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Analyzing Solutions High in Total Dissolved Solids for Rare Earth Elements (REEs) Using Cation Exchange and Online Pre-Concentration with the seaFAST2 Unit

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Cover Illustration: Photo of the seaFAST2 unit that attaches to the front end of an ICP-MS. Shown are the autosampler unit (on top of cart), peri-pump (in front of autosampler on cart), and valve system (on top right of autosampler). The actual separation chemistry is performed by an analytical column filled with a chelating resin (not pictured) that is attached in line to the valve system.

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Analyzing Solutions High in Total Dissolved Solids for Rare Earth Elements (REEs) Using Cation Exchange and Online Pre-Concentration with the seaFAST2 Unit

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Acronyms, Abbreviations, and Symbols

Term	Description
Ba	Barium
cps	Counts-per-second, measured on the ICP-MS
Eu	Europium
ICP-MS	Inductively coupled plasma mass spectrometer
ICP-OES	Inductively coupled plasma optical emission spectrometer
In	Indium
PAAS	Post-Archean Australian Shale
PPREE1	Designation for reference water from Paradise Portal, San Juan Islands
ppt	Parts-per-trillion
REEs	Rare Earth Elements, the 14 naturally occurring elements of the lanthanide series
TDS	Total dissolved solids, given in units of mass per volume (mg/L)

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The authors wish to thank Andy Ungerer in the Keck Collaboratory at Oregon State University (OSU) for his assistance and expertise with the ICP-MS. Additionally, Brian Haley (OSU) provided helpful input on the cation column procedure as well as with operating the seaFAST2 system.

ABSTRACT

The accurate quantification of the rare earth element (REE) dissolved concentrations in natural waters are often inhibited by their low abundances in relation to other dissolved constituents such as alkali, alkaline earth elements, and dissolved solids. The high abundance of these constituents can suppress the overall analytical signal as well as create isobaric interferences on the REEs during analysis. Waters associated with natural gas operations on black shale plays are characterized by high salinities and high total dissolved solids (TDS) contents >150,000 mg/L. Methods used to isolate and quantify dissolved REEs in seawater were adapted in order to develop the capability of analyzing REEs in waters that are high in TDS. First, a synthetic fluid based on geochemical modelling of natural brine formation fluids was created within the Marcellus black shale with a TDS loading of 153,000 mg/L. To this solution, 1,000 ng/mL of REE standards was added based on preliminary analyses of experimental fluids reacted at high pressure and temperature with Marcellus black shale. These synthetic fluids were then run at three different dilution levels of 10, 100, and 1,000–fold dilutions through cation exchange columns using AG50-X8 exchange resin from Eichrom Industries. The eluent from the cation columns were then sent through a seaFAST2 unit directly connected to an inductively coupled plasma mass spectrometer (ICP-MS) to analyze the REEs. Percent recoveries of the REEs ranged from 80–110% and fell within error for the external reference standard used and no signal suppression or isobaric interferences on the REEs were observed. These results demonstrate that a combined use of cation exchange columns and seaFAST2 instrumentation are effective in accurately quantifying the dissolved REEs in fluids that are >150,000 mg/L in TDS and have Ba:Eu ratios in excess of 380,000.

1. INTRODUCTION

The rare earth elements (REEs) are the 14 naturally occurring elements of the lanthanide series on the periodic table that are chemically similar and are often utilized as tracers of geochemical reactions and processes. The REEs share similar valence electron configurations and ionic radii gradually contract as atomic numbers increase, leading to predictable fractionations of the REEs by mass during physiochemical processes (Byrne and Sholkovitz, 1996; Elderfield et al., 1988). These relative fractionations of the REEs have been utilized to diagnose diverse geochemical processes such as groundwater flow (e.g., Johannesson et al., 1997a, 1997b), depositional environment in chert and shale lithologies (e.g., Murray et al., 1990), and pedogenetic processes (e.g., Laveuf and Cornu, 2009). For example, the dissolved REEs in ground waters are believed to reflect REE signatures of the rocks they flow through, thus providing a utility for tracing ground water flow paths (Johannesson et al., 1997a, 1997b). We submit that a similar potential also exists for the REEs to be useful as geochemical tracers of hydraulically fractured systems in unconventional natural gas operations, although such endeavors have yet to be undertaken. In recent years, the accelerated production of natural gas from black shale formations using directional drilling and hydraulic fracturing techniques has driven the need to document the fate of the water that returns from the well to the surface. The hydraulic fracturing process typically employs several million liters of water containing approximately 1% by volume of sand and chemical additives which are injected under high pressure into the well to fracture the shale formation and allow natural gas to flow to the surface (Haluszczak et al., 2013; Hayes, 2009). A portion of this water flows back to the surface, with compositions that can be highly altered compared to the waters at the time of injection (Blauch et al., 2009; Haluszczak et al., 2013; Hayes, 2009). Waters that return to the surface of the well, designated as flowback waters, are often enriched in salinity and total dissolved solids (TDS) and can reach TDS contents as high as 350,000 mg/L (Blauch et al., 2009; Dressel and Rose, 2010; Hayes, 2009). Growing concerns over the fate and handling of these returning waters highlight the need to understand the chemical composition of the waters and the potential for the release of contaminants from the shale formation into the returning flowback waters (Vidic et al., 2013). Using the REEs to trace geochemical processes occurring in flowback waters may help to address these ongoing issues in hydraulically fractured systems. However, the high TDS loadings of the flowback waters present significant analytical challenges to measuring dissolved REEs by mass spectrometry and must first be addressed before any evaluation on the potential utility of the REES as geochemical tracers can be conducted (measured on an inductively coupled plasma mass spectrometer, ICP-MS). This report presents one method using ion chromatography and online pre-concentration to accurately measure REEs in solutions that are high in TDS. The value of TDS that is considered "high" for flowback waters is not well-defined, but this report refers to high TDS loadings as those approximate to average flowback fluids (350,000 mg/L) (Blauch et al., 2009; Dressel and Rose, 2010; Hayes, 2009).

High concentrations of major cations (e.g., 1,000's mg/L) relative to concentrations of trace elements (e.g., 10's µg/L) reduce the ability of an ICP-MS to accurately detect the trace elements (Figure 1) due to low signal to noise ratios. This suppression of trace element signals is evident by monitoring an internal standard added to every standard and sample analyzed on the ICP-MS. In typical applications of REE analysis, indium (In) is chosen as the internal standard both because of a low natural abundance in environmental samples and an atomic mass of 115 amu that is close to the atomic mass range of the REEs. In samples that are high in TDS, signal

suppression is evident by the abrupt decrease in the 115In signal of the samples from the signal in the blanks and standards (Figure 1). While some variability is expected, values that fall outside of a heuristically defined ~10 % deviation from the 115In signal in blanks and standards are considered to be unreliable data (Figure 1). At those signals outside of the ~10 % window of the blanks and standards, accurately quantifying concentrations is less certain, since the signals of the standard curves and the samples are widely different (Figure 1).

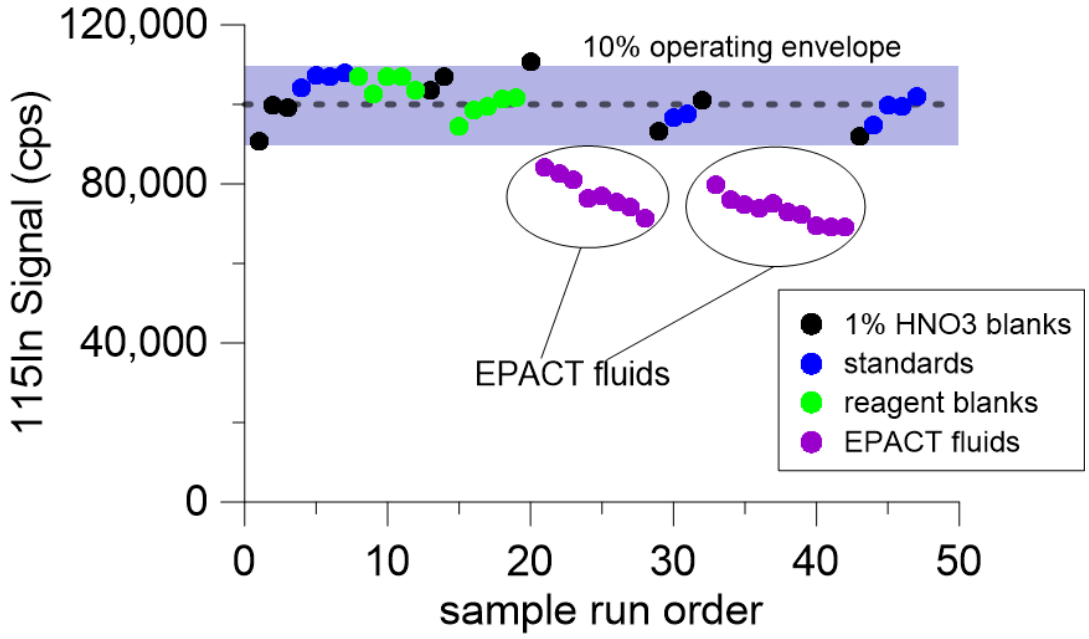

Figure 1: Signal suppression of high-TDS solutions on Thermo X-SeriesII. The shaded region marks the heuristically defined operating envelope of the 1 % HNO3 blanks and standards. The average 115In signal of the 1 % HNO3 blanks and standards is shown as the dotted line.

A high abundance of Ba^{2+} ions in solution can also create isobaric interferences on the REEs, and europium (Eu) in particular when analyzing solutions on an ICP-MS (Figure 2). The formation of barium oxides in the plasma creates a molecule that has a mass of 153 amu, the same isotopic mass that is typically measured for Eu. A similar interference is also present for ^{151}Eu, the other naturally occurring isotope of Eu. In general, the formation of oxides in the plasma is relatively low, and the ICP-MS is tuned to minimize oxide formation to below 2 % of elemental concentrations. With high concentrations of Ba and low concentrations of Eu, however, the formation of oxides can greatly impact the measured values of Eu (Figure 2). Evidence for barium oxide interferences can be qualitatively assessed through the appearance of a strong Eu anomaly, where Eu is greatly enriched in concentrations above that of the neighboring REEs (Figure 2).

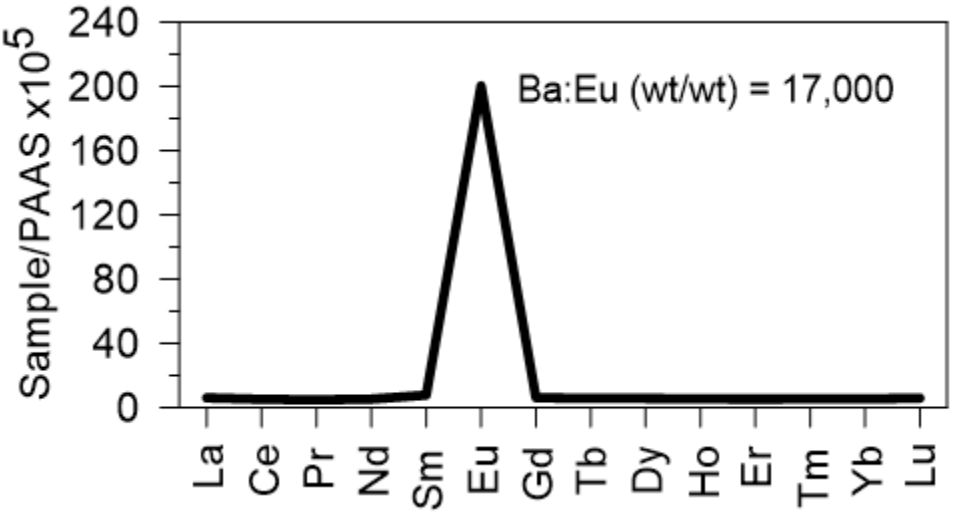

Figure 2: An example of isobaric Ba interference on Eu. Peaks in Eu are 4,000–6,000 times higher than the true values and show a drastic difference from neighboring elements. Ba:Eu ratios (wt/wt) are on the order of 17,000 at the time of analysis on the ICP-MS. Values of REEs are normalized to PAAS.

In order to obtain accurate measurement of the REEs in fluid phases, the REEs must be selectively isolated from the major constituents that cause signal suppression and isobaric interferences. In natural fluids such as seawater and sedimentary pore waters that are high in salinity (S ~ 35), common methods to effectively isolate the REEs include iron co-precipitation (e.g., Bayon et al., 2011), ion exchange chromatography (e.g., Haley and Klinkhammer, 2003), and chelating ligands (e.g., Abbott et al., 2015; Zhu et al., 2005). Fluids from hydraulically fractured systems, however, present a unique challenge in that concentrations of major cations and other dissolved constituents can be greatly elevated compared to seawaters (up to 350,000 mg/L) (Haluszczak et al., 2013; Hayes, 2009). For analyzing the REEs in such hypersaline solutions (2.0 m NaCl, 40 ppm Fe, 200 ppm dissolved organic carbon), Noack et al. (2015) presented a method using liquid-liquid extraction to isolate and analyze the REEs. This method proved successful at recovering a median value of 106% for all the REEs, with an initial loading of 500 parts-per-trillion (ppt) (Noack et al., 2015). Here a method of accurately quantifying the dissolved REE content of fluids from hydraulically fractured systems was pursued using a combination of ion exchange chromatography techniques and engineered technologies for ICP-MS analysis. To test these methods, an artificial saline solution was created that was based on geochemical modelling of formation fluids from the Marcellus black shale formation. Certified REE standards were added to this saline solution. The experimental solutions were then sent through cation exchange columns before going through a seaFAST2 unit attached to the ICP-MS. When using the online pre-concentration seaFAST2 unit (described below), Ba and other alkali and alkaline earth cations are typically washed out and eluted from the columns before the elution peak of the REEs. In cases of high Ba and other matrix ion concentrations, however, the Ba signal can extend into the elution peak for Eu and cause isobaric interferences (Figure 3). In the particular example shown in Figure 3, the concentration of Ba in the sample is 170 μM and the Ba signal on the ICP-MS is nearly 3 orders of magnitude higher than the signal of Eu. Thus, the importance of removing Ba before ICP-MS analysis is further highlighted in order to obtain an accurate quantification of Eu.

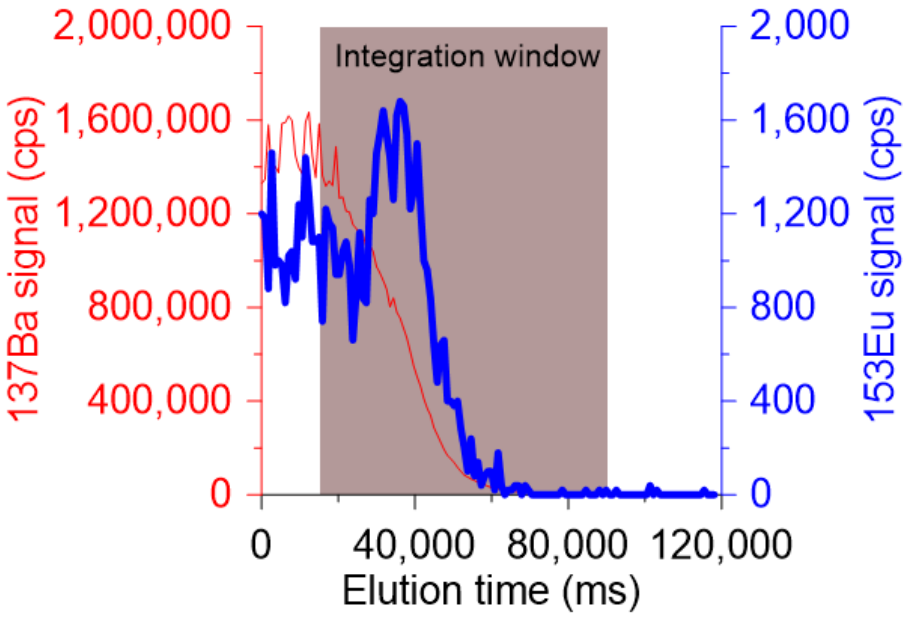

Figure 3: Elution window on seaFAST2 unit for 137Ba (red) and 153Eu (blue). The Ba signal extends into the Eu window and counts for Ba are 3 orders of magnitude greater than counts of Eu. Ba concentrations in this example are 170 µM.

2. METHODS

The fluids used in this study were created by adding chloride salts (from Alfa Aesar) to 18.2 MΩ (MQ) water to a final TDS loading of 153,000 mg/L (Table 1). The composition of this brine was based on geochemical modelling results of natural brine formation waters within the Marcellus black shale formation (Marcon et al., 2017). Compared to the hypersaline brines used by Noack et al. (2015) in their liquid-liquid extraction method, the undiluted concentration of the synthetic brine had the same order of magnitude for the concentrations of the major cations (Table 1). The amount of REEs that added to the solutions, however, were almost three orders of magnitude greater than the amount of REEs in the method of Noack et al. (2015); Noack et al. (2015) used standard amounts of 500 ppt for all the REEs, whereas this study added REEs in the ppb range (up to 420 ppb for Ce) (Table 1). Natural variability of the REEs in the environment, however, may vary between 2–4 orders of magnitude and the higher concentrations of the REEs should still be representative of natural brine formation waters (Noack et al., 2014). The REEs from single element standard solutions (Alfa Aesar, Specpure) were added in a concentration distribution consistent with Post-Archean Australian Shale (PAAS), used as a standard reference value (Taylor and McLennan, 1985). The total amount of REEs added was based on preliminary results from a laboratory experiment of high temperature and pressure reactions between organic-rich black shale and hydraulic fracturing fluid where the REEs in the reacted fluids were measured to be below 200 ng/mL. From this stock solution with standard additions of the REEs, three dilution levels were used; a 10-fold, 100-fold, and 1,000-fold series of dilutions. The rationale behind running a series of dilution levels was to determine the capacity thresholds of the cation columns, which were only previously calibrated for seawater samples at much lower concentrations of major cations. Samples to be run were prepared in triplicate. Blank runs of the brine without REE addition were also prepared. As a standard reference material, the acid mine drainage water from Paradise Portal in the San Juan Islands (designated PPREE1) was also analyzed to assess the external reproducibility of the method (Verplanck et al., 2001).

Table 1: Composition of experimental fluids

	Cations						Rare Earth Elements													
	µg/mL						ng/mL													
	Ba	Ca	Fe	K	Mg	Na	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Undiluted	2,300	21,000	70	1,200	2,200	20,000	200	420	50	180	30	6	20	4	20	5	20	2	10	2
10-fold dilution	230	2,100	7	120	220	2,000	20	42	5	18	3	0.6	2	0.4	2	0.5	2	0.2	1	0.2
100-fold dilution	23	210	0.7	12	22	200	2	4	0.5	2	0.3	0.06	0.2	0.04	0.2	0.05	0.2	0.02	0.15	0.02
1,000-fold dilution	2	21	0.07	1	2	20	0.2	0.4	0.05	0.2	0.03	0.006	0.02	0.004	0.025	0.005	0.02	0.002	0.01	0.002
PPREE1	0.01	348	68	0.9	35	8	80	161	21	92	20	6	24	4	22	4	12	1	8	1

The experimental fluids were first sent through cation exchange columns in the Class100 (ISO 5) clean room of the Keck Collaboratory at Oregon State University. The procedure to isolate the REEs through the cation columns was initially developed to process seawater samples, but is adapted here to evaluate the effectiveness in processing samples with a higher load of TDS (Appendix A). The resin used was the AG50-X8, 100–200 mesh cation exchange resin from Eichrom Technologies (C8-B500-M-H). The resin was filled to the 1.6 mL line of standard Poly-Prep® Chromatography Columns from Bio-Rad. Once filled with resin, the columns and resin were cleaned with aliquots of 6 M HCl. All acids were first distilled in a quartz still to remove trace contaminants. The resin was then conditioned with 1M HCl. Samples were prepared in 1M HCl solutions, in a total volume of 1 mL, and loaded onto the columns. Additional aliquots of 1M HCl and MQ water were loaded to gently wash the samples onto the columns. Major cations were washed out with volumes of 2M HNO_3. The REEs were collected in the final step with 6M HNO_3. After running through the cation columns, an aliquot of the fluids were analyzed on the Leeman Teledyne ICP-OES (inductively coupled plasma optical emission spectrometer) in the Keck Lab for major cations (Ba, Ca, Fe, K, Mg, Na). Standard error of these measurements, based on triplicate samples, was on average less than 10% for all of the major cations (Table 2). The samples after going through cation exchange columns were also measured for the REEs on a Thermo X-SeriesII ICP-MS.

After cation exchange columns, the fluids were prepared to run on a seaFAST2 unit attached as the sample introduction unit for the ICP-MS. The seaFAST2 system from Elemental Scientific, Inc. uses a chelation column with ethylenediaminetriacetic acid/iminodiacetic acid functional groups to selectively pre-concentrate transition metals and REEs while washing out alkali and alkaline earth matrix elements at pH ~7. An ammonium acetate buffer, prepared as 14.5 M ammonium hydroxide (ACS reagent, 28–30% as NH_3, CAS: 1336-21-6) and 17.4 M glacial acetic acid (ACS reagent, CAS: 64-19-7), conditions and loads the ion exchange column with the sample, washing out the matrix elements in the process. Following the washout of the sample matrix, quartz distilled 2 M HNO_3 acid with an internal standard spike of 1 ppb In elutes the REEs from the column and onto the ICP-MS for analysis. The method detection limits for the seaFAST2 unit are <400 ppq for all the REEs and blank values are below detection limits for every REE. External reproducibilities (1σ) are between 3–12% (n=7) for all the REEs. This reproducibility compares favorably to the values reported by Hathorne et al. (2012) of 3–11% (n=50) for seaFAST2 methodology.

3. OBSERVATIONS

The concentrations of dissolved constituents in the fluids were measured both after the initial processing through cation exchange columns and after running through the seaFAST2 unit and evaluated the relative efficiencies of both steps in the procedure. The REEs were also measured in the fluids after processing through cation columns and isobaric interferences with Ba were still present. Fluids were thusly sent through additional separation by the seaFAST2 unit and re-analyzed for recovered REE content.

3.1 MAJOR CATIONS AFTER CATION EXCHANGE COLUMNS

Dissolved Ba in the lowest dilution level was measured at an average of 10 µg/mL, corresponding to approximately 45% of the initial loading (Table 2). Dissolved Ba concentrations in the middle dilution level averaged 0.8 µg/mL, representing nearly 300% of the initial loading and indicating a possible contamination or blank issues with the cation columns at this concentration level (Table 2). The amounts of dissolved Ba in the highest dilution level and in PPREE1 were below the detection limit of 0.6 µg/mL (Table 2). Dissolved Ca was measured at an average of 30 µg/mL for the lowest level of dilution, an average of 5 µg/mL for the middle dilution level, and an average of 0.6 µg/mL for the highest level of dilution (Table 2). These concentrations correspond to 15%, 20%, and 30% of the initial concentrations, respectively, indicating that most, but not all, of the dissolved Ca is removed through cation exchange columns. For PPREE1, dissolved Ca was measured at 10 µg/mL, corresponding to 30% of the initial concentration (Table 2). Fe concentrations in the fluids varied widely among the dilution levels; for the lowest dilution level, dissolved Fe was measured at 0.6 µg/mL, representing nearly 90% of the initial loading values (Table 2). At the middle dilution level, dissolved Fe was measured at 0.07 µg/mL, whereas the initial concentration level in the fluids was 0.007 µg/mL (Table 2). Dissolved Fe was not detected in the highest dilution level (Table 2). In PPREE1 fluids, dissolved Fe was measured at 6 µg/mL, approximately 85% of the initial loading value (Table 2). Dissolved K concentrations were below limits of detection in the fluids processed through cation exchange columns (Table 2). Mg levels in the fluids were measured at 0.8, 0.4, and 0.75 µg/mL for the lowest, middle, and highest dilution levels, respectively (Table 2). For the middle and highest dilution levels, these values were greater than the initial loading concentrations, while for the lowest dilution level only about 3% of the initial loading was recovered (Table 2). For PPREE1 fluids, dissolved Mg was measured at 1 µg/mL, approximately 30% of the initial loading values (Table 2). Dissolved Na was measured at an average of 0.1 µg/mL at the lowest dilution level (<0.05% of the initial loading) and was below detection levels in the middle and highest dilution levels as well as in PPREE1 (Table 2).

Table 2: Dissolved major constituents after cation column processing. <DL represents values below the reported detection limits

Sample Designation	Ba		Ca		Fe		K		Mg		Na	
	µg/mL		µg/mL		µg/mL		µg/mL		µg/mL		µg/mL	
	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation
10-fold dilution	23	10.1	210	29	0.7	0.6	12	<DL	22	0.8	200	0.1
100-fold dilution	0.2	0.8	2	5	7.E-03	7.E-02	0.1	<DL	0.2	0.4	2	<DL
1,000-fold dilution	2.E-03	<DL	2.E-02	0.6	7.E-05	<DL	1.E-03	<DL	2.E-03	0.8	0.02	<DL
PPREE1	7.E-04	<DL	35	10	7	6	9.E-02	<DL	3	1	0.8	<DL
Detection limits	0.6		0.1		0.05		0.6		0.3		1.4	

At the highest concentration loaded onto the columns (corresponding to the lowest dilution level), the columns effectively remove 56% of the dissolved Ba. For high dilution levels, the relative removal of Ba was less, probably as a consequence of relatively high blank levels (Appendix B). However, even at these levels and considering that the amounts of REEs were also lowered due to the higher dilution factors, dissolved Ba still impinged an isobaric interference on Eu (Figure 4). For the other major cations, however, the cation columns appear to remove the amounts of K and Na very effectively, recovering < 5% of the initial K and Na amounts with the REE fraction. Dissolved Ca is reduced by approximately 70% (Table 2). Mg appears to be effectively removed when loaded at higher concentrations (>22 µg/mL), recovering < 4% of the initial Mg with the REE fraction. At lower concentrations of Mg in the initial fluids, the columns appear to have relatively high blank levels of approximately 0.7 µg/mL that mask the ability to detect lower concentrations (Appendix B). Similarly, dissolved Fe appears to have issues with blank levels in the cation column resin (Appendix B).

Besides Eu, which was affected by the levels of dissolved Ba, the remainder of the REEs displayed good recoveries after the cation columns, typically between 85–115% of the initial loadings (Appendix C). The highest dilution levels, however, were recovered at an average of 200% for all of the REEs (Appendix C). The REE concentrations of the acid mine drainage water (PPREE1) used as an external reference standard were recovered at values in good agreement with reported values from Verplanck et al. (2001) (Table 3).

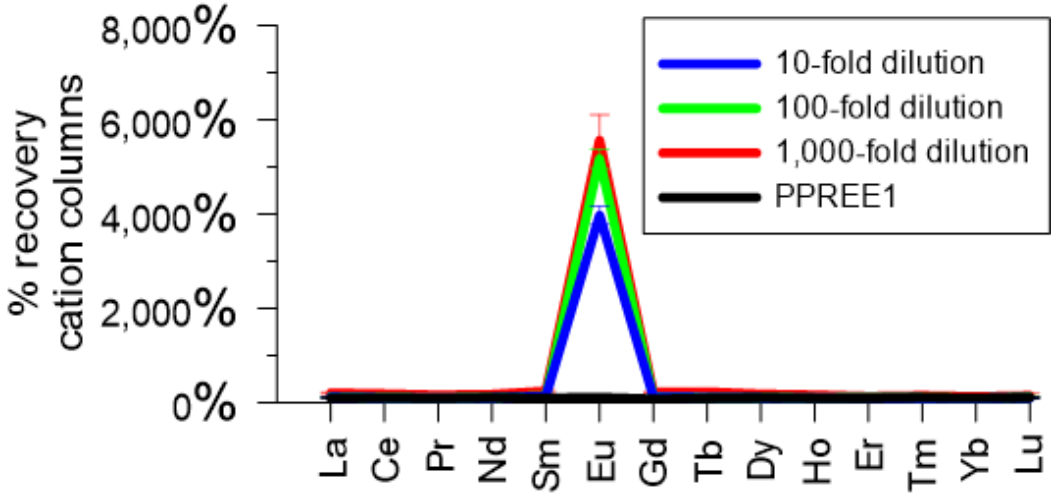

Figure 4: Recoveries of the REEs after cation column procedure.

3.2 REES AFTER SEAFAST2

Dissolved REEs in the fluids analyzed through the seaFAST2 unit attached to the ICP-MS generally showed good recoveries of the initial loadings, averaging between 90–105% for all of the REEs, except for the middle dilution level which showed lower recoveries of the light REEs and greater recoveries of the heavy REEs (Figure 5). This deviation is attributed to the ruptured peri-pump tubing during sample uptake of the middle dilution level samples, where the signal of the internal standard (115In) was lost. Once the peri-pump tubing was replaced, however,

internal standard recoveries returned to stable values and normal operation resumed. The middle dilution samples, however, were not revisited because the sample volume was consumed. Percent recoveries of the REEs in PPREE1 ranged from 80–110% and generally fell within error for reported values in Verplanck et al. (2001) (Appendix D). The percent recoveries across the REEs are stable, varying no more than 2.5% from the average recovery of 100% for the lowest dilution level and no more than 4% from the average recovery of 95% for the highest dilution level. The relative flatness of the percent recovery trend indicates that no fractionation of the REEs occurs during the cation exchange and seaFAST2 process. The overall conclusion drawn from these results is that the combined use of cation columns and the seaFAST2 unit are effective in accurately quantifying the REEs in a high TDS (153,000 mg/L) solution where the ratio of Ba:Eu (wt:wt) is approximately 38,000 initially. Samples that exhibit higher Ba:Eu ratios and/or higher TDS loadings may require additional runs through cation columns to effectively isolate the REEs prior to analysis by seaFAST2 and ICP-MS.

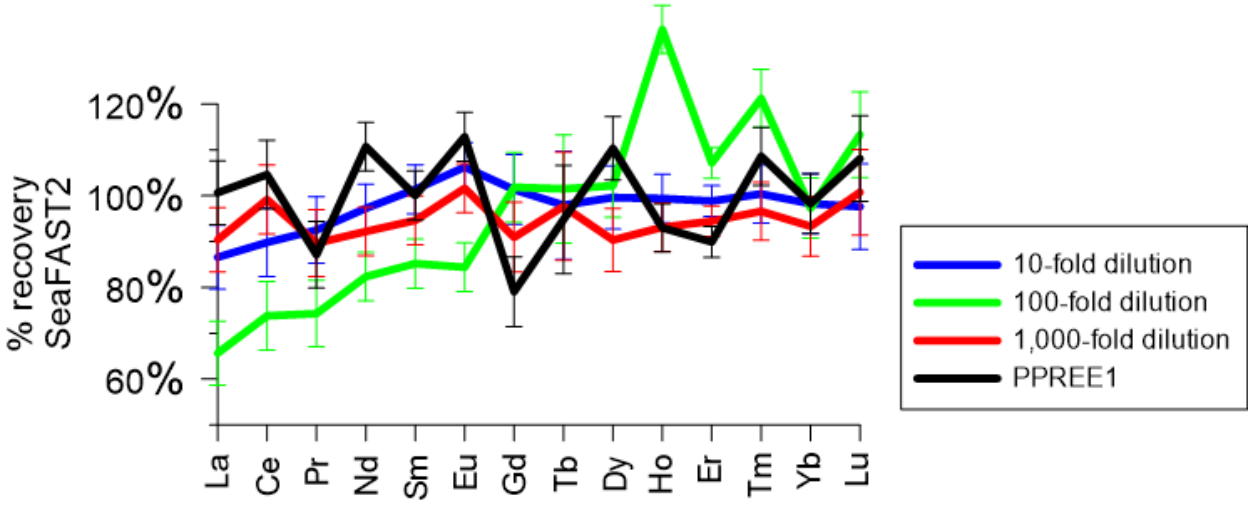

Figure 5: Recoveries of the REEs after processing through both cation columns and the seaFAST2 unit.

4. CONCLUSIONS

The cation exchange column procedures appear to be effective in removing the majority of the major cations in a synthetic fluid designed to mimic natural formation brines at 150,000 mg/L TDS. The exceptions are Ca, for which only approximately 70% of the initial loading is removed, and Ba, for which only approximately 56% of the initial loading is removed in the lowest dilution level. Despite the undetectable levels of dissolved Ba in the middle and highest dilution levels, the amount of dissolved Ba still present in solution proportionate to the REEs is enough to cause an isobaric interference on the ICP-MS. This suggests that the relative ratio of dissolved Ba and other major cations to the dissolved REE concentrations is the major determinant in accurately quantifying REE contents rather than absolute amounts. The initial ratio of Ba:Eu in the investigated fluids was approximately 380,000:1 on a mass basis. Once further removal of dissolved Ba was accomplished through the seaFAST2 unit, isobaric interferences on the REEs were not observed. The thresholds of the Ba:REE ratio that is needed for accurate measurement of the REEs is an area that will need further work, but fluids with ratios >380,000:1 and TDS loadings greater than 150,000 mg/L will likely require multiple runs through cation exchange columns in order to accurately isolate the REEs. Percent recoveries from using cation exchange in conjunction with seaFAST2 online pre-concentration range from 80–110%, and together appear to be effective at removing dissolved Ba and other major cations to the point where the REEs may be accurately determined. Fractionation of the REEs from this method is minimal; percent recoveries do not vary more than 2.5% for the lowest dilution level, and no more than 4% for the highest dilution level. Successful recovery of dissolved REEs using this coupled cation column/seaFAST2 method in an acid mine drainage reference water verifies that this method can accurately recover the REEs.

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APPENDIX A: CATION EXCHANGE COLUMN PROCEDURE

Table A1: Cation Exchange Column Procedure

Step	Volume	Notes
Load resin	1.6 mL	
6M HCl	2 x 3 mL	clean column
1M HCl	2 x 3 mL	condition column
SAMPLE	1 mL	load sample
1M HCl	3 x 1 mL	wash sample in
MQ	2 x 3 mL	
2M HNO_3	4 mL	
2M HNO_3	7 mL	
6M HNO_3	10 mL	elute REEs

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APPENDIX B: REE BLANK LEVELS OF THE CATION COLUMN/seaFAST2 PROCEDURE

TableB1: REE blank levels of the cation column/seaFAST2 procedure

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL	pg/mL
Cation Blank (n=5)	1.9	6.8	0.2	1.1	0.1	0.016	0.1	0.0	0.1	0.1	0.2	0.04	0.03	0.02

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APPENDIX C: DISSOLVED REE CONCENTRATIONS OF FLUIDS AFTER CATION COLUMNS

Appendix C1: Dissolved REE concentrations of fluids after cation columns

Sample designation	La		Ce		Pr		Nd		Sm		Eu		Gd	
	pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL	
	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation
10-fold dilution	2,000	2,358	4,168	4,214	461	457	1,770	1,837	293	404	58	2,289	246	301
100-fold dilution	200	254	417	444	46	47	177	195	29	44	6	298	25	31
1,000-fold dilution	20	41	42	78	5	7	18	31	3	7	0.6	32	2	5
PPREE1	8,040	8,093	16,100	16,841	2,120	1,847	9,230	10,219	2,030	2,031	595	671	2,380	1,882
Detection limits	2.E-04		0.9		0.3		1.0		0.4		0.04		0.1	

Sample designation	Tb		Dy		Ho		Er		Tm		Yb		Lu	
	pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL	
	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation	initial	after cation
10-fold dilution	37	41	246	259	52	52	152	147	21	20	147	134	21	21
100-fold dilution	4	4	25	27	5	5	15	17	2	2	15	13	2	2
1,000-fold dilution	0.4	0.8	2	4	0.5	0.9	2	2	0.2	0.3	1	2	0.2	0.3
PPREE1	365	346	2,200	2,427	443	412	1,190	1,070	148	161	820	806	112	121
Detection limits	0.02		0.5		0.1		0.1		0.01		0.5		0.03	

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APPENDIX D: DISSOLVED REE CONCENTRATIONS AFTER CATION COLUMNS AND seaFAST2 UNIT

Table D1: Dissolved REE concentrations after cation columns and seaFAST2 unit

Sample designation	La		Ce		Pr		Nd		Sm		Eu		Gd	
	pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL	
	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2
10-fold dilution	2,000	1,731	4,168	3743	461	426	1,770	1,721	293	297	58	61	246	249
100-fold dilution	200	131	417	308	46	34	1,77	146	29	25	6	5	25	25
1,000-fold dilution	20	18	42	41	5	4	18	16	3	3	0.6	1	2	2
PPREE1	8,040	8,121	16,100	15,951	2,120	1,820	9,230	9,595	2,030	1,787	595	591	2380	2014
detection limits	2.E-04		0.9		0.3		1.0		0.4		0.04		0.1	

Sample designation	Tb		Dy		Ho		Er		Tm		Yb		Lu	
	pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL		pg/mL	
	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2	initial	seaFAST2
10-fold dilution	37	36	246	245	52	52	152	150	21	21	147	144	21	20
100-fold dilution	4	4	25	25	5	7	15	16	2	3	15	14	2	2
1,000-fold dilution	0.4	0.4	2	2	0.5	0.5	2	1	0.2	0.2	1	1	0.2	0.2
PPREE1	365	308	2200	2142	443	377	1190	1132	148	162	820	686	112	124
detection limits	0.02		0.5		0.1		0.1		0.01		0.5		0.03	

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