC complexes is crucial for a comprehensive understanding of biogeochemical cycling of REEs in aquatic ecosystems.

Associated Content:

Supporting Information

detailed ICP-QQQ analytical methods; surface area analysis methods; 2-nitrobenzaldehyde actinometry; average photon flux; overall REE concentration distribution; scandium and yttrium concentration; PCA biplot of all treatment groups; ICP-QQQ operating conditions; ICP-QQQ detection limits; average total REE and DOC concentrations in variable groupings; individual REEs concentrations; DOC, total REE, LREE, and HREE concentrations; Spearman's rank correlation coefficients and p-values (PDF)

Conflict of Interest:

The authors declare no competing financial interest.

Acknowledgements:

DH was funded by LA Board of Regents LEQSF(2020-23)-RD-A-31. EW was supported by NSF CHE2038312, ICP-QQQ was awarded through an NSF MRI CHE2018417 (PZ). A special thank you to Mark Kelinske at Agilent Technologies for his constant support and expertise. Thanks to Zachary Redman for insights regarding actinometry and photochemistry.

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