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Utilizing Rare Earth Elements as Tracers in High TDS Reservoir Brines in CCS Applications

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Abstract

*In this paper we report the result of research associated with the testing of a procedures necessary for utilizing natural occurring trace elements, specifically the Rare Earth Elements (REE) as geochemical tracers in Carbon Capture and Storage (CCS) applications. Trace elements, particularly REE may be well suited to serve as *in situ* tracers for monitoring geochemical conditions and the migration of CO_2-charged waters within CCS storage systems. We have been conducting studies to determine the efficacy of using REE as a tracer and characterization tool in the laboratory, at a CCS analogue site in Soda Springs, Idaho, and at a proposed CCS reservoir at the Rock Springs Uplift, Wyoming. Results from field and laboratory studies have been encouraging and show that REE may be an effective tracer in CCS systems and overlying aquifers. In recent years, a series of studies using REE as a natural groundwater tracer have been conducted successfully at various locations around the globe. Additionally, REE and other trace elements have been successfully used as *in situ* tracers to describe the evolution of deep sedimentary Basins. Our goal has been to establish naturally occurring REE as a useful monitoring measuring and verification (MMV) tool in CCS research because formation brine chemistry will be particularly sensitive to changes in local equilibrium caused by the addition of large volumes of CO_2. Because brine within CCS target formations will have been in chemical equilibrium with the host rocks for millions of years, the addition of large volumes of CO_2 will cause reactions in the formation that will drive changes to the brine chemistry due to the pH change caused by the formation of carbonic acid. This CO_2 driven change in formation fluid chemistry will have a major impact on water rock reaction equilibrium in the formation, which will impart a change in the REE fingerprint of the brine that can measured and be used to monitor *in situ* reservoir conditions. Our research has shown that the REE signature imparted to the formation fluid by the introduction of CO_2 to the formation, can be measured and

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tracked as part of an MMV program. Additionally, this REE fingerprint may serve as an ideal tracer for fluid migration, both within the CCS target formation, and should formation fluids migrate into overlying aquifers. However application of REE and other trace elements to CCS system is complicated by the high salt content of the brines contained within the target formations. In the United States by regulation, in order for a geologic reservoir to be considered suitable for carbon storage, it must contain formation brine with total dissolved solids (TDS) > 10,000 ppm, and in most cases formation brines have TDS well in excess of that threshold. The high salinity of these brines creates analytical problems for elemental analysis, including element interference with trace metals in Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) (i.e. element mass overlap due to oxide or plasma phenomenon). Additionally, instruments like the ICP-MS that are sensitive enough to measure trace elements down to the parts per trillion level are quickly oversaturated when water TDS exceeds much more than 1,000 ppm. Normally this problem is dealt with through dilution of the sample, bringing the water chemistry into the instruments working range. However, dilution is not an option when analyzing these formation brines for trace metals, because trace elements, specifically the REE, which occur in aqueous solutions at the parts per trillion levels. Any dilution of the sample would make REE detection impossible. Therefore, the ability to use trace metals as *in situ* natural tracers in high TDS brines environments requires the development of methods for pre-concentrating trace elements, while reducing the salinity and associated elemental interference such that the brines can be routinely analyzed by standard ICP-MS methods. As part of the Big Sky Carbon Sequestration Project the INL-CAES has developed a rapid, easy to use process that pre-concentrates trace metals, including REE, up to 100x while eliminating interfering ions (e.g. Ba, Cl). The process is straightforward, inexpensive, and requires little infrastructure, using only a single chromatography column with inexpensive, reusable, commercially available resins and wash chemicals. The procedure has been tested with synthetic brines (215,000 ppm or less TDS) and field water samples (up to 5,000 ppm TDS). Testing has produced data of high quality with REE capture efficiency exceeding 95%, while reducing interfering elements by > 99%.

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Keywords: Rare Earth Elements; CCS; Geochemistry

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1. Introduction

The stabilization of CO_2 concentrations in the atmosphere will require a variety of technical and social solutions in order to make meaningful impact on global climate. In the United States there are regulatory standards requiring that CCS at both pilot and industrial scale be conducted in formations where water has a TDS greater than 10,000 ppm. As a result, to date CCS has been primarily focused on deep saline aquifers and depleted oil/gas reservoirs. These types of formations are good CCS targets because many of these systems are known to have trapped naturally occurring CO_2, hydrocarbons, and other fluids over geologic time. However, CCS activities in such formations can potentially displace high salinity formation fluids into potable aquifers due to over pressurization; or require that saline water be produced to manage reservoir pressure and control the CO_2 plume. Therefore, the ability to track the movement of these altered formation fluids in complex geologic settings will be a critical MMV goal to ensure environmental and regulatory compliance.

Using the natural geochemistry of saline formation fluids as *in situ* tracers to support MMV activities at CCS sites represents an important tool for understanding the interaction and migration of CO_2 affected fluids with reservoirs, cap rocks, and overlying potable aquifers. In addition to major elements (e.g., sodium, calcium, chloride, sulfate, etc.), trace elements, specifically the (REE), may be especially effective tracers. REE can provide a powerful tool for evaluating trends in water chemistry and transport (e.g., CO_2 impacts, mixing, and source zones) and are increasingly being used to evaluate aqueous systems in more detail than has traditionally been possible with major element analysis.

In recent years, a series of studies using REE as groundwater tracers have been conducted successfully at various locations around the world (Wood et al. 2006, Nelson et al. 2004, Johannesson et al. 1997a, Johannesson et al. 1997b, Johannesson et al. 2000, Ojiambo et al. 2003). In these studies, researchers were able to demonstrate that

REE can be used to trace water movement in a variety of aquifer types. Trace elements and REE have also been successfully used as *in situ* tracers to describe the evolution of sedimentary systems (Banner et al 1989, Bertram and Elderfield 1993, Gosselin et al 1992). This previous work is applicable to tracing CO_2 transport in CCS systems, because brine chemistry may be particularly sensitive to changes in local equilibrium caused by the addition of CO_2. Because brine within a targeted saline aquifer hosted formation will have been in chemical equilibrium with the host rocks for millions of years, the addition of large volumes of CO_2 will cause the brine chemistry to rapidly evolve due to the pH change caused by the dissolution of CO_2 in the brine and subsequent chemical interactions with reservoir and cap rocks. The altered geochemical signature imparted to the brine by these change may serve as an ideal tracer for fluid migration, both within the formation and should it migrate into surrounding formations. However, there are analytical challenges associated with measuring REE in natural aqueous systems. Special precautions must be taken to avoid contamination; water samples must be pre-concentrated prior to analysis, instrumental analyses must be conducted in short, careful runs; and extensive quality assurance/quality control procedures must be used.

1.1. REE Chemistry

The REE are a group of 15 elements including Lanthanides, atomic number 57-71, some classifications include scandium, yttrium as well. Despite their name the REE are not rare, and except for promethium are relatively plentiful in the earth’s crust, with bulk concentrations ranging to near 70 ppm. However, except for a few notable examples such as Byan Obo, China, they are not found in significant ore grade concentrations; the name “rare earth” is derived from this scarcity of economic deposits. The utility of REE as geochemical tracers is related to their remarkably uniform chemical properties with subtle but important systemic variations. The REEs are lithophile elements (elements enriched in the earth’s crust) that almost always occur naturally together because all are trivalent with Eu and Ce having additional oxidation states of [II] and [IV], respectively. The chemical uniformity of the REE is the result of the electrons in the 6s subshell being complexly filed, and the 4f electrons being very well shielded. The most significant difference in properties across the REE are decreasing ionic radii with increasing atomic number referred to as lanthanide contraction. Because of their similar chemical properties the REE readily substitute for one another.

The REE are commonly grouped into two packages the Light REE (LREE La – Sm) and the Heavy REE (HREE Gd – Lu). Less commonly a third group Middle REE (MREE Pm - Ho) is included. Because REE are among the least soluble trace elements, they are quite immobile during low temperature rock alteration, resulting in aqueous concentration of parts per trillion for most systems. Although the low concentration makes measuring aqueous concentrations of REE challenging, this attribute make the aqueous REE system extremely sensitive to perturbations, such as changes in digenesis cause by the addition of large volumes of CO_2 to a storage reservoir. Factors that affect the transport of the REE include, the distribution of REE in the host rock, the types, abundance, and stability of REE bearing minerals in the rock and the composition ligands, particularly carbonate in the formation brine and Cl in high temperature magmatic brines.

1.2. REE as a tracer

Although REE can provide a powerful tool for evaluating trends in water chemistry and transport (e.g., CO_2 impacts, mixing, and source zones) and are increasingly being used to evaluate aqueous systems, there are practical difficulties associated with accurately measuring REE in aqueous systems. The complexation of the REE, except under very acidic conditions, does not occur as hydrated trivalent ions; therefore, transport of REE in natural systems is dependent on soluble ligand complexes or, to a small degree, adsorption desorption reactions. REE are considered hard as defined by Pearson (1963), resulting in strong complexes with hard ligands (F, PO_4, and at high temperatures Cl). More than 98% of REE in and aqueous solution is the result of complexation with SO_4, CO_3 (Nelson et al. 2004, Sampson and Wood 2005). Therefore it would be expected that waters that with high concentrations of these ligands would have proportionally higher concentrations of REE.

In addition to the challenges mentioned previously, quantifying REE in brines present additional challenges because of high concentrations of interfering major elements ions. A goal of our ongoing research is develop methods and protocols to quantify REE in high TDS water that is characteristic of CCS in saline aquifers, and allowing the use of REE as a natural tracer of fluid-rock interactions and migrations

2. Methods

The parts per trillion concentration of REE in natural waters are at or below the detection limit for direct quantification by ICP-MS. However, preconcentrating samples overcomes this limitation. Our approach for quantifying REE uses two separate but related methods based on Strachan et al., 1989 and Stetzenbach et al., 1994; one for low TDS (less than 10,000 ppm) waters and one for higher TDS (10,000 to 200,000 ppm) brines. Both methods rely on a chromatographic separation of REE from other cations followed by elution and concentration of REE by up to 100 times for quantification using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). For lower TDS waters a HDPE gravity driven chromatographic column with ion exchange resin (Bio-Rad's AG 50W-X8) is used. For brines a borosilicate glass column with chelating resin (Bio-Rad's Chelex 100) is used. The more expensive chelating resin is used for brines because the high salinity caused the AG 50W-X8 to "clump" resulting in poor column performance. The two methods are described below.

2.1. Separation and preconcentration

Effective quantification of REE requires techniques that address their low concentrations in natural waters and analytical interferences from other cation in the waters. We addressed both of these issues using chromatographic approaches described below

2.1.1. Low TDS waters

Our low TDS procedure used AG-50W-X8 hydrogen form resin in the 200-400 mesh size, we have found that this size fraction results in a lower flow rate through the column and increase cation and REE capture efficiency. REE in each sample were concentrated by 50 or 100:1 by gravity feeding 1-2 liters of sample through a Bio-Rad Poly Prep AG 5W-X8, with 200 to 400 mesh resin gravity flow chromatography column with a 250 ml sample reservoir (the reservoir was not allowed to run dry and was capped through the process). After the sample was drained through the chromatography column, a 40-mL of 1.7 N ultra pure nitric acid was applied to the column to elute the divalent cations from the resin, leaving behind only the trivalent cation adsorbed to the AG 5W-X8 resin. The REE and other trivalent cations are then eluted from the resin using 10 mL of 8 N nitric acid and collected in an acid-washed Teflon container. The resulting eluent was evaporated to dryness at 60°C on a hot plate enclosed in a filter box to minimize contamination. The residual bead was dissolved in a 10-mL 1% nitric acid solution to obtain the final 50:1 or 100:1 concentration ratio. The sample is then placed in a triple acid washed sealed 15 ml centrifuge tube for ICP-MS analysis

The resin can be recycled several times using the regeneration procedure of Crock et al., 1984. Regeneration was accomplished by flushing the column with five pore volumes of 8.0 N nitric acid. This process converts the resin back to hydrogen form by removing all residual non-hydrogen cations. Finally five pore volumes of 18 MΩ H_2O were applied to the column removing nitric acid from the reservoir before the column is sealed for storage. Rigorous testing of the regenerated columns with known solutions showed no degradation of the AG-50W-X8 resin after more than twenty cycles.

2.1.2. High TDS brines

The high TDS procedure uses Chelex 100 Na form resin in the 200-400 mesh size modified after a procedure developed by Strachan et al., 1989. The pre-chromatography resin preparation in our procedure is similar to that presented in Strachan et al., 1989, though aliquot volumes are increased to maintain the aliquot/resin volume ratio. First 16.25 g of resin is added to and allowed to settle into an acid washed glass drip column, the resin is flushed with 50 ml of 2.5 N ultra pure nitric acid to convert the resin to hydrogen form and remove any non-hydrogen cations. The initial wash is followed by a wash with 50 ml of 18.2 MΩ H_2O to remove excess nitric acid from the column. The resin was then converted to ammonium form using 50 ml of 2.0 N ammonium hydroxide followed by 50 ml 18.2 MΩ H_2O wash to remove excess ammonium hydroxide and to achieve a neutral pH. The resin pH is adjusted to 5.2-5.4 concentrated ultra pure nitric acid. Because the resin characteristics are strongly dependent on pH it is important to maintain the resin pH close to the optimal pH of 5.3 for best cation capture.

Once the resin is prepared, the REE are in each sample are concentrated by 50 or 100:1 by gravity feeding 1-2 liters of sample through the column by first adding two 50 ml aliquots of sample to allow the resin volume to shrink before applying the remaining volume of sample. This is an important step as it allows the resin to shrink to its final volume without the formation of preferential flowpaths. Once the entire sample has passed through the column 250 mL of 18.2 MΩ H_2O was applied. The column is the eluted with a 25mL then two 50 mL aliquots of 1.0 M ammonium acetate (pH adjusted to to 5.3 with nitric acid) to remove the mono- and divalent cations. 250 mL 18.2 MΩ H_2O is applied to the column to remove excess ammonium acetate. Next two 100 mL aliquots of 2.5N nitric acid are applied to the column to elute REEs and other trivalent cations into an acid washed 50ml Teflon beaker. This is followed by a wash of 10 mL 18.2 MΩ H_2O. The collected eluent is evaporated to dryness at 60°C on a hot plate enclosed in a filter box to minimize contamination. The resultant precipitate is dissolved (for 12 hours) using 10 ml 1% nitric acid to achieve 50 or 100 time REE enrichments relative to the original sample. The REE concentrate is placed in a triple acid washed sealed 15 ml centrifuge tube for ICP-MS analysis.

To recharge the columns for storage and reuse, 3 pore volumes of 2.5 M nitric is added to remove residual cations and convert resin to the hydrogen form. This is followed by an 18.2 MΩ H_2O wash to remove the acid from the resin. Finally, at least three pore volumes of 2.0 M ammonium hydroxide is applied until the effluent pH is 10, to converting the resin to ammonium form, which is ideal for storage. The column containing the regenerated resin is then sealed for storage. The regeneration procedure will allow the resin to be stored for several months. Prior to use the column must be prepared as described above. The regenerated resin has been tested with no degradation of the Chelex 100 Na form resin after twenty cycles.

2.2. Sample collection

Prior to each sample collection, or laboratory preparation two 500–mL, high-density polyethylene bottles were acid washed using 5% trace metal grade nitric acid for a minimum of 2 days. After the acid wash, the bottles were triple rinsed with 18.2 MΩ H_2O and then refilled with 18.2 MΩ H_2O, sealed, and placed into acid-washed plastic Ziploc bags. Prior to filling the bottles, the deionized water was discarded; and replaced with sample water or synthetic brine. Personnel wearing new nitride gloves did all sample collection; gloves were change between each step of process (bottle filling, preservation, labeling). Each sample was collected from the fastest flowing portion of the stream or spring or as far from the edge as possible. Prior to collecting the sample, the pH, temperature and alkalinity of the water were measured and recorded. For field samples, each were collected using a Geotech peristaltic pump pushing water through precleaned, acid-washed Teflon tubing. Water was purged through the sampling apparatus until the temperature, pH and conductivity stabilized. The samples were filtered using a 0.45-um Gelman Sciences high–capacity, in-line filter capsule with polyether sulfone membrane, dispensing water directly into acid-washed polyethylene bottles. The samples were then acidified to pH <2, using ultra pure nitric acid and sealed with Parafilm. To minimize the potential for environmental contamination, the exterior of the sample containers were rinsed thoroughly with 18.2 MΩ deionized water, placed into acid-washed plastic bags, and the bagged sample containers were placed in a cooler with dry ice for transport back to the laboratory. The only deviations from this procedure were at aquifer wells that had fixed piping. In these cases, the Teflon tubing and filter was connected to the existing piping; otherwise the samples were filtered and preserved as detailed above.

2.3. Analytical

REEs were analyzed after preconcentration in triplicate with using an Agilent 7500a ICP-MS, with a Babington nebulizer and electron multiplier detector. By preconcentrating the samples, we were able to remove 99% of the divalent cations, which increases the REE detection by decreasing the formation of interfering oxides (specifically BaO^+) in the plasma and lowering the overall background interference.

Analyses were to be considered reliable if plasma oxide formation (as measured by ^{156}CeO/^{140}Ce) was less than 0.5%.. The largest contributor to the oxide interference is the formation of BaO^{+}, which interferes with ^{139}La, ^{146}Nd, ^{147}Sm, ^{175}Lu, and, specifically ^{152}Sm and ^{151}Lu. Because the separation and preconcentration methods used in our study are extremely effective in removing interfering ions, especially Ba, analysis has not required correction for oxides.

Instrumental drift is accounted for by periodically analyzing a fixed concentration Rh internal standard, instrument blanks, and REE standards. All analyses were corrected by comparison to these known samples. Instrument drift was encountered, especially when larger numbers of samples were analyzed. Over time, the ICP-MS procedure was altered to minimize instrumental drift, including running fewer samples during a single series, increasing wash time, adding a small amount HF to facilitate rinse efficiency and including more blanks (deionized water) between samples. The standards used to make up the calibration solutions for the ICP-MS were obtained from Inorganic Ventures Inc. The standards were also used to spike known samples to test for instrumental drift. Blanks were run every 10 samples and were made up of DIW and 5% ultra pure nitric acid. .

3. Results

The above described procedures were tested using 14 synthetic laboratory brines made from reagent grade salts (NaCl >> CaCl2 > MgCl2 > KCl) with TDS from 7,500 to 215,000 ppm and NASS-6 certified seawater reference sample obtained from the National Research Council Canada. These samples were either spiked with known amount of REE or in the case of the NASS-6 reference seawater, were established reference material with REE concentration measured and documented.

Once the procedure were tested and verified using the synthetic brines and reference seawater, they were applied to waters from two CCS relevant locations the low TDS Soda Springs, Idaho natural CCS analogue site and the high TDS University of Wyoming Carbon Management Institute CCS test site on the Rock Springs Uplift in west-central Wyoming.

3.1. Methods verification

Our analytical methods described above were thoroughly tested and verified to assess their efficacy for application to CCS relevant brines. The results of this testing is reported below.

3.1.1. Synthetic brines

Early on during the development and testing of the REE separation procedures on synthetic brines we experienced a great deal of difficulty with contamination. The analytical results exhibited a significant amount of light REE (LREE) contamination especially La (figure 1 black trend line). The saw-tooth effect observed for the Heavy REE (HREE) in figure 1 is common and reflects the Oddo-Harkins effect (Oddo, 1914 and Harkins 1917) where atoms with even atomic number have a higher natural abundance than do their neighbors with odd atomic numbers. Initially, LREE enrichment was attributed to particulate mobilized by a major HVAC cleaning and reconstruction in the laboratory facility, as research using La had previously been conducted in a neighboring laboratory. Consequently the experiments were moved to another laboratory at the University of Idaho campus. The ICP-MS was thoroughly cleaned, all the tubing, rinse containers and anything else that could have been contaminated was replaced. However, the LREE contamination continued to persist. We then suspected that the reagent grade salts being used to make up the synthetic brine were the source of the observed REE contamination. This suspicion was supported by the pronounced Oddo-Harkins effect observed for all processed brines, indicating a natural component for the source of REE contamination. To test the salt contamination hypothesis, the chromatographic separations were conducted in a box constructed from HEPA filters to minimize any potential atmospheric contamination. Great care was used, and the filter box was only opened to place and remove samples. Additionally, a large pressurize Sentry Air Systems forced air HEPA filtration system was moved into the lab proximal to the filter box. Once the potential for external contamination was reduced, we proceeded to test the possibility that the reagent grade salts were responsible for the anomalous LREE contamination. The synthetic brines were made up as before using the same suite of salts. However, this time before the brines were spiked with REE, half were passed through the chromatography column to remove any REE that may have been present from the salts used to make the brines. Both sets of brines were then spiked with 5 ppb REE and passed through the chromatography column as described in section 2.1.2 to preconcentrate the REE. The resulting data (figure 2 red trend line) shows that the samples passed through the column prior to being spiked had REE concentrations of 5 ppb as expected. However, the brine samples that were not passed through the chromatography column prior to being spiked with REE had the same LREE contamination as previously observed (figure 2 black trend line) indicating that the salts used to make up the synthetic brines were the source of LREE contamination of approximately 2 ppb at 75 g/l. These results also confirmed that our procedure for quantitatively separating REE is effective for simple brines with TDS up to 200 g/l. Twenty-four additional synthetic brines across a range of TDS from 20,000 ppm to more than 200,000 ppm were then tested. The resulting data showed a REE capture efficiency exceeded 95% across the entire TDS and REE concentration range, giving us confidence that the procedure could successfully be applied to CCS relevant natural systems.

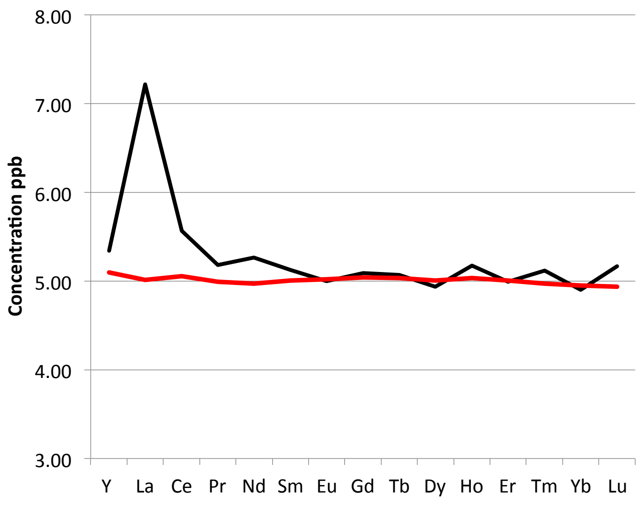

Figure 1 Results from test of the high TDS Chelex resin extraction of REE. Black trend show the results of the chromatography of a 5 ppb REE solution using reagent grade salts. A clear contamination of the sample in LREE especially La is obvious. The red trend line show the results of the same experiment after running the synthetic brine solution thought the extraction column prior to spiking with REE

3.1.2. NASS Standard

Reference seawater standard (NASS-6) was analyzed using the high TDS method to evaluate the suitability of the method for waters with more complex compositions. The National Research Council Canada (NRCC) has rigorously characterized and documented (Lawrence 2007) NASS-6 for it use as a chemical standard for ocean water. Two 500 mL NASS-6 reference standards were processed as described in section 2.1.2. They were also spiked with 1 ppb yttrium to quantify the REE recovery efficiency of the method.

The results of showed that background corrected measure REE concentrations were within 0.2% (Ln) to1.9% (La) of the concentrations reported by NRCC; this is less than the 3% uncertainty we associate with our general ICP-MS analysis.

3.2. CCS Systems

In order to assess the suitability of REE as a potential tracer for CCS settings, our methods were tested with samples that exhibit a range of water chemistry and rock types. Waters from the CO_2 charged Soda Springs CCS analogue site were analyzed to evaluate the suitability of REE's to quantify the CO_2 driven water rock interaction at this unusual site. There are two types of water at the Soda Springs, a deep carbonate sourced CO_2 charged water that that is believed to be the result of the interaction between acidic magmatic fluids and Paleozoic carbonates deep in the basin. There is also a shallow fresh water system, which overlies the CO_2 rich water and is recharged by seasonal precipitation and leakage from a reservoir located at the head of the basin. The deeper CO_2 charged system is naturally pressurized, and wells that penetrate through the basalt cap rock into the CO_2 aquifer, often results in geysering wells, that can shoot water more than 30 meters into the air. The second set of CCS relevant water was collected from the Rock Springs Uplift; a large structure located in west central Wyoming that has been studied for is large theoretical capacity to store CO_2. A single sample of formation brine from the Weber (~90,000 ppm TDS) and Madison (~75,000 ppm TDS) formations were collected. The Madison Formation is comprised of a thick sequence a marine carbonates, while the Weber Formation is primarily a diagenetically altered siliciclastic. Because of the differences in rock type, the very long residence time of the brine, and the presence of sealing formations between them, these brines provided an ideal test for both the high TDS procedures ability to delineate differences in REE chemistry between formations in stable sedimentary basins.

3.2.1. Soda Springs, Idaho

Samples collected from Soda Springs were analyzed for REE using the low TDS procedure (section 2.1.1). The resulting chondrite normalized data are presented in figure 2, showing a very positive Eu anomaly. This Eu anomaly is consistent with the anomaly reported by Olny (2012), for travertine precipitated at the same springs. The presence of the Eu anomaly in both the water and the travertine collected from the same CO_2 charged springs provide strong evidence for the interaction between deep acid CO2 changed waters and the basalt flows that cap the valley. The very strong Eu anomaly in the Soda Springs system provides is evidence for interaction of the upward migrating CO_2 charged waters with the basalts that cap the system. The Eu anomaly in these data may be explained by the dissolution of plagioclase within the basalt caprock, where plagioclase is preferentially dissolved releasing a disproportionate amount of Eu[II] which is substituted for Ca[II] in the feldspar into the aqueous phase. The high aqueous Eu concentration occurs as stable carbonate complexes (carbonate complexes predominate at near-neutral to basic pH, Wood, 1990), and is precipitated in the travertine in the proportion found in the water due to rapid CO_2 degassing of the waters. The total REE concentration varies across sampled springs with the highest concentration and the smallest Eu anomaly at Octagon Spring. More investigation is needed to explain the high REE concentration and small Eu anomaly observed in the Octagon Spring water. However, it is likely that the variability in REE concentration and the near identical Eu anomaly at the other sample locations is due to non selective adsorption onto clays in the near subsurface.

Drill cuttings from monitoring wells drilled into the basalt provided by the Monsanto Corporation Soda Springs operations, show significant secondary mineralization in the basalts at depth, with the pore space and fractures being completely filled with primarily carbonate precipitate. Additionally, the observation that the CO_2 system at Soda Springs is over pressured below the basalt contact suggests that that normally permeable basalt has been sealed by mineralization resulting from CO_2 basalt interactions providing further evidence supporting the explanation of the Eu anomaly in the groundwater and travertine at the site. Our results from the Soda Springs study site suggest that REE may potentially be used to assess processes within a CCS target formations and to track CO_2 impacted waters such sites.

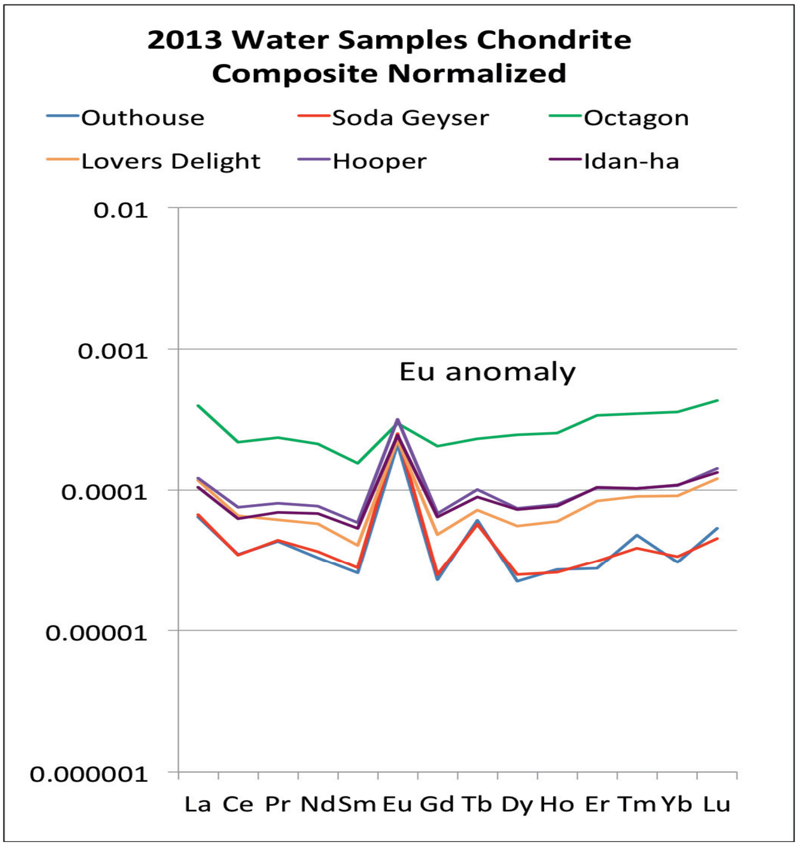

Figure 2 Graphs of ICP-MS measured REE concentrations from water samples taken from Soda Springs, Idaho normalized to chondrite composite (Wakita et al., 1971). The graph on the left shows the normalized REE concentrations of the samples collected in 2012 or prior, with only ½ of the REE being retained by the column. The graph on the right shows the normalized REE concentrations samples collected after 2012, with near 100 percent of the REE captured. Discrepancies in the REE trends for the samples (particularly in EU) are apparent between the two figures.

3.2.2. Rock Springs Uplift, Wyoming

Brine samples from Weber and Madison formation collected from the Rock Springs Uplift were analyzed for REE using the high TDS procedure (section 2.1.2). Extreme care was exercised with the Rock Springs Uplift samples (collected at the end of the water production cycle) as they were irreplaceable and the only true formation brines available for this study. The resulting chondrite normalized from the Weber and Madison brines are presented in figure 3. Both brines show LREE enrichment and like seawater both brines have a slightly negative Ce anomaly although the anomaly is much less pronounce in the brines than in seawater. Both samples have positive Gd anomalies. The largest differences between the two formation brines are the very positive HREE enrichment observed in the Weber brine and the HREE depletion in the Madison Brine and the higher REE concentration of REE in the Madison Formation. The relatively high REE concentration in the Madison Formation is expected, as the Madison Formation is a carbonate-dominated system. The data suggest that although the two formations have some similarities in their REE distributions, the HREE enrichment and the significantly higher REE concentration of in the Madison Formation indicate that these two formations are hydrologically isolated from each other as expected. Although we were only able to analyze two brine samples, our results indicate that are analytical methods are robust that REE may applicability in understanding the fate of CO2 in CCS systems sited in saline formations.

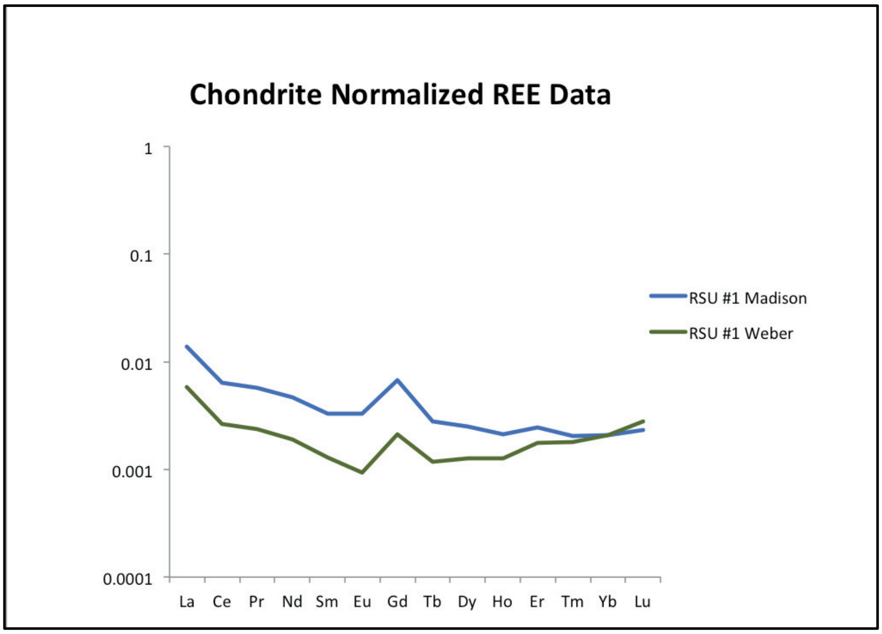

Figure 3 Graphs of ICP-MS measured REE concentrations from water samples taken from Soda Springs, Idaho normalized to chondrite composite (Wakita et al., 1971). The graph on the left shows the normalized REE concentrations of the samples collected in 2012 or prior, with only ½ of the REE being retained by the column. The graph on the right shows the normalized REE concentrations samples collected after 2012, with near 100 percent of the REE captured. Discrepancies in the REE trends for the samples (particularly in EU) are apparent between the two figures.

3.2.3. CO_2 impacted vs unimpacted waters

Although only two systems have been evaluated to date, there are some important inferences that can be drawn from the Soda Springs and the Rock Springs Uplift results. First, the chondrite-normalized concentration of REE's in deep formation brines are several orders of magnitude high than they are lower TDS water. Second, if Soda Springs system is representative of CO_2 waters that have migrated from their place or origin into an adjacent formation, then the REE chemical signature of the may be useful for early detection of displaced formation brines impinging into overlying potable aquifers. The ability for early detection of migration would be highly desirable to CCS operators, regulators and other vested parties. Another important characteristic of the data is the enrichment of LREE relative to chondrite in the unimpacted waters, indicating that these waters are close to equilibrium and are not undergoing rapid diagenesis. In contrast, the Soda Springs water has a flatter trend with a slight HREE enrichment; more indicative of a system that is undergoing relatively rapid change.

4. Summary

The objectives of this work are a small part of the overall goal of demonstrating the efficacy of using REE as tracers in CCS or other relevant environments. The first objective was to develop methodology to measure REE across a range of CCS environments, from fresh water to high TDS saline formation fluid. Our effort resulted in two procedures, one for high TDS brine and one for low TDS water. Both of the procedures are equally effective in concentrating REE and removing interfering ions so they can be analyzed by ICP-MS. The high TDS procedure is slightly more involved, but both procedures are inexpensive and can be easily in most laboratories that do trace metal work. The sampling procedures needed to support these REE preconcentration procedures in more involved than standard water analysis, but would not be overly burdensome to apply to a CCS Pilot or industrial application.

The second objective was to demonstrate that REE can be applied as a natural tracer across a wide range geologic environments and CCS applications. REE have a long history of use as tracers in magmatic, ore deposit, and more recently groundwater studies. The ability to use existing water chemistry to track flow in the subsurface is appealing for a variety of reasons; most importantly it does not rely in introduction of a thoroughly mixed tracer into the system. In our study we evaluated REE from three formations or systems, the Madison and Weber Formations in the Rock Springs Uplift, Wyoming, and a naturally leaking CO_2 system at Soda Springs, Idaho. In each of these systems were we able to us REE to elucidate the effectiveness of the seals capping the formations at the Wyoming location and the specific water-CO_2-mineral reactions that are occurring in the Soda Springs system.

The procedures and mythologies described in this paper will be field tested at the Big Sky Carbon Sequestration Partnerships Saline CO_2 storage Pilot at Kevin Dome Montana. Additional samples will be collected from collaborators throughout the CCS community with the goal of sufficiently testing REE such that they will routinely be applied as tracers as the CO_2 storage technology matures.

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